SYNTHESIS AND PHYSIO-CHEMICAL STUDIES OF SOME TERNARY COMPLEXES CONTAINING VITAMIN AS ONE OF THE LIGANDS

THESIS
SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENT FOR THE DEGREE OF MASTER OF PHILOSOPHY (M.PHIL) IN CHEMISTRY

BY

MOHAMMAD SALIM

DEPARTMENT OF CHEMISTRY
BANGLADESH UNIVERSITY OF ENGINEERING AND TECHNOLOGY (BUET)
DHAKA-1000, BANGLADESH

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CANDIDATE`S DECLARATION

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

Mohammad Salim
(Candidate)
M. Phil Student
Roll No. 040203205 F
Department of Chemistry
BUET, Dhaka, Bangladesh

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Mohammad Salim
Author

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CONTENTS

Abstract

Ternary complexes provide models for metalloenzymes and several other biological processes involving metal ions. These have great functional values in nature, such as in blood (hemoglobin) which is an iron-complex and functions as the oxygen carrier of the blood stream. 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=Ascorbic Acid (AsA), Pyridoxine (Pyri), Nicotinic Acid (Nia) and L=α-alanine(α-ala), Glycine(gly), Phenylalanine(ph-ala), and 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 statistical, 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.

Ternary complexes containing Pyridoxine (Pyri) are found to be more stable than the corresponding complexes containing Ascorbic Acid(AsA) and Nicotinic acid(Nia). With respect to ligand L, the stability of ternary complexes increases in order: glycine < α-alanine < phenylalanine < tyrosine. Ternary complexes of Ni(II) are found to be less stable than the corresponding Cu(II) and Zn(II) complexes.

The formation of the complexes have been confirmed by UV spectral studies and Cyclic Voltammogram.

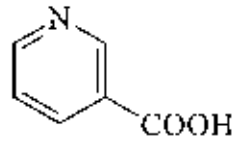
INTRODUCTION

INTRODUCTION

1.1 General Introduction

Bioinorganic chemistry is a specialized field that spans the chemistry of metal-containing molecules within biological systems. This field is concerned with the control and use of metal ions in biochemical processes. Although bioinorganic chemistry includes the study of artificially introduced metals (e.g: medicinally), many natural occurring biological processes (such as respiration) depend upon molecules containing inorganic elements, such as metalloproteins and these natural processes are also studied by bioinorganic chemistry [1]. Metal complex is a branch of bioinorganic chemistry, where metals play very important roles in biological system [2].

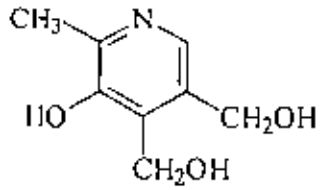
The complexes [3], in which a metal is bound to two different ligands are called mixed ligand complexes. Such systems are also known as ternary complexes. It is now generally agreed that ternary complexes are usually formed in a solution containing metal ions and two different suitable ligands. The knowledge about the chemical structure, physiological role, deficiency diseases and available sources of vitamin are essential for human life [4]. Recent studies involved an investigation of the coordination behavior of some vitamins as biological important ligands, which are essential chemicals for the maintenance of normal metabolic functions.



Nicotinic acid

Nicotinic acid, also known as niacin or vitamin B_3 is a water soluble vitamin whose derivatives such as NADH, Nicotinamide adenine dinucleotide (NAD), NAD^+ and Nicotinamide adenine dinucleotide phosphate (NADP) play essential roles in energy metabolism in the living cell and DNA repair [5]. It is very important for human life because it reduces very low density lipoprotein (VLDL) or bad cholesterol [6] and increase high density lipoprotein (LDL) or good cholesterol in blood. It also removed toxic chemicals from the body. Niacin deficiency leads to disease pellagra, a disease with symptoms that include sunburn, diarrhea, irritability, swollen tongue and mental confusion. High dose of niacin may elevate blood sugar, thereby worsening diabetes mellitus [7] and may cases of facial flushing and itching.[8]

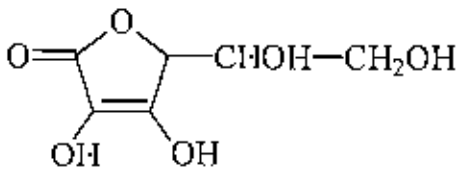
Pyridoxine also called vitamin B_6 serves as coenzyme and is involved in the metabolism of protein and carbohydrates, the production of insulin and red and white blood cells, the synthesis of neurotransmitters, enzymes and prostaglandins. Pyridoxal (PL), Pyridoxine (PN), Pyridoxamine (PM), Pyridoxal 5- phosphate (PLP), Pyridoxine 5-phosphate (PNP) and Pyridoxamine 5- phosphate (PMP) are six forms of vitamin B_6. PLP is the active coenzyme form and has the most importance in human metabolism.



Pyridoxine

Pyridoxine helps the body to absorb and metabolize amino acids, to use fats and to form red blood cells. Pyridoxine deficiency may results smooth tongue, skin disorders, dizziness, nausea, anemia and kidney stones.

Ascorbic acid or vitamin C is the enolic form of 3-oxo-L gulofuranolactone. Ascorbic acid behaves as a vinylogous carboxylic acid, where the double bond ("Vinyl") transmits electron pairs between the hydroxyl and the carbon.



Ascorbic acid

Ascorbic acid is the ascorbate ion. In living organisms, ascorbate is an antioxidant, as it protects the body against oxidative stress [9] and is a cofactor in several vital enzymatic reactions. Ascorbic acid deficiency causes scurvy in humans.

The biochemical reactions [10] taking places in solution involve organic molecules with potential coordinating sites and also strongly coordinating transition metal ions. In living tissues and fluids, [11,12] 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 is to be expected. Ternary complexes [13,14] have been implicated in the storage of metal ions and their transport through membranes in the biological system [12,15]. Taking every thing together, one is not surprised any more about Wood's conclusion [16], "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 the metal ion and ligands similar to those present in biological fluid and living tissues [10,11]. The formation [17] and stability [11,12] 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 [18] .This results in a large body of data involving metal binding sites or models [19] and structures formed [20]. The study of mixed ligand complexes is also important from fundamental coordination chemistry in point of view. 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 [21]. 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.

The formation of ternary complex can be considered to take place in three different ways, as follows [22].

$M + A + L \leftrightarrows MAL \qquad K^{M}_{MAL} = \dfrac{[MAL]}{[M][A][L]} \ldots\ldots\ldots (I)$

$MA + L \leftrightarrows MAL \qquad K^{MA}_{MAL} = \dfrac{[MAL]}{[MA][L]} \ldots\ldots\ldots (II)$

$ML + A \leftrightarrows MLA \qquad K^{ML}_{MLA} = \dfrac{[MLA]}{[ML][A]} \ldots\ldots\ldots (III)$

From eq (I) and (II) we find,

$$\log K^{MA}_{MAL} = \log K^{M}_{MAL} - \log K^{M}_{MA} \ldots\ldots\ldots (IV)$$

From eq (I) and (III) we find

$$\log K^{ML}_{MLA} = \log K^{M}_{MLA} - \log K^{M}_{ML} \ldots\ldots\ldots (V)$$

On a quantitative basis, the stability of ternary complexes can be expressed in terms of the difference in the tendency of a ligand (A or L) to bind with the free metal ion and with the metal ion already bound to another ligand (L or A) and is represented by $\Delta\log K$.

$$\Delta\log K = \log K^{MA}_{MAL} - \log K^{M}_{ML} = \log K^{ML}_{MLA} - \log K^{M}_{MA} \ldots\ldots (VI)$$

It is evident form the eq^{n}(VI) that the influence of both ligands is mutual and of the same size in the formation of ternary complexes. Both ligands are either stabilized or destabilized in their coordination to the metal ion equally.

$\Delta\log K$ must be a constant because it is the result from subtraction of two constants. From statistical consideration $\Delta\log K$ is expected to be negative. This is because when the first ligand (A) combines with a given multivalent (hydrated) metal ion, it has more coordination position

available for bonding than when it combines with metal ion already bonded to another ligand (L). Hence the order $\log K^{M}_{MA} > \log K^{ML}_{MLA}$ usually holds and one expects to observe negative values for Δlog K.

The Δlog K value is the measure of the stability of ternary complexes. Greater the value of Δlog K greater will be the stability of complexes. The stabilization factor governiug Δlog K depends on the coordinating member of the metal ion and the denticity of the ligand.

The difference ($\log K^{M}_{MAL} - \log K^{M}_{MA}$) is generally about 0.5 to 0.8 log units for monodentate ligauds and about –1 to –2 log unit for bidentate ligands [23] .In the cases 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 [24] i.e the statistical factor is $\frac{5}{12}$ and accordingly $\Delta\log K_{oh}$ = -0.4. For square plane (sp) a factor of $\frac{1}{4}$, 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 Jahn-Teller inversion to be rapid [23], there are eight equivalent attacking positions for the first ligand can vary from one to four depending on the relative rates of inversion. Hence the statistical value is between $\frac{1}{8}$ and $\frac{4}{8}$ and ΔlogK = -0.9 (or -1.1) to –0.3 . In case of Cu^{2+} and the ligands that introduce a strong ligand field, the statistical expression $\Delta\log K\ \frac{do}{cu}$ = -0.9 is considered to be most

appropriate one [25]. Hence an experimentally determined value of ΔlogK, more or less negative than –0.9 indicate that, the ternary complex is favoured less or more respectively. So the value of ΔlogK is affected by the nonstatistical factors depending on the natures of the ligands A and L and structure of the metal ion in some cases [26].

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 coloring pigments which impart colors to the plants and flowers contains ions likes Cu(II), Fe(II), Fe(III), Co(II) etc.

Among the vitally important biochemical processes [27] which are influenced by the various metal ions are (i) transmission of the nerve pulses in the animal body, (ii) maintenance of the osmotic pressure in the animal and plant bodies are controlled by various metal ions [28].

The activation of enzymes are controlled by various metal ions. The enzymes from yeast and many bacteria are activated by Fe^{2+}, Co^{2+}, or Zn^{2+} ions [29].

Some metal ions play remarkable contradictory physiological roles in different concentration and in different chemical form. Thus while Copper 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 a number of other disease in man and animal [30]. Cu (II) complexes with DL-aspetric acid, L-prolin, DL-methionine and L-glutamic acid have similar toxicities to mice [31]. Copper and Zinc complexes have shown marked beneficial action in physiological disorders.

1.3 LITERATURE REVIEW

The study of ternary complex in solution provides simpler models for the more complicated biochemical reactions. The synthetic ternary complexes with metal atom bound to two different ligands mimic the metalloenzymes with the metal ion bridging the carrier ligands and substrate.

This understanding has directed the attention of chemists to study of dynamic equilibria in the formation of metal complexes, involving the metal ion and ligands similar to those present in biological fluids and living tissues. The formation and stability of such complexes have been extensively studied. Some of these important and related to present research work have been reviewed and briefly presented here:

(1) Additional stability of (MAL) was observed if L coordinates through O⁻, O⁻, (e.g. oxalic acid) [32]. It has been shown that ΔlogK is positive in the complex [CuAL], due to lowering in repulsion between metal dπ electron and the ligand electrons and finally neutralization of the ternary complex result [33,34].

(2) Beda E. Fischer and co-workers [35] observed the participation of Co^{+2} and Ni^{+2} in biological system. They suggested that S ligands may have π accepting qualities.

(3)(i) P.G. More and co-workers studied the synthesis, spectral, thermal and antibacterial studies on Copper (II) and Zinc(II) complexes using NNO donor schiff bases [36]. It is observe that Cu(II) and Zn(II)

complexes show enhanced antibacterial activity as compared to the ligand.

(ii) Mixed ligand chelates of some multidentate heterocycles with Cobalt (II) and Nickel(II) have been studied by P.T Arasu et al [37]

(4) An interesting relationship of the stability of Cu(II) and Ni(II) ternary complexes is observed if one of the ligands is tridentate ligand [38,39,40]. 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

(5) H. Sigel and coworkers [41] have also observed that in the systems [Cu(DET)(L)] [where DET = diethylenetriamine, L= bidentate L-alanineamide], ΔlogK is more negative.

(6)(i) Y. J. Israeli studied [42] the formation constants of mixed ligand complexes of Cu(II) and Ni(II) with NTA and various aminoacids.

(7)(ii) J. P. Tandon and coworkers [43] 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.

(7) J. I. Watters and O. Yamauchi [44,45] 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. P. K. Bhattacharya and

coworkers [46,47,48] have further elaborated the effect of negatively charged on the stability constant in terms of electronic repulsion concept.

(8) The effect of steric hindrance between the bulky side groups on the coordinating ligands L and L′ on the stability of the ternary complexes has been studied by P. C. Parikh et al. and W.E. Bennett et al [49,50]. They reported that if the two ligands involved in the formation of the ternary complex have substituted groups on the front or back side of the second ligand coordinates with the metal ion forming the ternary complex resulting in less stable complex. For example [MAL] complexes where L=N-substituted ethylenediamine due to steric hindrance of the alkyl groups on the nitrogen of the ligands of N-substituted ethylenediamine.

(9) The order of the stabilization observed by H. Sigel et al. and P. K. Bhattacharya et al.[51,52] in ternary complexes containing two chelate rings are as follows:
Two five-membered rings > One five-membered ring and One six-membered ring > Two six-membered rings.

(10) 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 M. V. Chidambaram et al and P. J. Patel et al [53,54]. This has been repeatedly confirmed [55-59] by other workers.

(11) Study of M(dpx)(pyrocatecholate) complexes [60] of the later members of the first transition 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.

(12) In another series of ternary diamines, P. K. Bhattacharya and corworkers [46,47,54,61] 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) imidazoline.

(13) The complexes containing aromatic amines and pyrocatechol derivatives have been studied by P. K. Bhattacharya and coworkers [61,62] also by H. Sigel and coworkers[63]. Both groups conclude that the electron density over the donor site of L has significant influence over the stability of the ternary [CuAL] complexes. Electron withdrawing substitution on L lower the stability of the complex and electron donating subsistent increases it.

(14) In ternary complex [M(bipyridyl)(ATP) [64,65,66] the nucleotiede 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 part of the nucleotide as confirmed by formation constant studies and NMR studies.

(15) In the complex [Cu(ATP)(Try)] [67] 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 [68] such as [Cu(phenylalanine)(norvalinate)] [69] a flexible hydrophobic interaction has been shown. Interligand interaction has also been proposed in [Cu(phe)(Try)] [70] where (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 histidine in addition to the hydrophobic interaction between two ligands.

(16) M. M. Taqui Khan and coworkers have determined the formation constants with complexes of adenine nucleotides with variety of metal ions [71-77]. 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 [71,77,78].

(17) A. Oriodi and coworkers [77] have carried out X-ray study of [M(bipy) (ATP)] complex. According to them there are two types of stacking interactions (i) Intarmolecular and (ii) Intermolecular.

(18) H. Sigel et al.[78] have synthesized the mixed ligand 2,2'-bipyridyl-Cu^{2+} - nucleotide complexes exist in a folded form 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.

(19) An interesting research on synthesis, crystal structure and magnetic properties of tetrakis [diaqua(μ-1,3-dimethylviolurato)-Copper(II)] tetraperchlorate dihydrate have been investigated by L. E. Colacio et al [79]. The structure of this complex is square planar. From variable temperature magnetic susceptibility measurements the compound was found to exhibit a very strong antiferromagnetic character.

(20) 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 M. Barandika et al [80] . The results indicate that the anitiferromagnetic contribution of the global coupling constant is decreased.

(21) 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, L. K. Thompson and coworkes [81-83] experimentally confirmed the angle dependence of the crossover between ferro and anitiferromagnetic couplings for a variety of copper (II) dimers.

(22) According to a recent study by O. Kahn and coworkers [84] based on experimentally obtained spin density maps for a particular copper (II) dimer exhibiting di-μ-N_3, bridges, neither of the mechanisms cited above is co-operative.

(23) T. Murakami et al [85] have investigation on the stabilities and spectral properties of five coordinate mixed ligand Cu(II) complexes containing penta- methyl diethylenetriamine and α-amino acid.

(24) The μ-(η'-N: η^2 -O,O)-nitrito dinuclear compounds [Ni(μ-NO_2 $(NCS)_3$ $(Medpt)_2$]. H_2O and [Ni (μ-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 A. Escuer et al [86]. They reported that thiocyanate ligand appears to stabilise the

tridentate coordination mode of the nitrito ligand and the dinuclear compounds shows antiferromanetic character.

(25) H. Hoffmann and Yeager [87] 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)].

(26) Cis-trans isomerism in complexes of the kinetically labile cupric ion was reported by K. Tomita, [88] who suggested that while bis-glycinatocopper(II) monohydrate adopts a cis configuration, the dihydrate of this complex exists as the trans isomer.

(27) Synthesis and X-ray crystallographic studies on Cu(II) complexes with alanine have been investigated by R. D. Gillard et al [89] . They prepared light blue platelets and dark blue prismatic crystals of bisalaninatocopper(II) and they concluded that these represent trans and cis modifications respectively.

(28) D.L. Leussing et al [90] studied mixed Ni(II) and Zn(II) complexes involving glyoxalate and the amino acids e.g. glycine, α-alanine and α-aminoisobutyric 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.

(29) Mixed ligand complexes involving amino acid dithiocarbamates substituted phosphines and Ni(II) have been reported by S. Thirumaran et al [91]. They observed that all complexes are diamagnetic. Thermal decomposition of dithiocarbamate moiety proceeds through the formation of [Ni $(SCN)_2$ pph_3].

(30) M. Enamullah et al [92] have determined the proton-ligand and metal-ligand formation constants of phthalic acid with some transition metal ions such as Zn(II), Ni(II) Co(II) and Cd(II). It was found that the metal ions Zn(II) and Cd(II) form complexes at low ionic strength, $I \leq 0.1M$. Above this ionic strength such as I = 0.15 M, these ions seem to be inactive towards complexation with phthalate ions. The metal ions Co(II) and Ni(II) showed no appreciable complexation even at very low ionic strength, I = 0.02 M.

(31) G. R. Cayley and Hague [93] 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 $[Zn(pada)]^{2+}$.

(32) F. Nobuo et al.[94] have studied an interesting research on trinuclear cu^{II} Mn^{II} Cu^{II} complexes of an oxamide dioxime ligand and finally these have been extended to a bimetallic magnetic compound.

(33) T. H. Tarafder [95] 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.

1.4 AIM OF THE PRESENT INVESTIGATION

Coordination chemistry has embraced the most divers' branches of science and technology recently with its multidimensional uses. This coordination chemistry phenomenon has tremendous significance to life science. This was observed [96] 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.

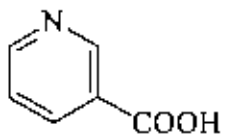
Previous studies involved a research work on the coordination behavior of some vitamins as biologically important ligands which are essential chemicals for the maintenance of normal metabolic functions. Recent studies also involve tyrosine as ligand, which regulate the endogenous analgesic activity of the peptides [97]. Lack of part studies and the fact that mixed ligand complexes could be expected to be more biologically active [98] than binary complex prompted us to undertake the present work.

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 Nicotinic acid (Nia), Pyridoxine (Pyri) and Ascorbic acid (AsA) and L refers to glycine, α-alanine, phenylalanine, and tyrosine. 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 [99,100]. The formations of the complexes have been confirmed by CV (Cyclic Voltammogram) and UV spectral studies.

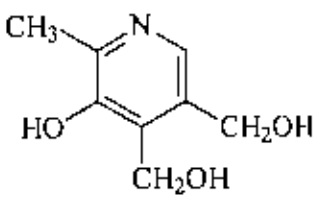
1.5 Ligands and their structure

In the present investigation, the formation constant as well as the stability constant of ternary complexes of the type [MAL] have been determined by using biological important ligands. In these complexes A refers to Nicotinic acid (Nia), Pyridoxine (Pyri) and Ascorbic acid (AsA) L refers to glycine (Gla), α–alanine (α-ala) phenylalanine, and tyrosine (Tyro). The structure of ligands (A and L) used in this study are as follows –

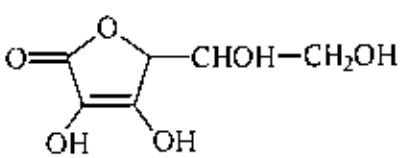
1. Nicotinic acid (Nia):



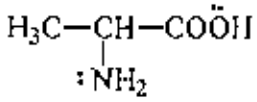
2. Pyridoxine (Pyri):



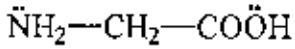
3. Ascorbic acid (AsA):



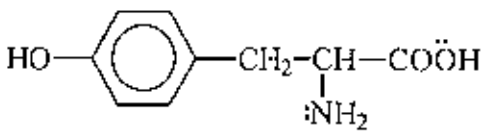
4. α-alanine (α-ala):



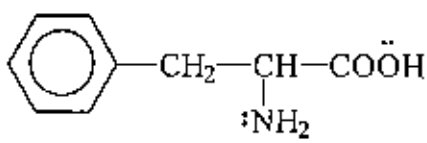
5. Glycine (gly) :



6. Tyrosine (Tryo) :



7. Phenyl alaline (Ph-ala) :



EXPERIMENTAL AND RESULT & DISCUSSION

EXPERIMENTAL

2.1 Apparatus and Chemicals

Apparatus

TOA pH-meter HM-2OS, Del Micro Computer with SCOGS Computer Programm, Carl Zeiss UV visible Spectrophotometer with CM Quartz Cell, Cyclic Voltammogram, Microburette and Glasswares of Pyrex glass were used. The microburette was calibrated to 0.01 mL by the method described by Vogel [101]. The measuring flask of various capacities, pipettes etc were also calibrated.

Chemicals

All the chemicals used were of analytical-reagent grade or the highest purity available. Doubly distilled de-ionized water, which is non-absorbent under ultraviolet radiation, was used. The important chemicals and solvent utilized throughout the experiments were listed below:

1) Sodium Perchlorate
2) Nicotinic acid
3) Pyridoxine
4) Ascorbic acid
5) Glycine
6) α- alanine
7) Phenylalanine
8) Tyrosine.
9) Perchloric acid (70%) [E. Merch, Germany]

2.2 Preparation of Metal Perchlorate

Metal Perchlorate was prepared from analytically pure metal carbonate by treatment with 70% perchloric acid (AR). The treatment was done in the following way:

About 100 ml 70% perchloric acid was taken in a 250 ml beaker and than metal perchlorate e.g. copper carbonate was added slowly with continuous steering. The addition of copper carbonate was continue until the bubble were disappears. Access amount of copper carbonate was added and kept it 12 hours to ensure the complete of the reaction. Than water-alcohol mixture was added with continuous steering and filtered. The resulting solids were filtered, washed with ethanol till free from excess acid and recrystallized several times from ethanol.(Copper perchlorate is partially soluble in alcohol).Copper perchlorate solution was also standardized by iodometric titration. Nickel perchlorate and zinc perchlorate were prepared with the same method.

Stock solution of perchloric acid, sodium hydroxide and sodium perchlorate were prepared in carbonate free double distilled de-ionized water. Carbonate free sodium hydroxide solution was prepared according to the literature method [102] and standardized by standard oxalic acid solution. Standard perchloric acid solution was prepared from AR 70% acid by proper dilution and titrated with standard alkali.

2.3 Synthesis of [Cu(Pyri)(α-ala)] complex

A solution containing equimolar amount of the ligands pyridoxine (5.0mmol) and α-alanine(5.0mmol) in 40ml water, was added to a solution of copper perchlorate(5.0mmol) dropwise. Than added a solution of NaOH (0.02M) dropwise till the precipitation was completed. The resulting solid was filtered, washed with water-alcohol mixture, followed by pure alcohol and dried in air. The crystals were grown from the conc. aqueous solution and subjected to XRD studies.

2.4 Elemental analysis of [Cu(Pyri)(α-ala)] complex

The complex was analysed for copper by acid decomposition, followed by iodometric titration and by complexometric titration with EDTA using pyrocatechol violet indicator in analytical laboratory. The result was recorded in the table no-2.2.13

2.5 Potentiometric Determination Stability Constant

Irving Rossotti titration technique [102,103] has been used to determine the formation constants of the ternary complexes using SCOGS (Stability Constant of Generalized Species) computer program [99,100]

The activity coefficient of H^+ under experimental condition has been considered to be equal to 1 and the value of the ionic product of water 14.167 has been used.

For the determination of the protonation constants of the ligands(L) the following sets of solution (50 cm^3) were prepared.

1) 0.02M $HClO_4$, 0.002M ligands(L) and 0.178M $NaClO_4$.
2) 0.02M $HClO_4$, 0.005M ligands(L) and 0.175M $NaClO_4$.

For the determination of the formation constants of the binary complexes ML, ML_2, where M= Cu(II), Ni(II) and Zn(II), L=Ascorbic acid, Pyridoxine, Nicotinic acid, α-alanine, Phenylalanine, Glycine and Tyrosine, the following sets of solution (50cm^3) having M:L in the ratio of 1:1 was prepared.

1) 0.02M $HClO_4$, 0.002M metal perchlorate, 0.002M ligands(L) and 0.176M $NaClO_4$.

For the determination of the formation constants of the ternary complexes [MAL], M= Cu(II), Ni(II) and Zn(II), A=Ascorbic acid, Pyridoxine, Nicotinic acid, L= α-alanine, Phenylalanine, Glycine and Tyrosine, the following solution (50cm^3) having M:A:L in the ratio 1:1:1 were prepared.

1) 0.02M $HClO_4$, 0.002M metal perchlorate, 0.002M ligand (A), 0.002M ligand (L) and 0.174M $NaClO_4$

All the prepared sets were titrated potentiometrically against standard (0.02M) sodium hydroxide solution. In all the cases acid concentration was kept 2.00×10^{-2} M and the total ionic strength (I) of the solution was

maintained at 0.2M. Titration of each sets were carried out twice to check the reproducibility of data.

All the titrations were carried out in aqueous medium and the temperature was maintained at 25°C±1°C during the progress of titration. Titration 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 solution 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 ($HClO_4$), 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 on. 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 [51,104]. 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 (2.2.1 to 2.2.3). The values of formation constants for the ternary complexes and Δlog K have been presented in Table (2.2.4 to 2.2.12). pH titration curves have been presented in Fig. 2.2.1-2.2.9 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 2.2.10 to 2.2.18.

EXPERIMENTAL DATA

Table – 2.2.1: 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	$\log K_1^H$	$\text{Log } \beta_2^H$	$\log K_{CuL}^{Cu}$	$\log K_{CuL_2}^{Cu}$
α-alanine	9.13	12.73	5.56	9.54
phenylalanine	9.20	11.12	4.80	8.55
Glycine	9.54	12.49	6.02	10.45
Tyrosine	9.56	16.88	4.78	8.81
Nicotinic acid	4.40	13.70	7.02	13.88
Pyridoxine	8.80	13.62	12.68	18.28
Ascorbic acid	11.25	15.29	11.75	19.36

Table – 2.2.2: 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	$\log K_1^H$	$\text{Log } \beta_2^H$	$\log K_{NiL}^{Ni}$	$\log K_{NiL_2}^{Ni}$
α-alanine	9.13	12.73	7.60	13.69
Glycine	9.54	12.49	6.30	12.57
Phenylalanine	9.20	11.12	7.46	14.12
Tyrosine	9.56	16.88	7.38	14.28
Nicotinic acid	4.40	13.70	6.31	7.96
Pyridoxine	8.80	13.62	9.94	16.23
Ascorbic acid	11.25	15.29	9.02	16.65

Table – 2.2.3: 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 β_2^H	log K_{ZnL}^{Zn}	log $K_{ZnL_2}^{Zn}$
α-alanine	9.13	2.73	4.64	8.60
Glycine	9.54	12.49	4.94	9.26
Phenylalanine	9.20	11.12	4.28	8.35
Tyrosine	9.56	16.88	4.18	8.27
Nicotinic acid	4.40	13.70	5.13	9.47
Pyridoxine	8.80	13.62	7.28	13.68
Ascorbic acid	11.25	15.29	8.86	14.12

Table – 2.2.4: Stability constant of mixed ligand complexes [Ni(AsA)(L)] in aqueous medium with I = 0.2 M ($NaClO_4$) at 25°C ± 1°C.

System	log K_{NiAL}^{Ni}	log K_{NiA}^{Ni}	log K_{NiAL}^{NiA}	log K_{Nil}^{Ni}	ΔlogK
[Ni(AsA)(α-ala)]	16.40	9.02	7.38	7.60	-0.22
[Ni(AsA)(Gly)]	14.79	9.02	5.77	6.30	-0.53
[Ni(AsA)(Ph-ala)]	16.42	9.02	7.40	7.46	-0.06
[Ni(AsA)(Tyro)]	16.60	9.02	7.58	7.38	0.20

Table – 2.2.5: Stability constant of mixed ligand complexes [Cu(AsA)(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(AsA)(α-ala)]	17.17	11.75	5.42	5.56	-0.14
[Cu(AsA)(Gly)]	17.54	11.75	5.78	6.02	-0.23
[Cu(AsA)(Ph-ala)]	16.68	11.75	4.93	4.80	0.13
[Cu(AsA)(Tyro)]	16.78	11.75	5.03	4.78	0.25

Table – 2.2.6: Stability constant of mixed ligand complexes [Zn(AsA)(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(AsA)(α-ala)]	13.56	8.86	4.70	4.64	0.06
[Zn(AsA)(Gly)]	13.72	8.86	4.86	4.94	-0.08
[Zn(AsA)(Ph-ala)]	13.42	8.86	4.56	4.28	0.28
[Zn(AsA)(Tyro)]	13.43	8.86	4.57	4.18	0.39

Table – 2.2.7: Stability constant of mixed ligand complexes [Ni(Pyri)(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(Pyri)(α-ala)]	17.43	9.94	7.49	7.60	-0.11
[Ni(Pyri)(Gly)]	15.76	9.94	5.82	6.30	-0.48
[Ni(Pyri)(Ph-ala)]	17.36	9.94	7.42	7.46	-0.04
[Ni(Pyri)(Tyro)]	17.65	9.94	7.71	7.38	0.33

Table – 2.2.8: Stability constant of mixed ligand complexes [Cu(Pyri)(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(Pyri)(α-ala)]	18.19	12.68	5.51	5.56	-0.05
[Cu(Pyri)(Gly)]	18.52	12.68	5.84	6.02	-0.18
[Cu(Pyri)(Ph-ala)]	17.68	12.68	5.00	4.80	0.20
[Cu(Pyri)(Tyro)]	17.93	12.68	5.25	4.78	0.47

Table – 2.2.9: Stability constant of mixed ligand complexes [Zn(Pyri)(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(Pyri)(α-ala)]	12.12	7.28	4.84	4.64	0.20
[Zn(Pyri)(Gly)]	12.25	7.28	4.97	4.94	0.03
[Zn(Pyri)(Ph-ala)]	12.02	7.28	4.74	4.28	0.46
[Zn(Pyri)(Tyro)]	12.25	7.28	4.97	4.18	0.79

Table – 2.2.10: Stability constant of mixed ligand complexes [Ni(Nia)(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(Nia)(α-ala)]	13.56	6.31	7.25	7.60	-0.35
[Ni(Nia)(Gly)]	12.06	6.31	5.75	6.30	-0.55
[Ni(Nia)(Ph-ala)]	13.37	6.31	7.06	7.46	-0.40
[Ni(Nia)(Tyro)]	13.84	6.31	7.53	7.38	0.15

Table – 2.2.11: Stability constant of mixed ligand complexes [Cu(Nia)(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(Nia)(α-ala)]	12.33	7.02	5.31	5.56	-0.25
[Cu(Nia)(Gly)]	12.57	7.02	5.55	6.02	-0.47
[Cu(Nia)(Ph-ala)]	11.62	7.02	4.60	4.80	-0.20
[Cu(Nia)(Tyro)]	11.97	7.02	4.95	4.78	0.17

Table – 2.2.12: Stability constant of mixed ligand complexes [Zn(Nia)(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(Nia)(α-ala)]	9.60	5.13	4.47	4.64	-0.17
[Zn(Nia)(Gly)]	9.71	5.13	4.58	4.94	-0.36
[Zn(Nia)(Ph-ala)]	9.27	5.13	4.14	4.28	-0.14
[Zn(Nia)(Tyro)]	9.59	5.13	4.46	4.18	0.28

Table- 2.2.13: Analytical data of [Cu(Pyri)(α-ala)] complex

Compound	Color	%M Obtained	%M Theoretical
[Cu(Pyri)(Gly)]	Light Green	19.4	19.6

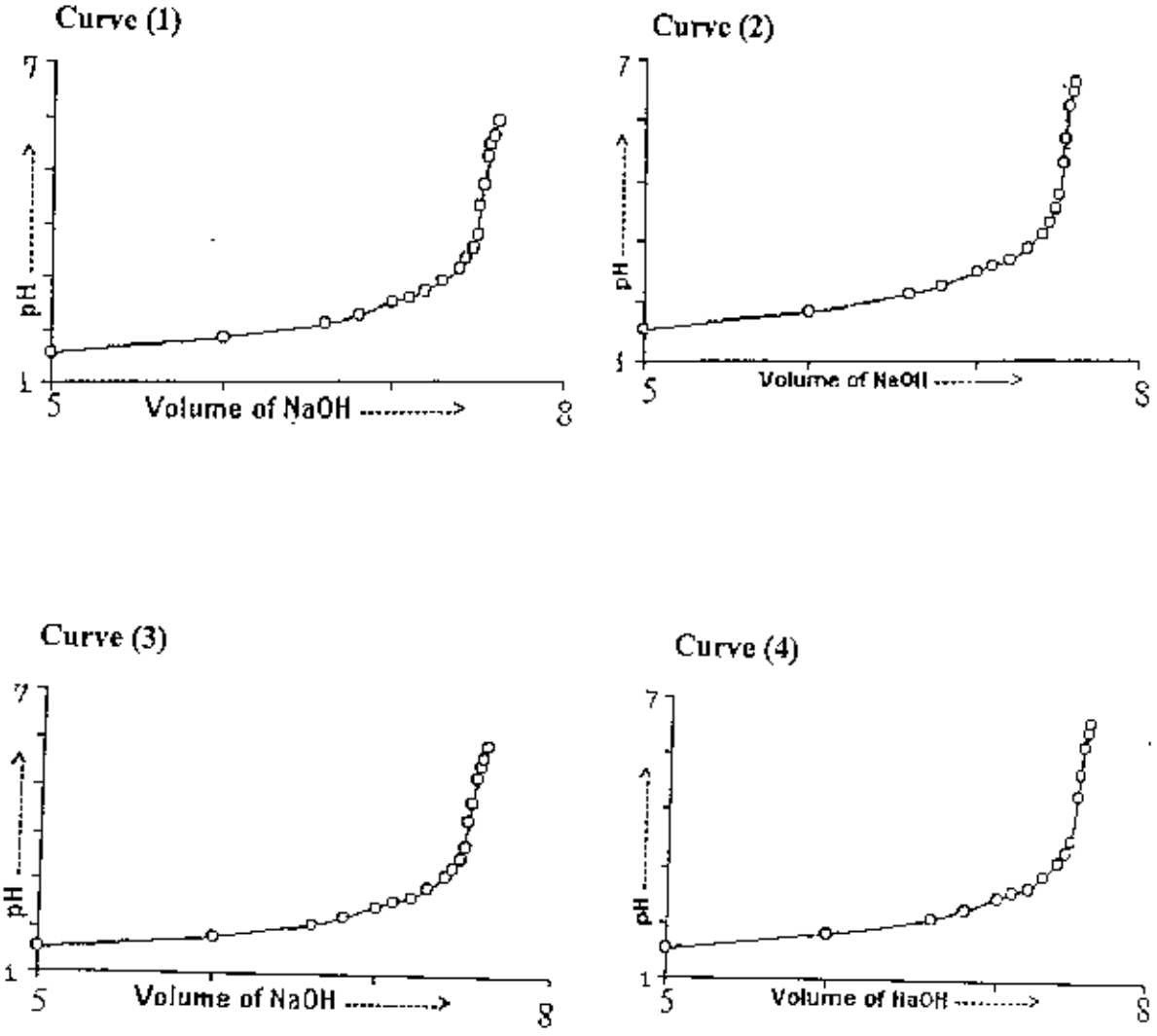


Fig- 2.2.1: Potentiometric titration curves of aqueous solutions containing metal ions, Ascorbic Acid (AsA) and L. (each 0.001M).
Curve (1) Cu^{2+} + AsA + Glycine
Curve (2) Cu^{2+} + AsA + α-alanine
Curve (3) Cu^{2+} + AsA + Phenyl alanine
Curve (4) Cu^{2+} + AsA + Tyrosine

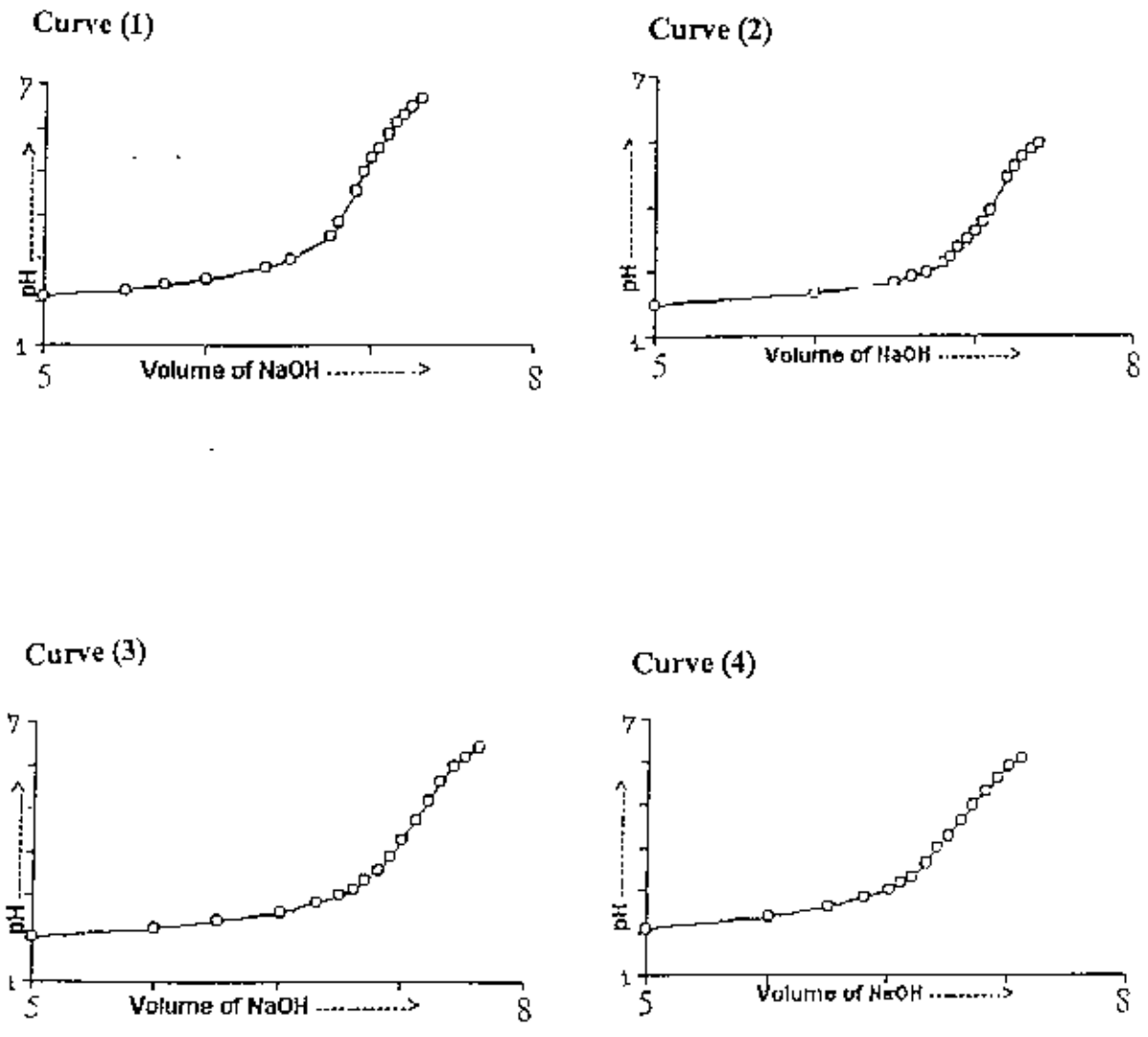


Fig- 2.2.2: Potentiometric titration curves of aqueous solutions containing metal ions, Ascorbic Acid (AsA) and L. (each 0.001M).
Curve (1) Ni^{2+} + AsA + Glycine
Curve (2) Ni^{2+} + AsA + α-alanine
Curve (3) Ni^{2+} + AsA + Phenyl alanine
Curve (4) Ni^{2+} + AsA + Tyrosine

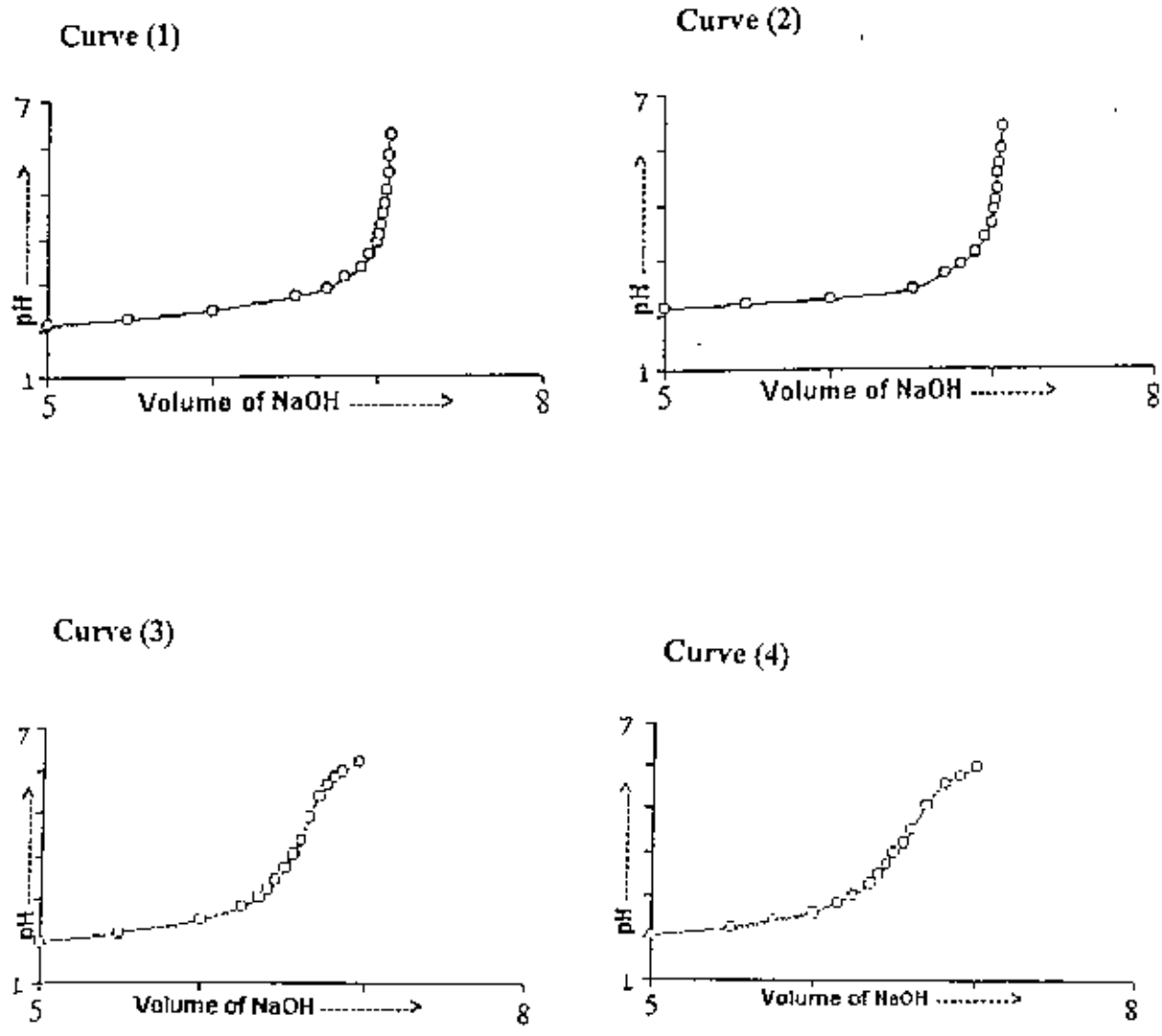


Fig- 2.2.3: Potentiometric titration curves of aqueous solutions containing metal ions, Ascorbic Acid(AsA) and L. (each 0.001M).
Curve (1) Zn^{2+} + AsA + Glycine
Curve (2) Zn^{2+} + AsA + α-alanine
Curve (3) Zn^{2+} + AsA + Phenyl alanine
Curve (4) Zn^{2+} + AsA + Tyrosine

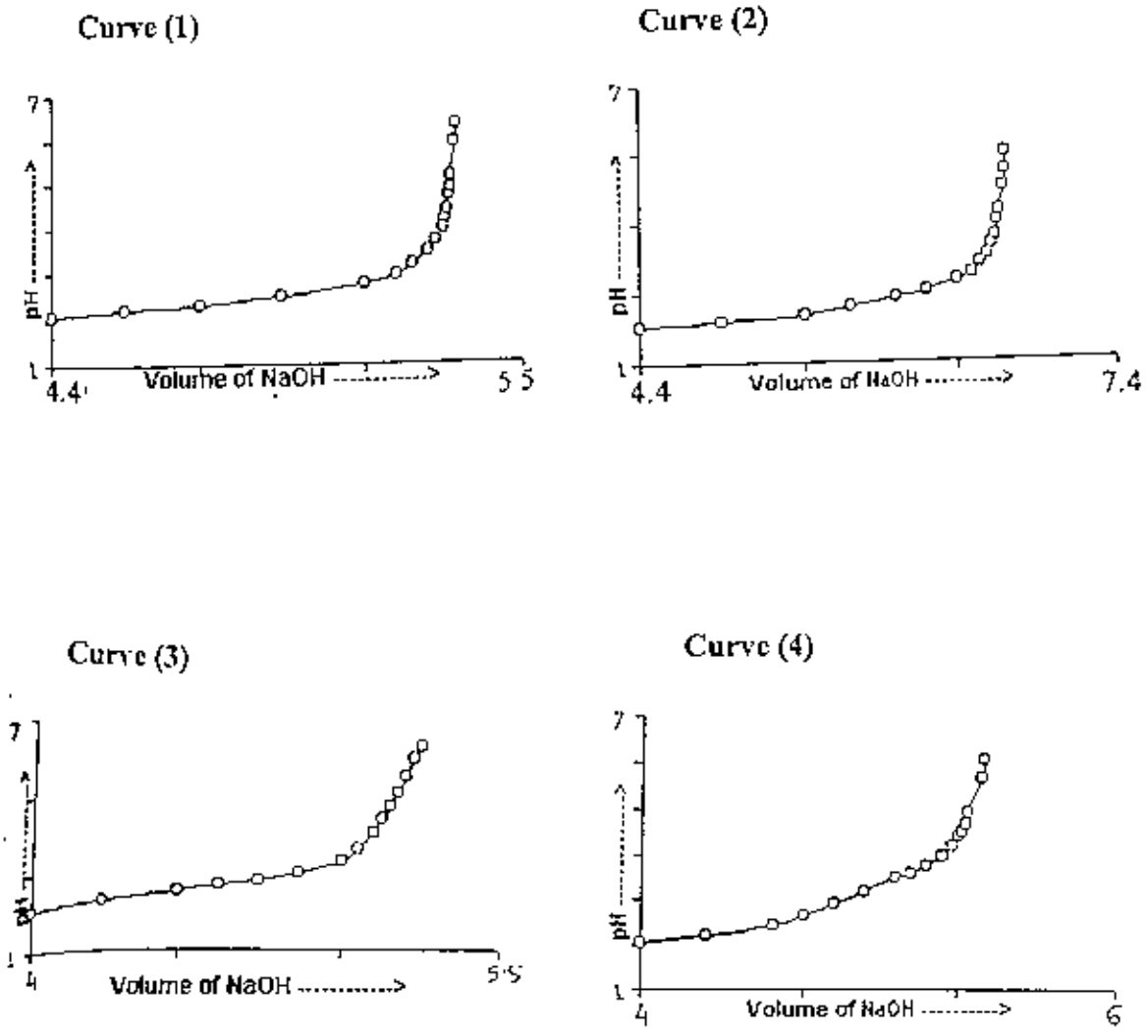


Fig- 2.2.4: Potentiometric titration curves of aqueous solutions containing metal ions, Nicolinic acid(Nia) and L. (each 0.001M).
Curve (1) Cu^{2+} + Nicotinic acid + Glycine
Curve (2) Cu^{2+} + Nicotinic acid + α-alanine
Curve (3) Cu^{2+} + Nicotinic acid + Phenyl alanine
Curve (4) Cu^{2+} + Nicotinic acid + Tyrosine

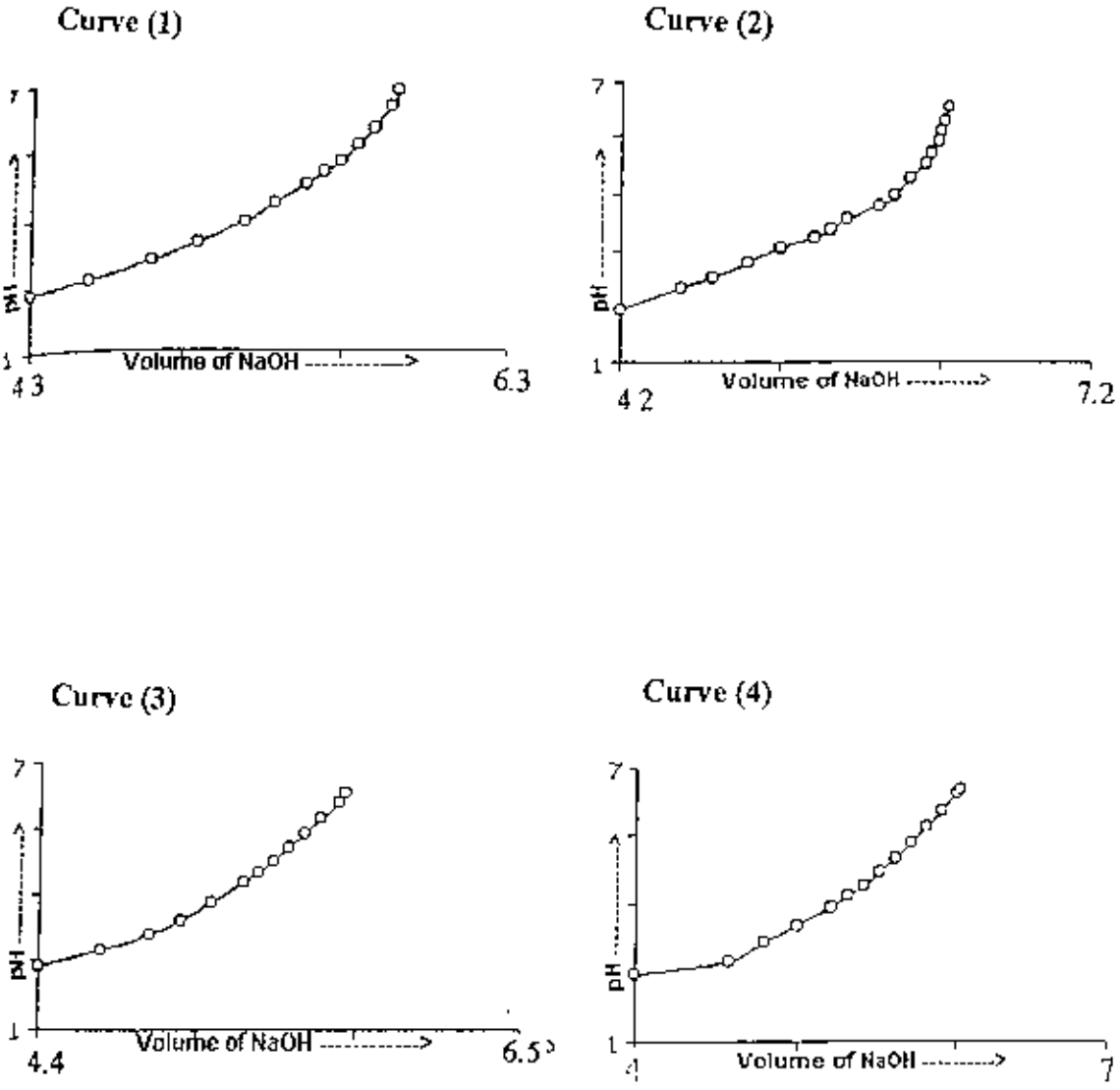


Fig- 2.2.5: Potentiometric titration curves of aqueous solutions containing metal ions, Nicotinic acid (Nia) and L. (each 0.001M).
Curve (1) Ni^{2+} + Nicotinic acid + Glycine
Curve (2) Ni^{2+} + Nicotinic acid + α-alanine
Curve (3) Ni^{2+} + Nicotinic acid + Phenyl alanine
Curve (4) Ni^{2+} + Nicotinic acid + Tyrosine

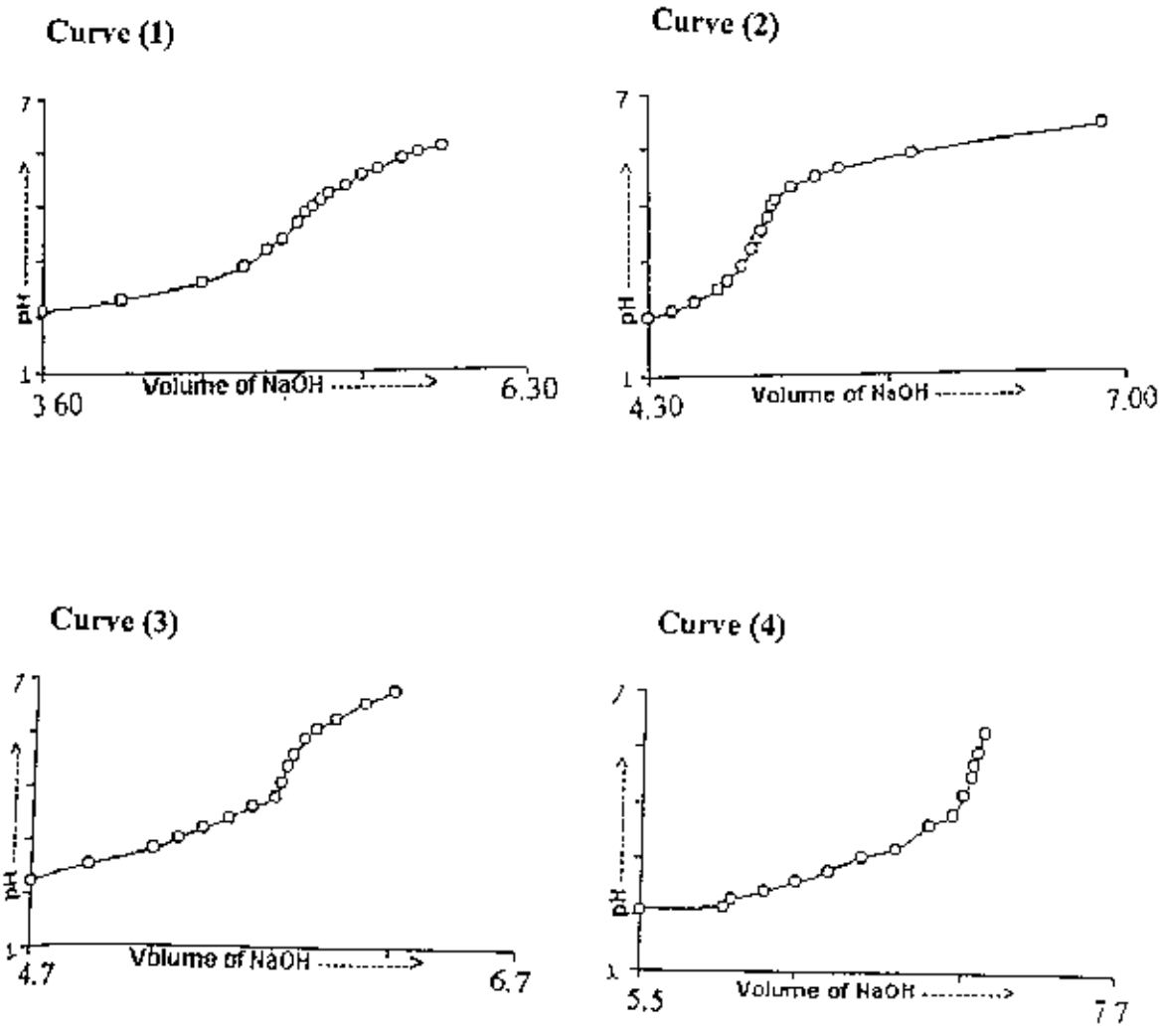


Fig- 2.2.6: Potentiometric titration curves of aqueous solutions containing metal ions, Nicotinic acid (Nia) and L. (each 0.001M).
Curve (1) Zn^{2+} + Nicotinic acid + Glycine
Curve (2) Zn^{2+} + Nicotinic acid + α-alanine
Curve (3) Zn^{2+} + Nicotinic acid + Phenyl alanine
Curve (4) Zn^{2+} + Nicotinic acid + Tyrosine

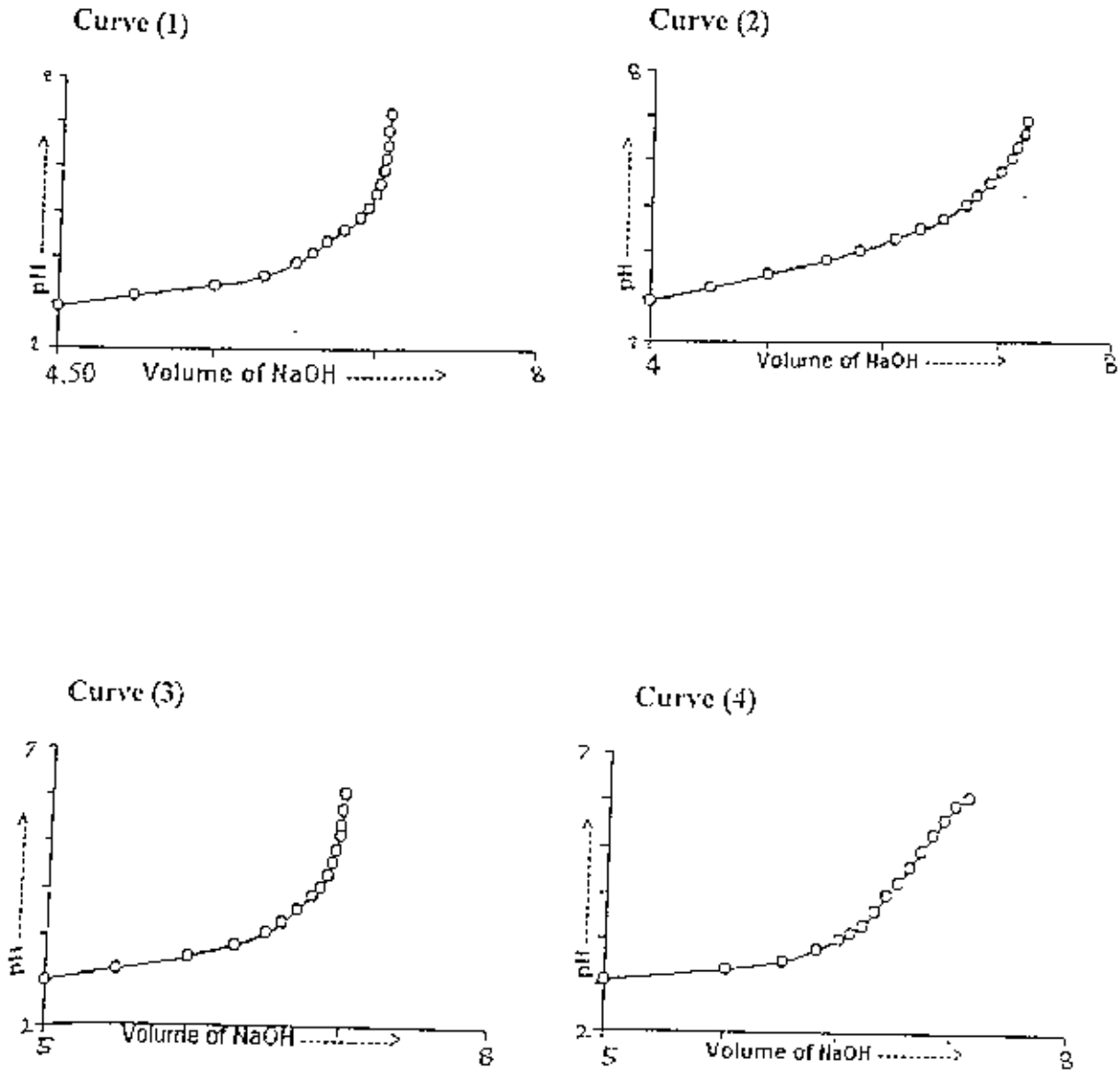


Fig- 2.2.7: Potentiometric titration curves of aqueous solutions containing metal ions, Pyridoxine (Pyri) and L. (each 0.001M).
Curve (1) Ni^{2+} + Pyridoxine + Glycine
Curve (2) Ni^{2+} + Pyridoxine + α-alanine
Curve (3) Ni^{2+} + Pyridoxine + Phenyl alanine
Curve (4) Ni^{2+} + Pyridoxine + Tyrosine

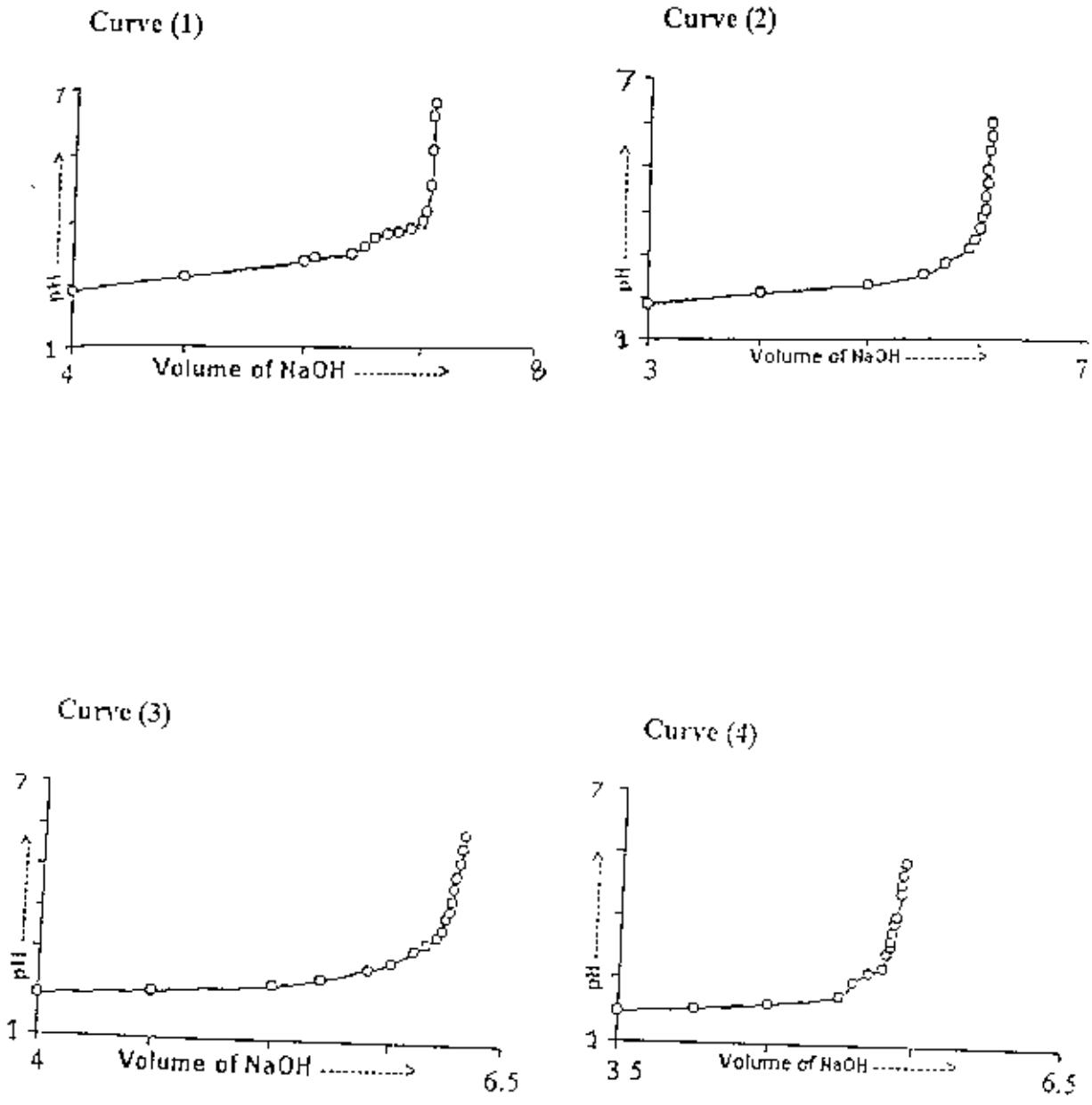


Fig- 2.2.8: Potentiometric titration curves of aqueous solutions containing metal ions, Pyridoxine (Pyri) and L. (each 0.001M).
Curve (1) Cu^{2+} + Pyridoxine + Glycine
Curve (2) Cu^{2+} + Pyridoxine + α-alanine
Curve (3) Cu^{2+} + Pyridoxine + Phenyl alanine
Curve (4) Cu^{2+} + Pyridoxine + Tyrosine

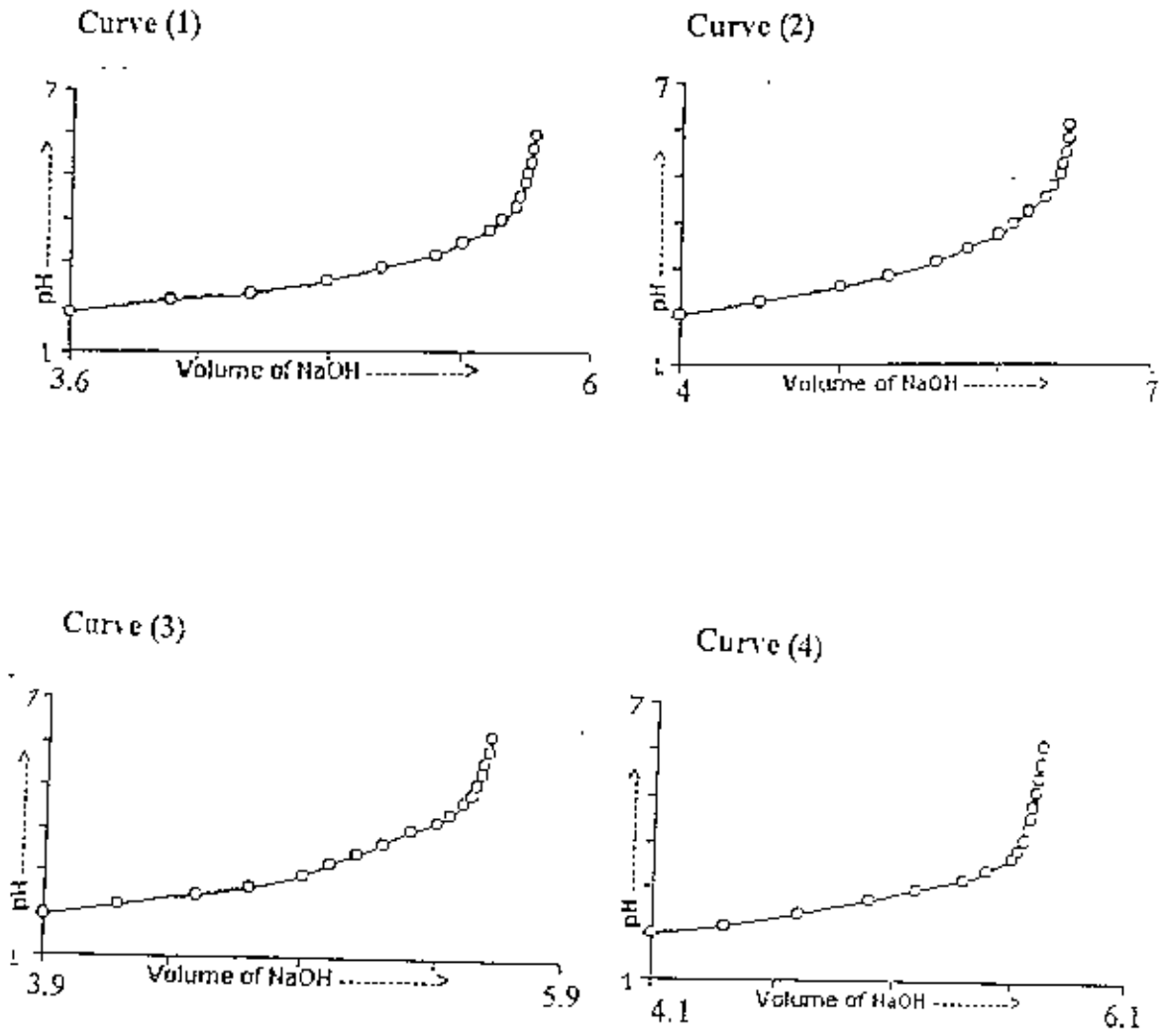


Fig- 2.2.9: Potentiometric titration curves of aqueous solutions containing metal ions, Pyridoxine (Pyri) and L. (each 0.001M).
Curve (1) Zn^{2+} + Pyridoxine + Glycine
Curve (2) Zn^{2+} + Pyridoxine + α-alanine
Curve (3) Zn^{2+} + Pyridoxine + Phenyl alanine
Curve (4) Zn^{2+} + Pyridoxine + Tyrosine

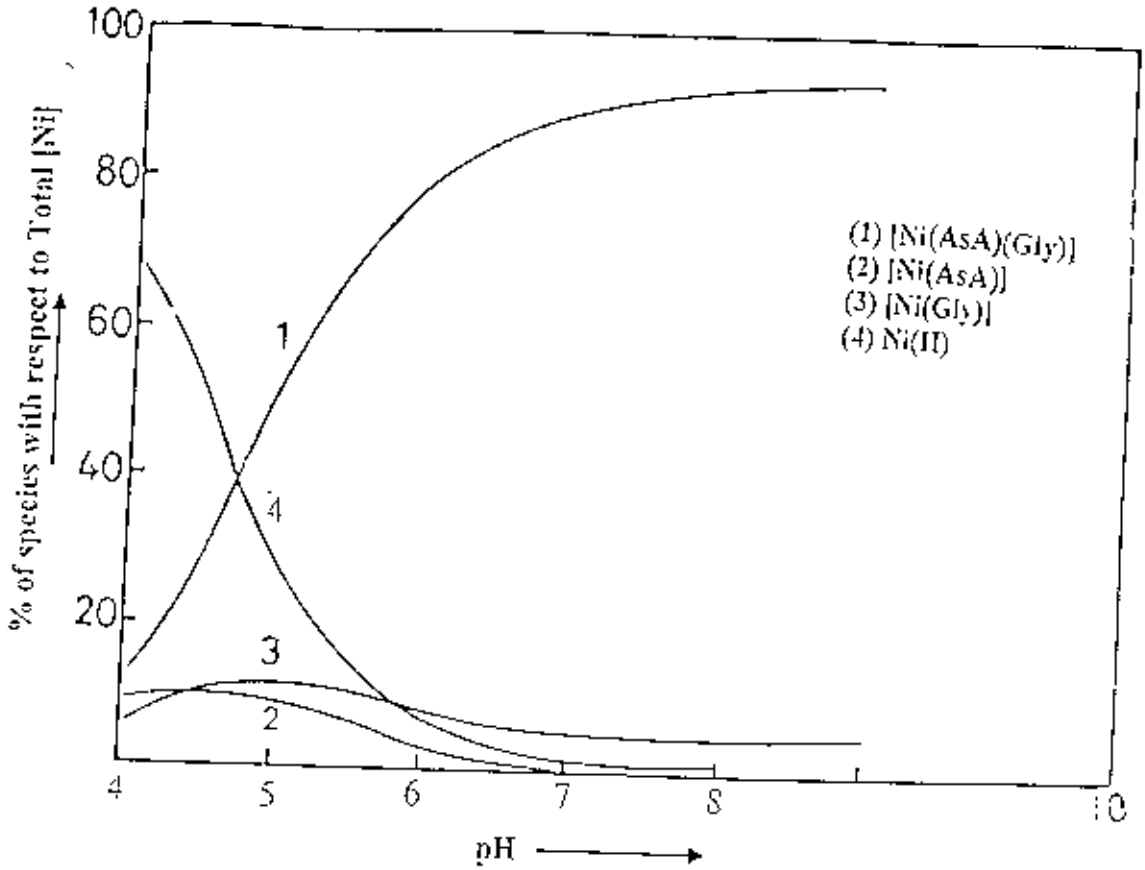


Fig – 2.2.10: Species distribution diagram for the [Ni (AsA) (Gly)] ternary system showing the formation percentages relative to total concentration of the metal as the function of pH.

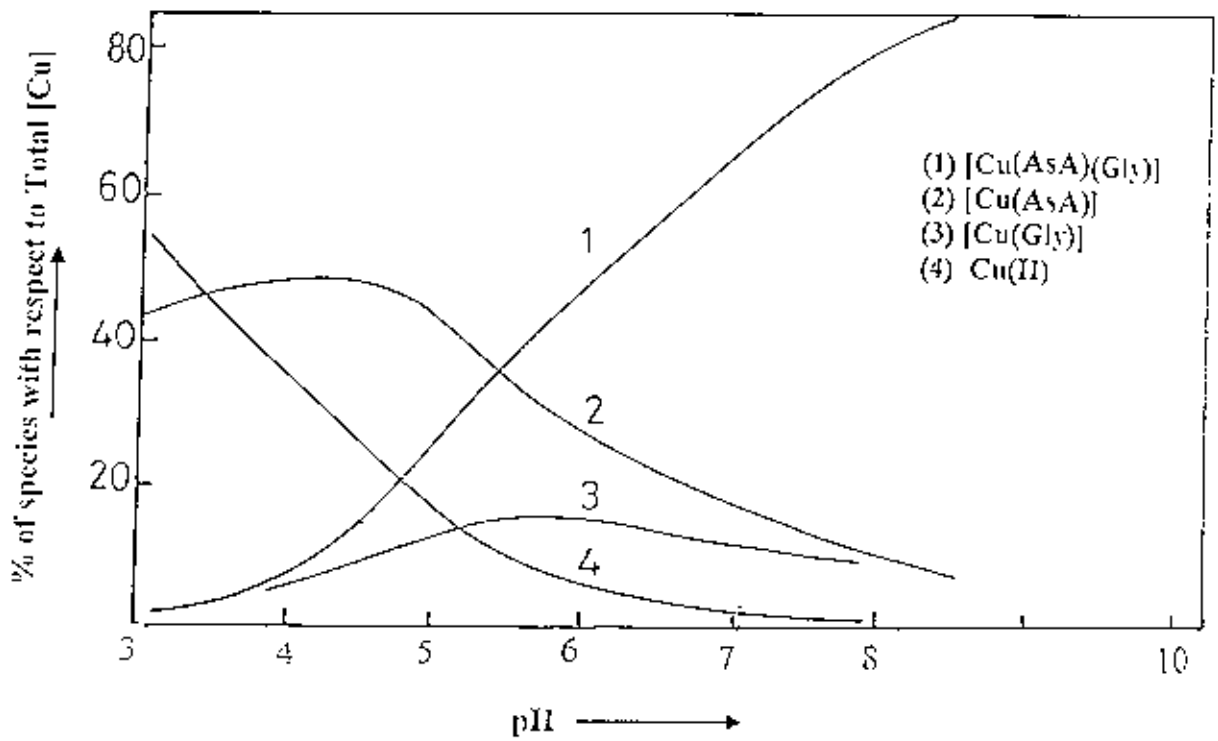


Fig – 2.2.11: Species distribution diagram for the [Cu (AsA) (Gly)] ternary system showing the formation percentages relative to total concentration of the metal as the function of pH.

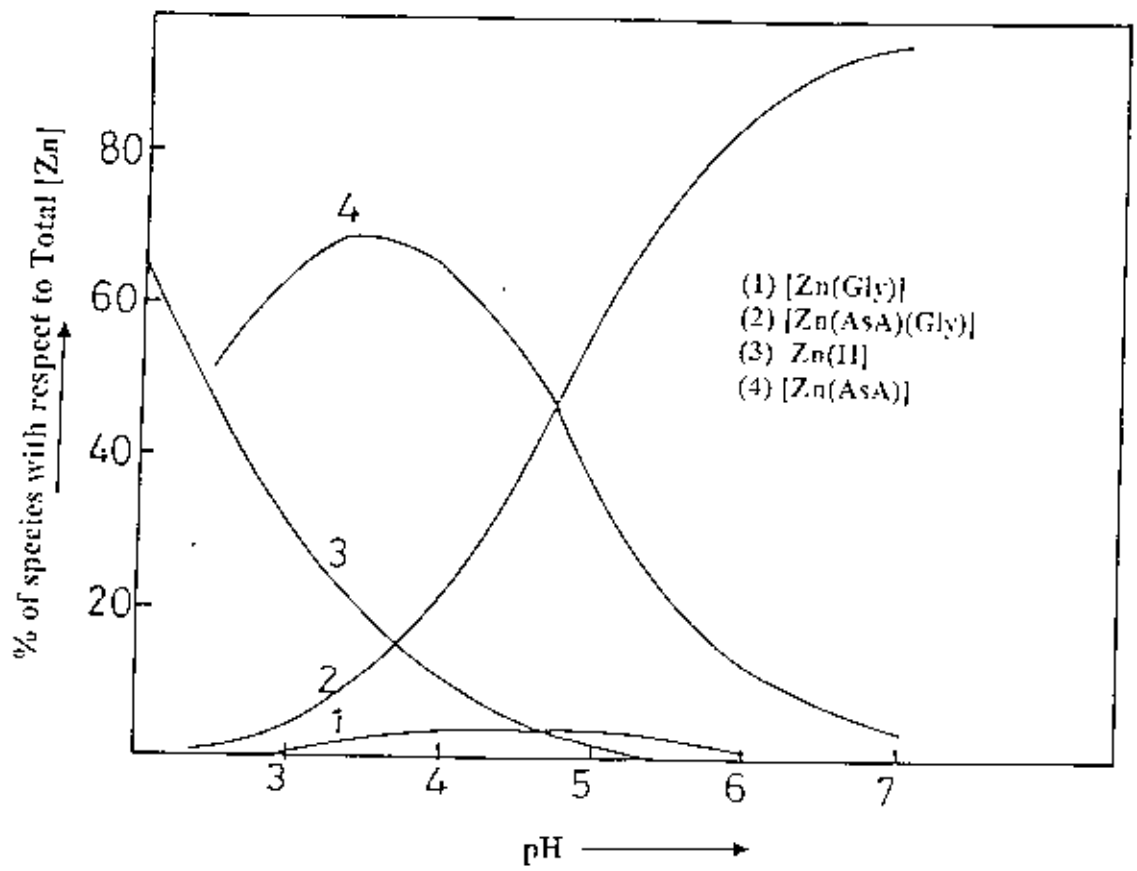


Fig – 2.2.12: Species distribution diagram for the [Zn (AsA) (Gly)] ternary system showing the formation percentages relative to total concentration of the metal as the function of pH.

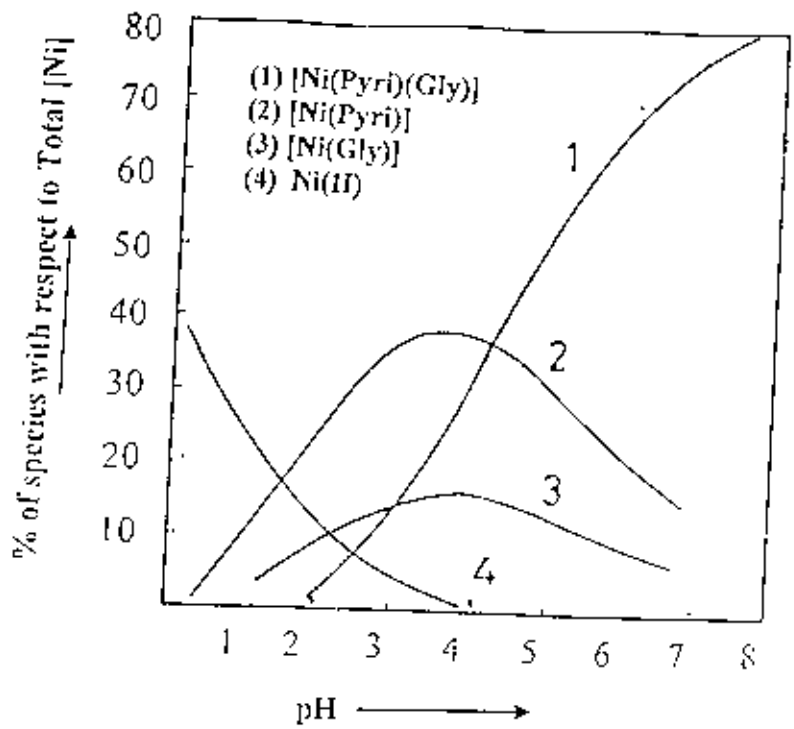


Fig – 2.2.13: Species distribution diagram for the [Ni (Pyri) (Gly)] ternary system showing the formation percentages relative to total concentration of the metal as the function of pH.

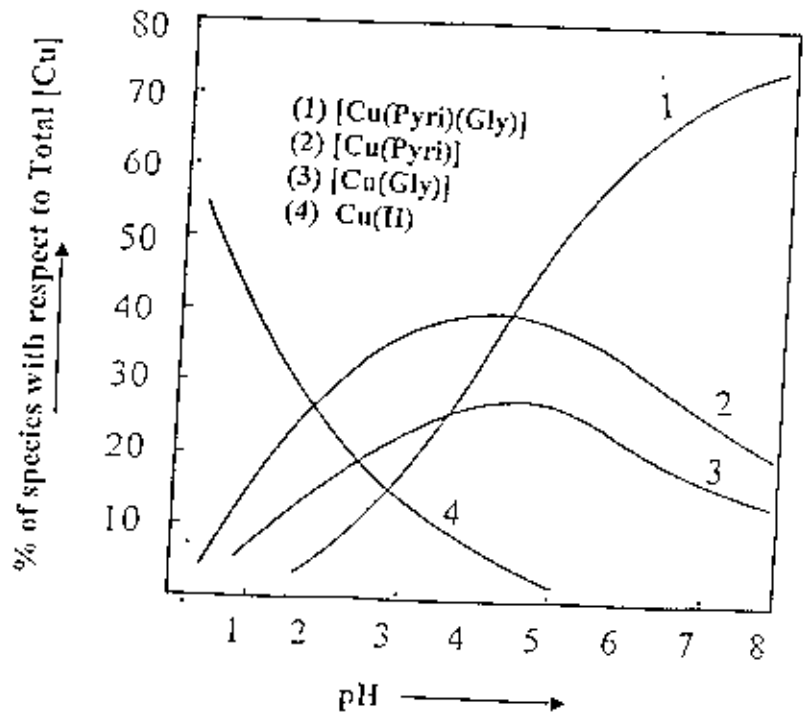


Fig – 2.2.14: Species distribution diagram for the [Cu (Pyri) (Gly)] ternary system showing the formation percentages relative to total concentration of the metal as the function of pH.

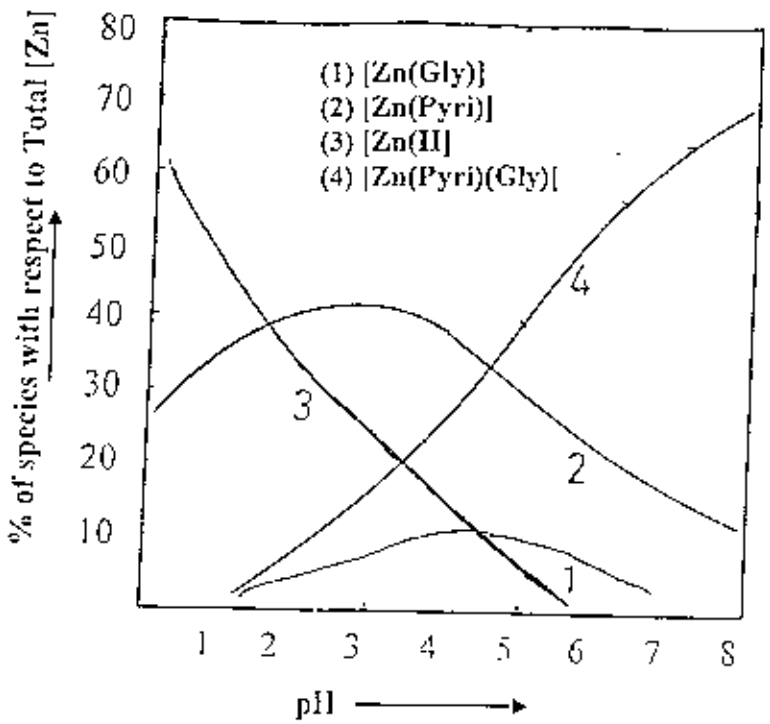


Fig – 2.2.15: Species distribution diagram for the [Zn (Pyri) (Gly)] ternary system showing the formation percentages relative to total concentration of the metal as the function of pH.

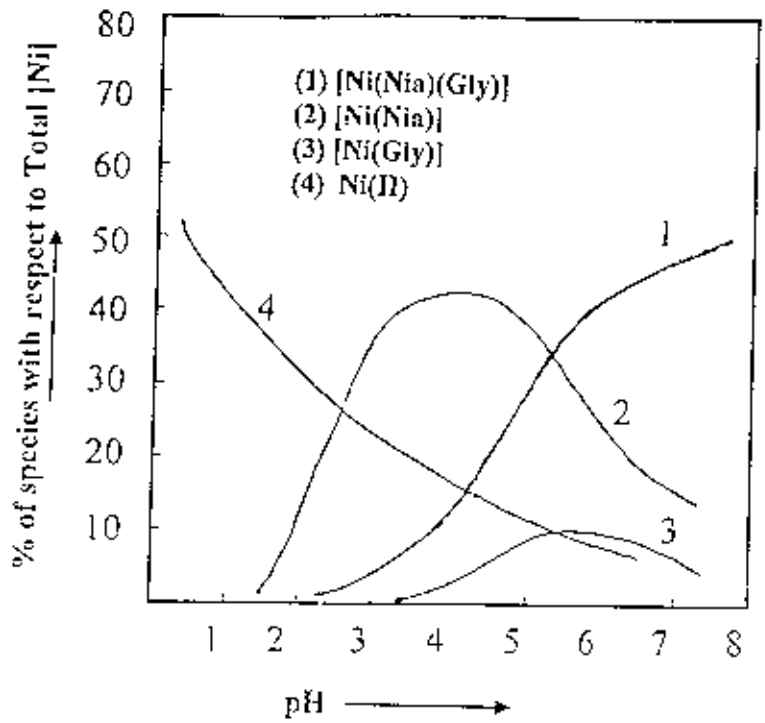


Fig – 2.2.16: Species distribution diagram for the [Ni (Nia) (Gly)] ternary system showing the formation percentages relative to total concentration of the metal as the function of pH.

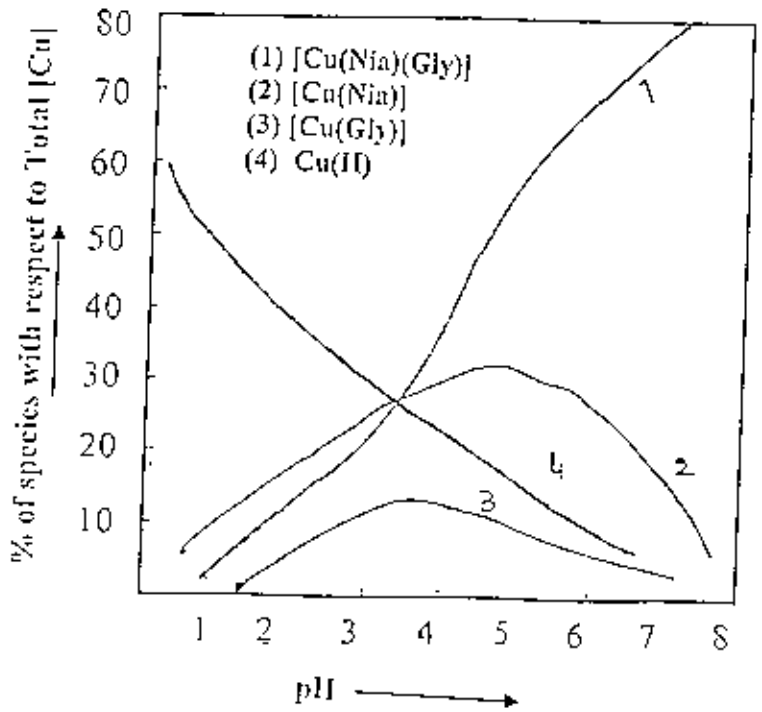


Fig. 2.2.17: Species distribution diagram for the [Cu (Nia) (Gly)] ternary system showing the formation percentages relative to total concentration of the metal as the function of pH.

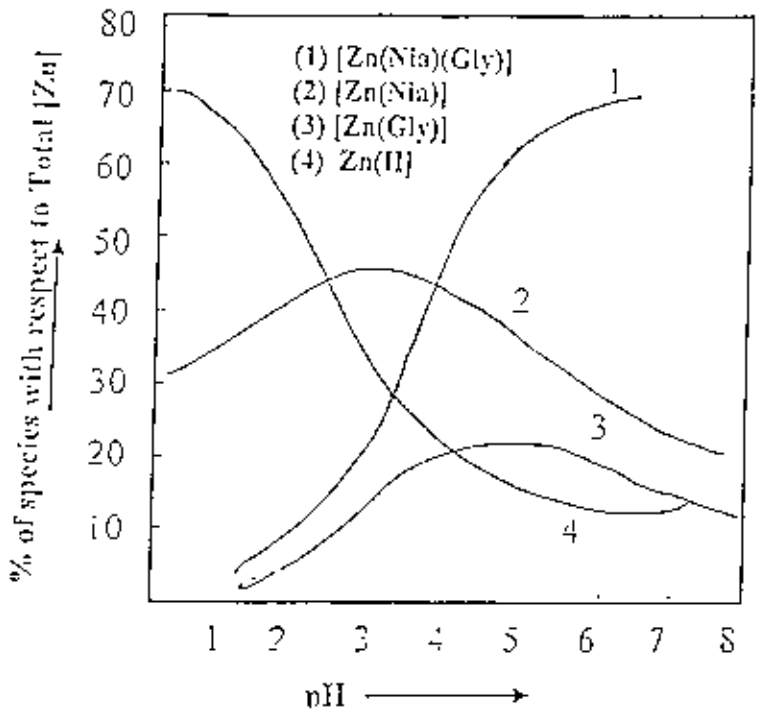


Fig. 2.2.18: Species distribution diagram for the [Zn (Nia) (Gly)] ternary system showing the formation percentages relative to total concentration of the metal as the function of pH.

RESULTS AND DISSCUSSION

Results & Discussion

[M(AsA)L] system

Stability constant of ternary complexes [MAL] type where M =Cu(II), Ni(II) & Zn(II), A =Ascorbic Acid (AsA), and L =glycine(gly), α-alanine (α-ala), phenylalanine (ph-ala), and tyrosine (tyro).

The analysis of the representative species distribution curves (fig-2.2.10 to 2.2.12) shows that in the pH range 1.5-3.5, M(II) (free metal ion) is the major species. In the pH range 3.5- 5, [ML] and [MA] is predominating and in the pH range 5-6 the species [MAL] is exist. The percentage of all other species is less than 1% in case of [M(AsA)(L)] system. This is because ascorbic acid (AsA) forms stable binary complex M-AsA (MA) at low pH and L combines with [MA] to form [MAL] ternary complex.

It is observed that in all cases of L, 1st protonation constant is grater than the 2nd protonation constant and $\log K_1$ is grater than $\log K_2$ and this is expected from statistical consideration. Only two protonation constants of Ascorbic Acid could be determined. These correspond to those for the phenolic OH. The protonation of the phenolic OH is reduced because of the presence of double bond in the furine ring.[105]

It is observed that for the complexes [Cu(AsA)(L)], [Ni(AsA)(L)] and [Zn(AsA)(L)]; where L = ph-ala and tyro, ΔlogK value (Table no-2.2.4 to 2.2.6) is less negative than the complexes where L =gly and α-ala. This is because of intramolecular interligand interaction. These amino acids (L) are bidentate, hence occupy two equatorial positions or one equatorial and one axial position. The non-coordinated side group, phenyl and hydroxy

phenyl ring of phenylalanine and tyrosine respectively come over furine ring of ascorbic acid [fig-2.5.1(C)] and hence non covalent hydrophobic interaction is possible [106]. This intramolecular interligenal interaction stabilizes the ternary complex leading to less negative Δlogk or positive Δlogk values.

Another reason for positive values of Δlogk in [Cu(AsA)(L)], [Ni(AsA)(L)] and [Zn(AsA)(L)] where L = Tyrosine is due to hydrogen bonding between the phenolic OH of the side group of tyrosine and carbonyl O of ascorbic acid. However, no such H-bonding interaction is possible for phenylalanine, glycine and α alanine. This electrostatic H-bonding intraction [fig-2.5.1(d)] results stable ternary complex of positive or less negative Δlogk values. [107]

In case of Cu(II) complexes Δlogk value (Table no-2.2.5) is less negative then that of Ni(II) complexes (Table no-2.2.4) i.e. Cu^{2+} form stable complex than Ni^{2+}. This is because of d^9 electronic configuration of Cu^{2-}, which is subjected to Jahn-Teller distortion effect. Distortion splits the degeneracy, lower symmetry and there by increase stability of the complex[108]. There is an additional stabilization of the octahedral complex due to distortions [109] and hence Cu(II) form more stable complex.

It is interesting fact that for the complexes of [M(AsA)(L)] where M = Zn(II), L = gly, α-ala, ph-ala and tyro shows less negative or positive Δlogk values (Table no-2.2.6). Though this fact is not run as expectation from the statistical value. This observation indicates that the complex

[Zn(AsA)(L)] is more stable as compared to the (Cu(AsA)(L)] and [Ni(AsA)(L)] complexes (Table no-2.2.5 & 2.2.4), where L = gly, α-ala, ph-ale, and tyro. This can be explained on the basis of the 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 ligands in its coordination sphere. If different types of ligand coordinate to the central metal ion easily i e accommodate the space in there coordination sphere, the rate of the formation of ternary complexes will move in a favourable direction and stable complexes will be formed. When a bulky gronp is either attached to or present near the donor atom of a ligand mutnal repulsion among the ligands occurs and consequently the metal-ligand bond is weakened. Thus 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 fonn 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 [110].

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(AsA)(L)] > [Cu(AsA)(L)] > [Zn(AsA)(L)]

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

Besides of the fact Zn(II) have coordination number 4 and it follows sp^3 hybridization in forming complex [110] i.e. its complex fits into tetrahedral geometry. It prefers a tetrahedral geometry [111] over on octahedral and

square planar, as the ligand-ligand repulsion is minimum in a tetrahedral geometry. This is due to the fact that in a tetrahedral geometry the four ligands are situated at the four corners of a regular tetrahedron. The angular distance [112] between them is 109°28′. But in an octahedral and a square planar structure the ligands are situated at on 90° angle about the central metal ion. This leads to close proximity of ligands in an octahedral and sqnare planar structure. Hence octahedral and square planar structure shows higher ligand-ligand mutual repulsion over the ligand-ligand mutual repulsion in a tetrahedral structure. The complex of metal ion e.g. Cu (II) and Ni(II) shows square planar and octahedral geometry. Hence the complex [Zn(AsA)(L)] undergo higher stability over the stability of [Cu(AsA)(L)] and [Ni(AsA)(L)] complexes.

[M(Pyri)(L)] system

Stability constant of ternary complexes [MAL] type where M =Cu(II) Ni(II) and Zn(II), A =Pyridoxine(Pyri) and L =glycine(gly) α-alanine(α-ala), phenylalanine(ph-ala) and tyrosine(tyro).

The analysis of representative species distribution curves (plot of concentration of various species) as a function of pH (fig-2.2.12 to 2.2.15) shows that in the pH range 1-3 M(II) is the Major species. In the pH 3-5 [MA], [ML] is the major species and in the pH range 5-7 [MAL] exist. The percentage of the species $[ML_2]$, $[MA_2]$ are very less. This indicates that the formation of [MAL] ternary complexes takes place by simultaneous coordination of A and L with the Metal ion.

$$M + A + L \rightarrow MAL$$

It is observed that in all cases of L, 1st protonation constant is grater than the 2nd protonation constant and $\log K_1$ is grater than $\log K_2$ and this is expected from statistical consideration. Only two protonation constants of Pyridoxine could be determined. These correspond to those for the phenolic OH and pyridyl nitrogen (tertiary amine).

It is reported that for the complexes of [M(Pyri)(L)] where M =Cu(II), Ni(II) & Zn(II), ΔlogK value (Table no-2.2.7 to 2.2.9) is less negative even positive for L =ph-ale and tyro than L =gly & α-ala. This is because of intramolecular interligand interaction. These amino acids are bidentate, which occupy two equatorial positions or one equatorial and one axial position. The non-coordinated side group of phenyl and hydroxyphenyl of phenylalanine and tyrosine respectively come over the pyramidal ring of pyridoxine leading to an intramoleculer stacking interaction [fig-2.5.2(C)].

This interligand interaction stabilizes the ternary complex landing to less negative ΔlogK or positive ΔlogK.

Another reason for extra stabilization (positive ΔlogK) of tyrosine complex is due to hydrogen bonding between the phenolic OH of the side group of tyrosine and alcoholic O of pyridoxine. However, no such H-bonding interaction is possible for ph-ala, α-ala & gly. This electrostatic H-bonding interaction [fig-2.5.2(D)] results stable ternary complex of positive or less negative ΔlogK value.

It is also observed that Δlogk value is more negative for the Ni(II) complexes (Table no-2.2.7) compared to Cu(II) complexes (Table no-2.2.8) in case of glycine, α- alanine, phenylalanine and tyrosine. This is because of Jahn-Teller effect.

The complexes [Zn(Pyri)(L)] are more stable as compared to the [Cn(Pyri)(L)] and [Ni(Pyri)(L)] complexes, where L = gly, α-ala, ph-ala and tyro. This can be explained on the basis of the size of metal atom which involves in complexion. With the increase in size of the metal atom, the ligand can donate electron pairs more easily to the central metal ion. For this, the steric effect between bulky group of ligand is decreased in complex compound and hence more easily it can form complexes of greater stability. The size of the atom is expressed in terms of atomic radii. The atomic radii of the Zn (1.25A°) metal atoms are higher than that of the atomic radii of Cu (1.17 A°) and Ni (1.15A°) metal atom [110]. For this reason, in our present investigation the [Zn(Pyri)(L)] complexes acquires higher stability compared to the stability of [Cu(Pyri)(L)] and [Ni(Pyri)(L)] complexes.

Besides of the fact that Zn(II) have coordination number 4, and it complex fits into a tetrahedral structure. It prefers a tetrahedral geometry over an octahedral or square planar, as the ligand-ligand repulsion is minimum in a tetrahedral geometry [111]. This is due to the fact that the four ligands are situated at the four corners of a regular tetrahedron. The tetrahedral angle is 190°28′. But in an octahedral and a square planar structure the ligands are situated at a 90° angle about the central metal ion [112]. 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 repulsion over ligand-ligand mutual repulsion in tetrahedral structure. The metal ion Ni(II) and Cu(II) in complex shows octahedral and square planar geometry. Hence the complex [Zn(Pyri)(L)] undergo higher stability over the [Cu(Pyri)(L)] and [Ni(Pyri)(L)] complexes.

It is also observed that [M(Pyri)(L)] complex is more stable than [M(AsA)(L)] and [M(Nia)(L)] complexes. This is because of M → N tertiary amine π - interaction. As a result the electron density over the metal ion is reduced. Thus the σ- bonding tendency of L to combine with $[MA]^{2+}$ is increase. So M → A, π-interaction goes on increase and the ternary complex is stabilized more.

[M(Nia)(L)] system

Stability constant of ternary complexes [MAL] type where M =Cu(II), Ni(II) & Zn(II), A =Nicotinic acid(Nia) and L =glycine(gly), α-alanine(α-ala), phenylalanine(ph-ala) and tyrosine(tyro).

The analysis of the representative species distribution curves (Fig-2.2.16 to 2.2.18) shows that in the pH range 1-3, metal ion is the major species. In the pH range 3-5, the species [MA] [ML] is predominating. In the pH range 5-7, the species [MAL] exist.

It is observed that for the complexes of [M(Nia)(L)] where M =Cu(II), Ni(II) & Zn(II), ΔlogK value (Table no-2.2.10 to 2.2.12) is less negative even positive for L =ph-ala and tyro than L =gly & α-ala. This due to the fact that intramolecular interligand interaction involves in complex. The non-coordinated side group of phenyl and hydroxyphenyl of phenylatanine and tyrosine respectively come over the pyridyl ring of the Nicotinic Acid [fig-2.5.3(C)] and hence non covalent hydrophobic interaction is possible. This intramolecnlar interligand interaction stabilizes the ternary complex, leading to more positive ΔlogK values.

Another reason for extra stabilization of tyrosine complex is due to hydrogen bonding between the phenolic OH of the side gronp of tyrosine and carboxylic O of Nicotinic Acid [fig-2.5.3(D)]. However, no such H-bonding interaction is possible for ph-ala, α-ala & gly. This electrostatic H-bonding interaction results stable ternary complex of positive or less negative ΔlogK valne.

It is investigated that for the complexes of [M(Nia)(L)] type the ΔlogK values are more negative in case of Ni(II) complexes (Table no-2.2.10) compared to Cu(II) complexes (Table no-2.2.11). This is because of the presence of Jahn-Teller effect.

It is also reported that for the complexes of [M(Nia)(L)] where M = Zn(II), L = gly, α-ala, ph-ala and tyro shows less negative ΔlogK values (Table no-2.2.12) as compared to [Cu(Nia)(L)] and [Ni(Nia)(L)] complexes (Table no-2.2.11 & 2.2.10) 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 to the central metal ion and form stable ternary complex. The size of the metal atom is expressed in terms of atomic radii. The atomic radii of Cu(II), Ni(II) & Zn(II) are as follow-

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

A mutual repulsion among the ligands in a ternary complex decreases in the following order-

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

For this reason, in our present investigation, the [Zn(Nia)L)] complexes acquires higher stability as compared to the stability of [Cu(Nia)(L)] and [Ni(Nia)(L)] complexes.

Another reason is Zn(II) has coordination number 4, and it follow sp^3 hybridization in forming complexes i.e. its complex fits into a tetrahedral geometry. It prefers a tetrahedral geometry [111] over octahedral or square planar, as the ligand-ligand repulsion is minimum in a tetrahedral geometry. This is due to the fact that in tetrahedral the angular distance between ligands is 109° 28′ . But in octahedral and square planar structure of Ni(II) & Cu(II) complexes follows the angular distance of <L-M-L is 90° . This leads to closely space of ligands which unstabilizes the complex.

UV SPECTRA MEASUREMENT

ELECTRONIC SPECTRA MEASUREMENT

Ultraviolet and visible spectra can give qualitative knowledge of electronic properties. The absorption of light in the UV, visible region (200-800nm) by a metal ion depends on the electronic transition within the ion and also on the type and strength of ligand to metal bonding.[113] The transition consists of usually nonbonding or bonding orbital to the next higher energy orbital i.e. antibonding π. In general the ions and complexes of elements in the first two transition series absorb broad bands of visible radiation in at least one of their oxidation states and are, as a consequence, colored. Here absorption involves transitions between filled and unfilled d-orbital with energies that depend on the ligands bonded to the metal ions. The energy differences between these d-orbital (and thus the positions of the corresponding absorption peaks) depend on the position of the element in the periodic table, its oxidation state and the nature of the ligand bonded to it. In fact a complex may be identified by its absorption characteristics, i. e. based on the positions of the maxima and the minima in the absorption spectrum and their intensities (absorbance or molar extinction coefficient values).

Many investigators [114] have carried out research on electronic spectra of metal carbonyls. They have been proposed that $[Zn(CO)_4]^{2-}$ is more stable than the well-know $[Ni(CO)_4]$.

Absorption spectra of $[Ti(H_2O)_6]^{3-}$ have been observed by T. M. Dunn et al. [115]. Absorption of light by $[Ti(H_2O)_6]^{3+}$ ion involving a shift of an electron from t_{2g} level to e_g level. This transition gives the $[Ti(H_2O)_6]^{3+}$ ion its purple color.

According to the well-know concept of average environment introduced by C. K. Jorgensen and R. D. Hancock [116,117], the wave numbers of the bands of an octahedral complex MA_xB_{6-x} will approximately be obtained by interpolation between the wave numbers of the corresponding bands of the pure complexes MA_6 and MB_6.

Two geometrical isomers (Cis and Trans) of the complex MA_3B_3 have been investigated by Nakamoto et al.[118] . These investigations have been carried out by absorption spectra. They proposed that the Trans isomer is more stable than the Cis isomer.

Several investigators [118-120] carried out research work on the charge transfer spectra of Fe^{3+}, $[FeCl_2]^{2+}$ and $[FeBr_2]^{2+}$ species. They observed that the strong bands moves to longer wavelengths in complexes of Fe^{3+}, as the ligand becomes more easily oxidized.

Electronic spectra of the complexes of oxoanadium (IV) with salicylaldimine and 2-hydroxy-1-naphthyldiamine were recorded by P.K Bhattacharya [121] .The electronic spectra predicts that the complexes of oxovanadium (IV) have square pyramidal structure with coordinating atoms of the schiff base in the square plane and the oxygen atom in the axial position.

Ultraviolet and visible spectral studies of the complexes of copper (II) with 1,10-phenanthroline, catechol and o-phenylenediamine were investigated by J. P. Patel et al. [122]. These complexes show that the greater stability of the mixed ligand complex is due to lowering in repulsion between metal dπ-electrons and the ligand electrons.

H. Kabir [123] investigated the electronic spectra of the complex of Cu(II) & Ni(II) with tryptophane, catechol, glutamic acid. ATP & malonic acid. The complexes of Ni(II) are more stable than those of the complexes of Cu(II) when one the ligands is tridentate.

Recently Nargis Jahan Ara [124] investigated the electronic spectra of the complex of Cu(II), Co(II) & Ni(II) with thiamine, riboflavin, glycine and tryptophans. The complexes of Cu(II) are more stable than those of the complexes of Ni(II) when one of the ligand is bidentate.

In the present investigation, our aim is to observe the electronic spectra of the compounds of M, [MA], [ML], and [MAL] where M= Cu(II), Ni(II) and Zn(II); A=Pyridoxine and Nicotinic Acid; L= Glycine(Gly). Solution of [MA], [ML] were prepared by mixing M(II) and A in 1:1 ratio: M(II) and L in 1:1 ratio. 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. A Carl Zeiss UV-visible spectrophotometer, with CM Quartz cell was used for the electronic spectral measurements. Electronic spectra were obtained in the range of 800-200nm in aqueous media. The absorption bands of the complexes in UV region results from d-d, n- π and π- π^* electronic transitions. The pattern of maxima, in longer wavelength which is due to the metal to ligand charge transfer transition. The UV visible spectra of the samples are shown in fig-2.3.1 to 2.3.15. The results of electronic spectra measurement are summarized in the Table-2.3.1

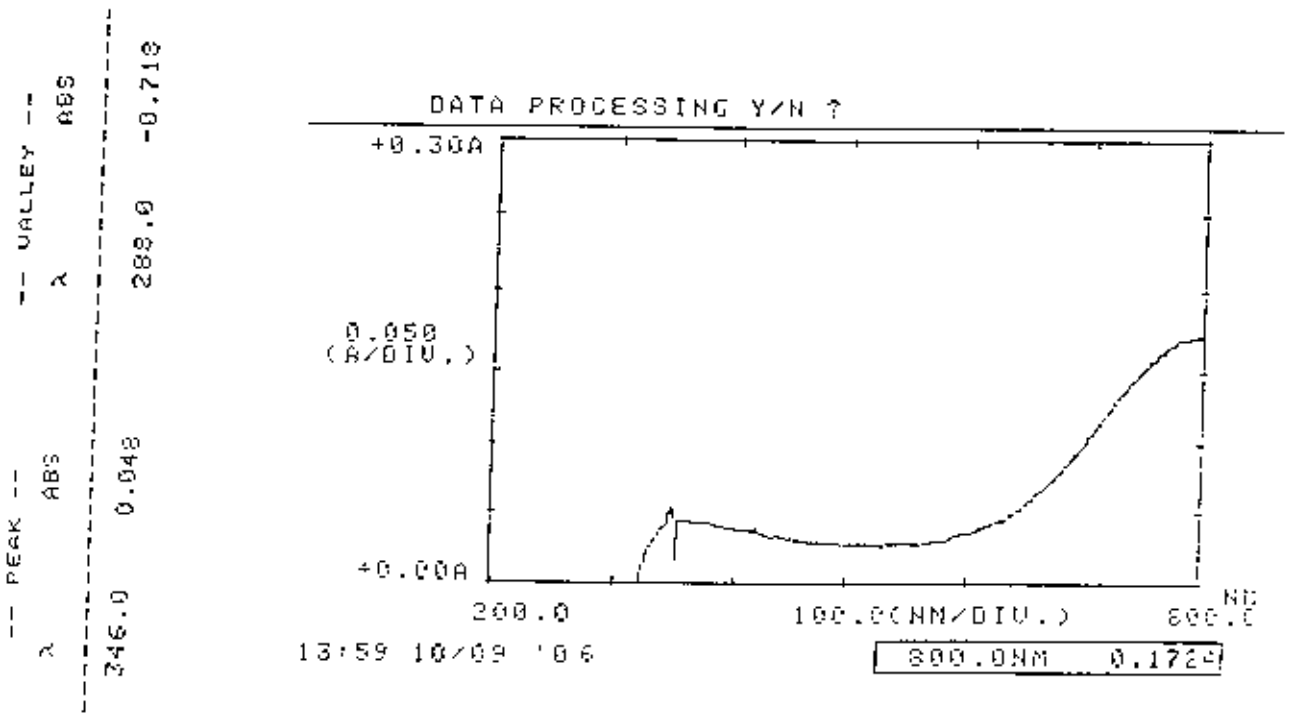


Fig. 2.3.1: UV Spectra of Copper perchlorate, $Cu(ClO_4)_2$.

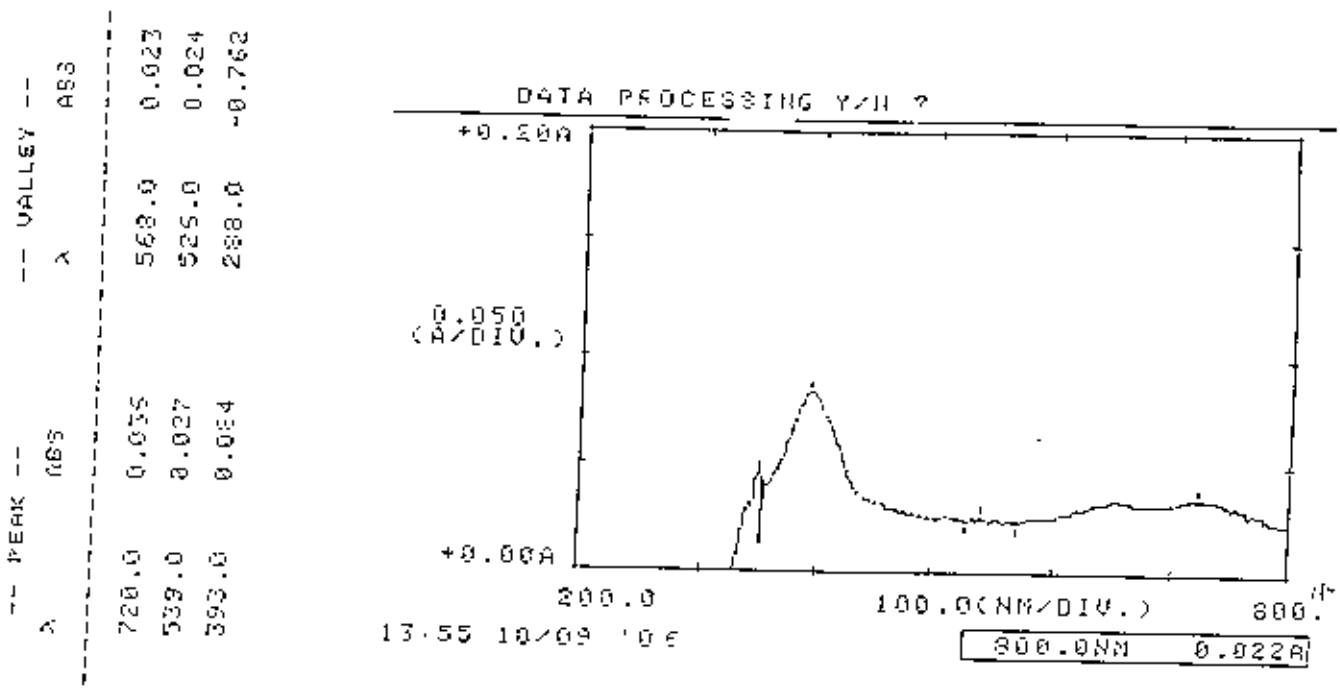


Fig. 2.3.2: UV Spectra of Nickel perchlorate, $Ni(ClO_4)_2$.

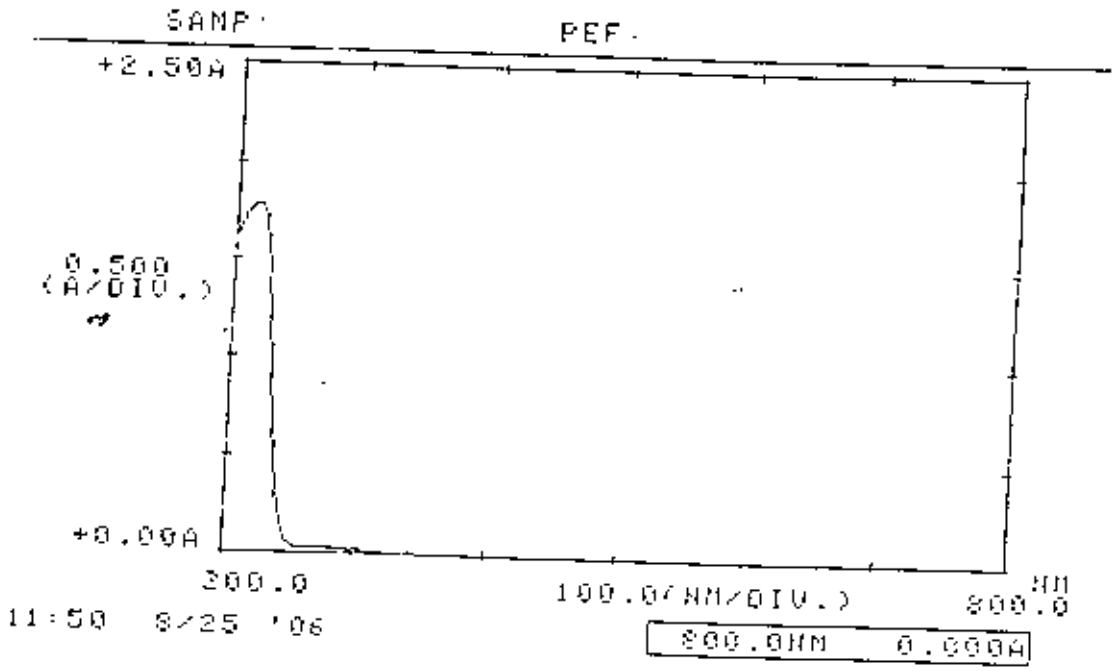


Fig. 2.3.3: UV Spectra of Zinc perchlorate, $Zn(ClO_4)_2$.

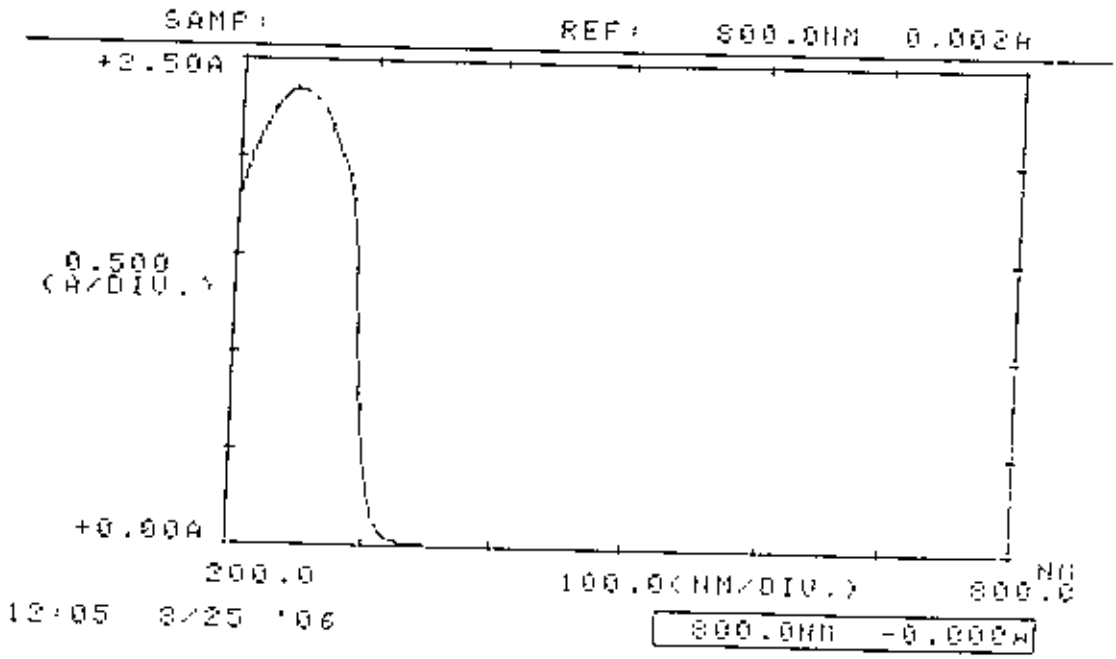


Fig. 2.3.4: UV Spectra of the complex [Cu(Nia)].

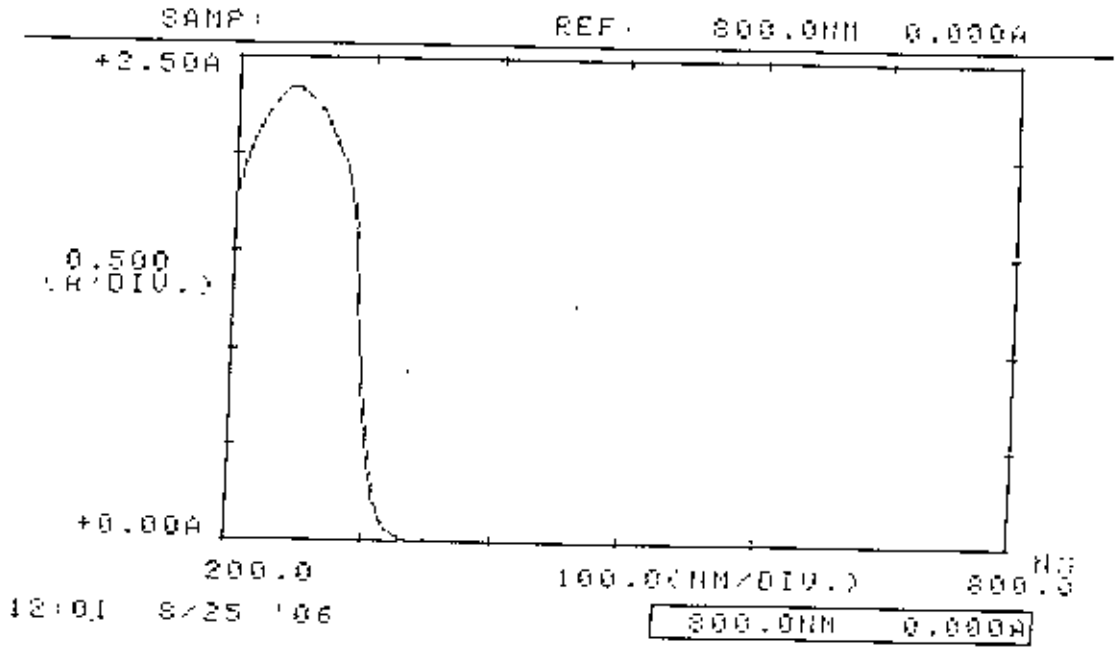


Fig. 2.3.5: UV Spectra of the complex [Ni(Nia)].

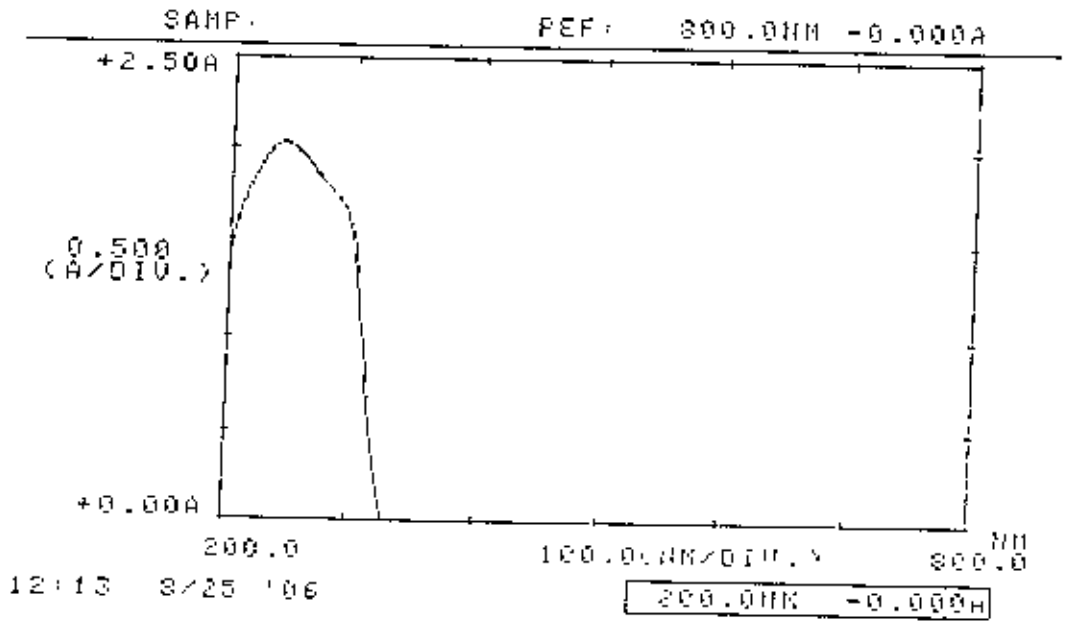


Fig. 2.3.6: UV Spectra of the complex [Zn(Nia)].

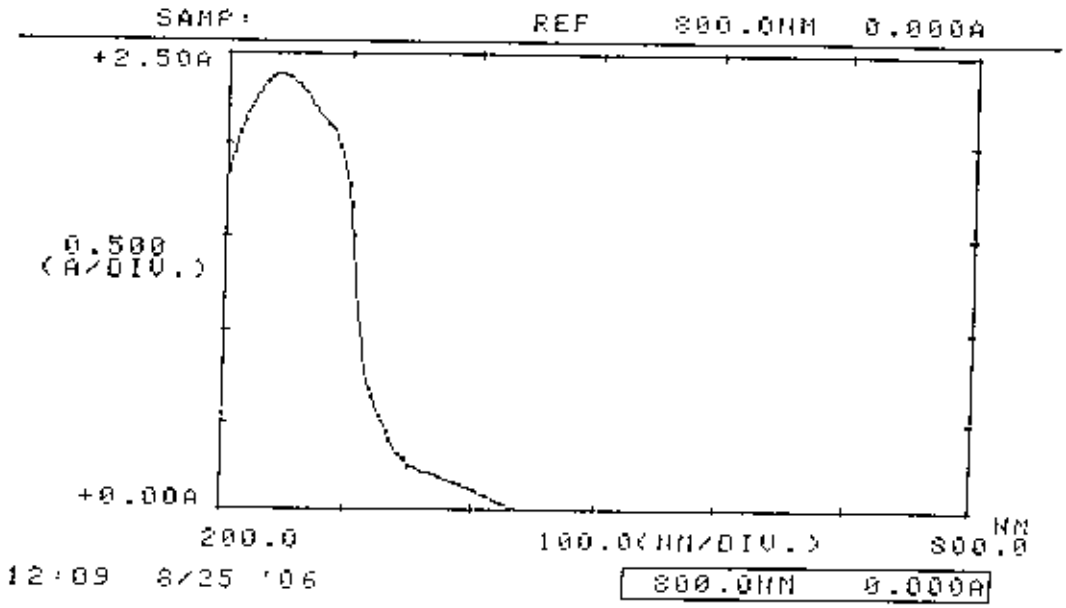


Fig. 2.3.7: UV Spectra of the complex [Cu(Pyri)].

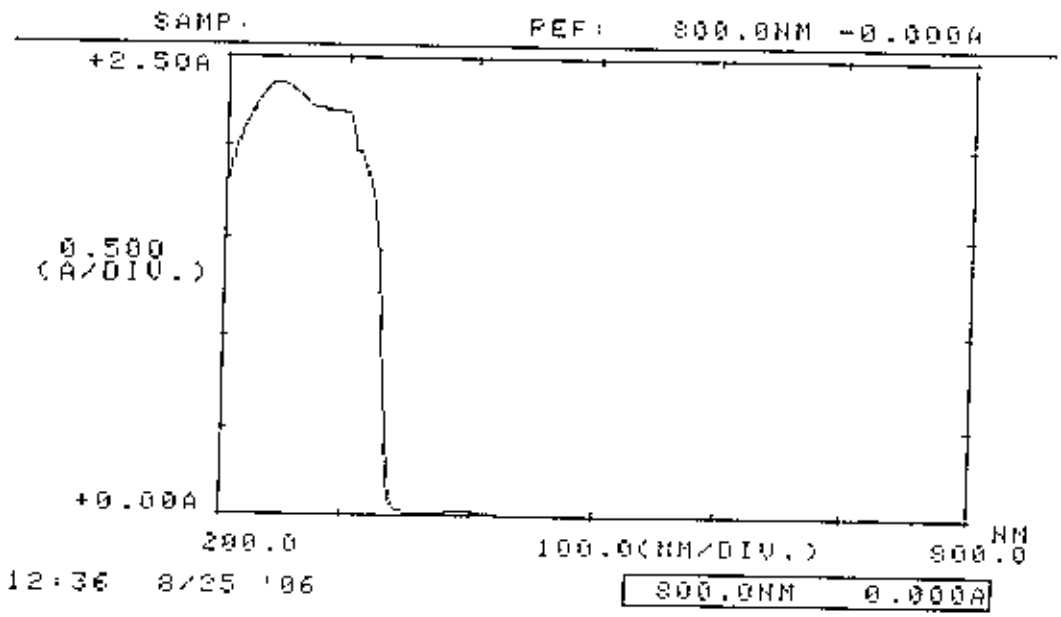


Fig. 2.3.8: UV Spectra of the complex [Ni(Pyri)].

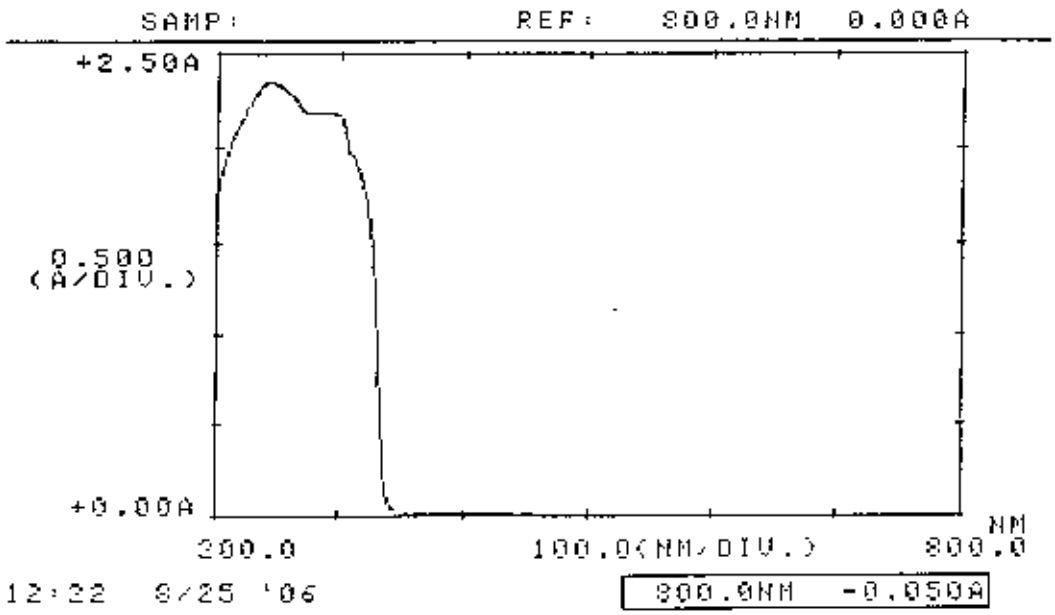


Fig. 2.3.9: UV Spectra of the complex [Zn (Pyri)].

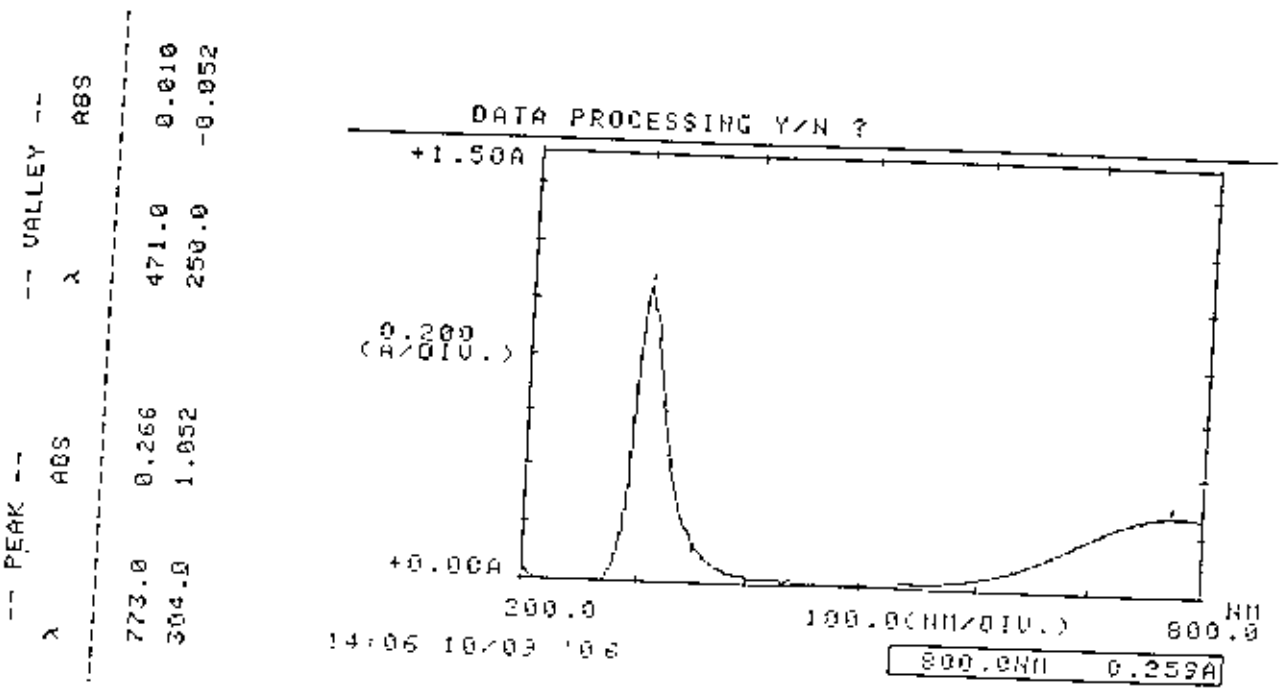


Fig. 2.3.10: UV Spectra of the complex [Cu(Nia)(Gly)].

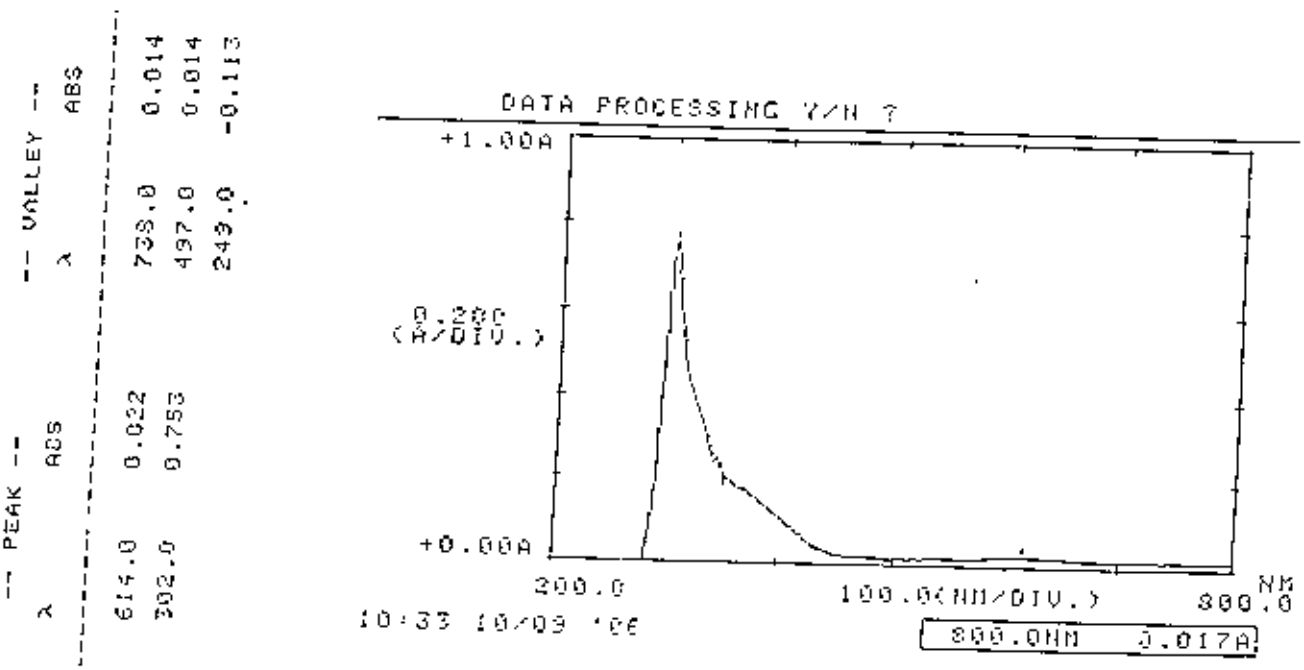


Fig. 2.3.11: UV Spectra of the complex [Ni(Nia)(Gly)].

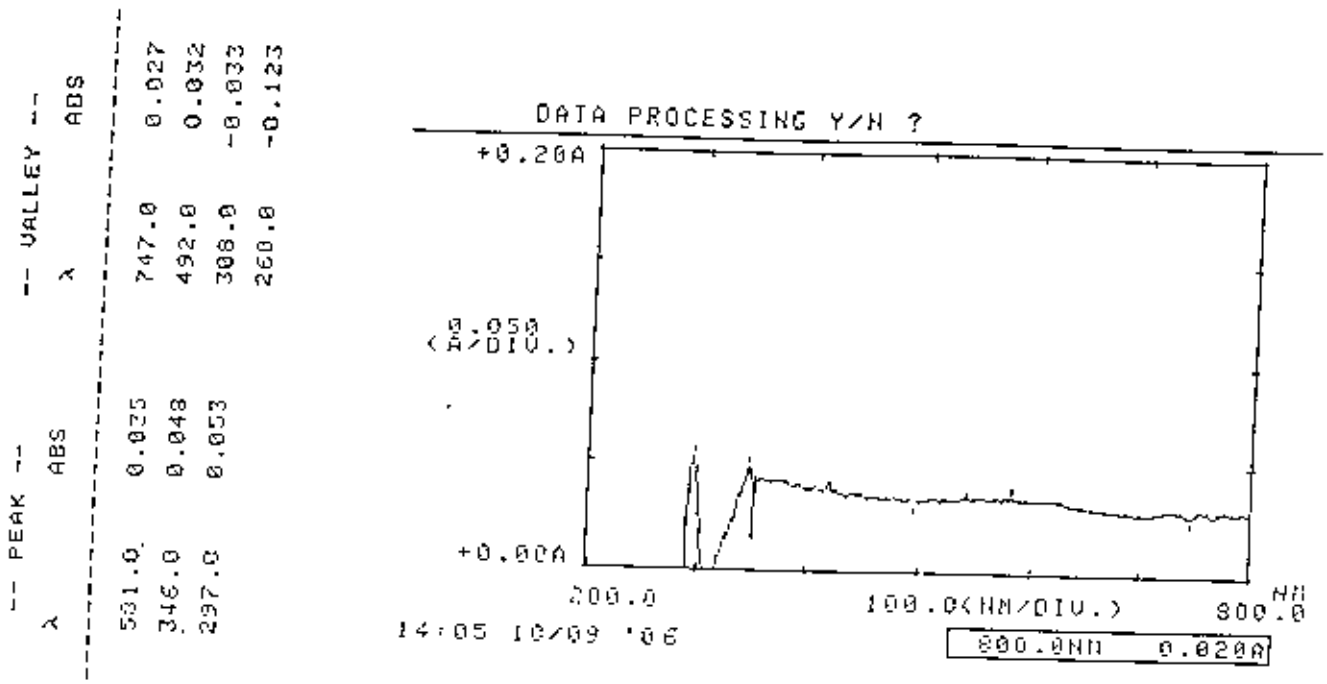


Fig. 2.3.12: **UV Spectra of the complex [Zn(Nia)(Gly)].**

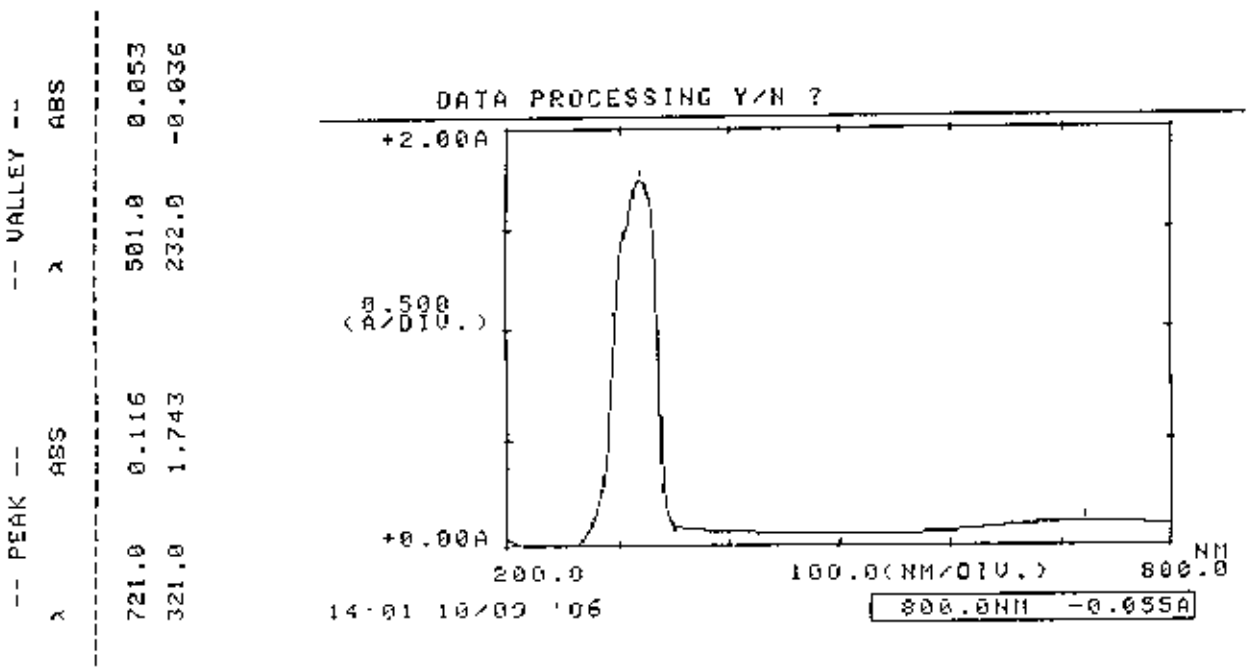


Fig. 2.3.13: UV Spectra of the complex [Cu(Pyri)(Gly)].

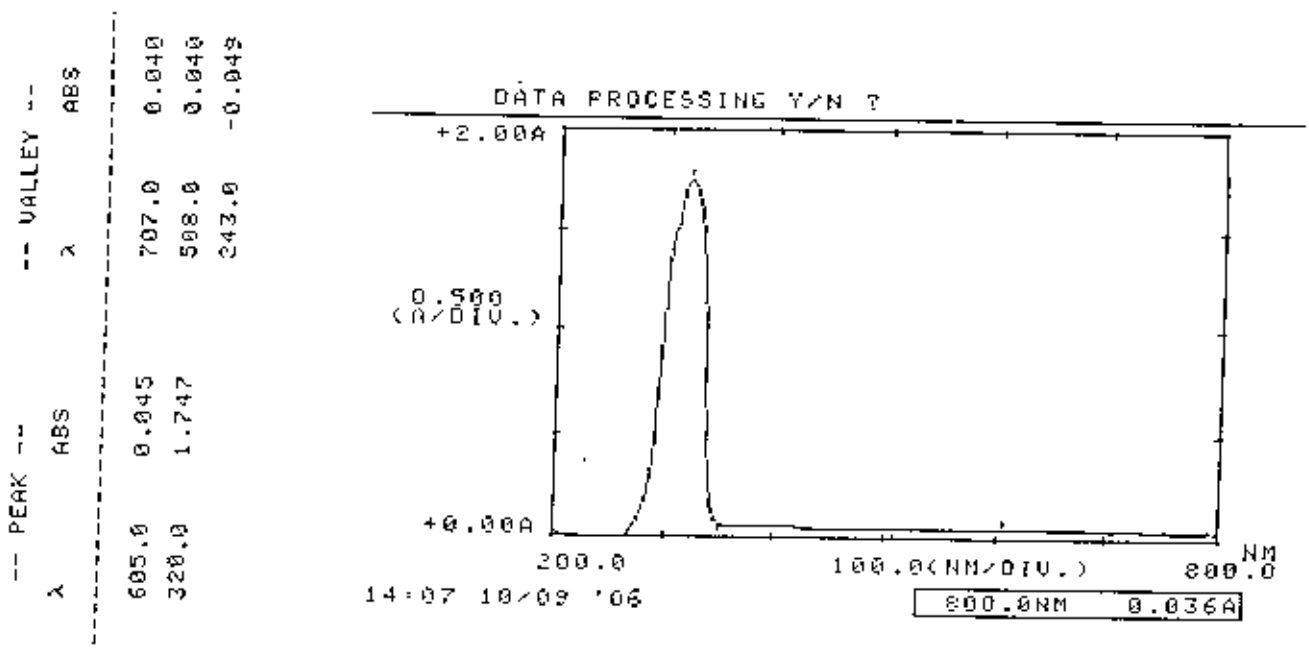


Fig. 2.3.14: UV Spectra of the complex *[Ni(Pyri)(Gly)]*.

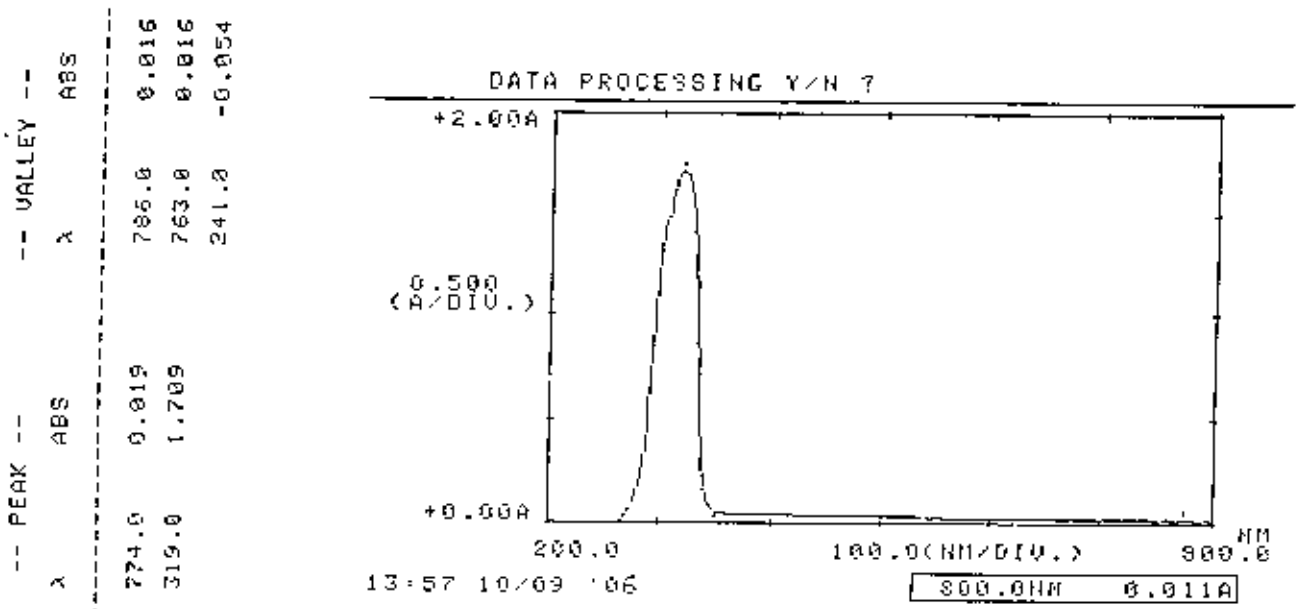


Fig. 2.3.15: UV Spectra of the complex [Zn (Pyri)(Gly)].

Table-2.3.1: UV visible spectral data of some Cu(II), Ni(II) and Zn(II) complexes:

Compounds	Maximum Wave Length(λ_{max})nm		
$Cu(ClO_4)_2$	346		
$Ni(ClO_4)_2$	393		
$Zn(ClO_4)_2$	214		
[Cu(Nia)]	241		
[Ni(Nia)]	241		
[Zn(Nia)]	240		
[Cu(Pyri)]	299	241	
[Ni(Pyri)]	297	241	
[Zn(Pyri)]	294	242	
[Cu(Nia)(gly)]	773	304	
[Ni(Nia)(gly)]	614	302	
[Zn(Nia)(gly)]	581	346	297
[Cu(Pyri)(gly)]	721	321	
[Cu(Pyri)(gly)]	605	320	
[Cu(Pyri)(gly)]	600	319	

RESULTS AND DISSCUSSION

RESULT & DISCUSSION

The spectral bands of Cu(II), Ni(II) and Zn(II) as a metallic perchlorate are at 346nm, 393nm, & 214nm. The absorption spectra of [MA] e.g. [Cu(Nia)], [Ni(Nia)] and [Zn(Nia)] exhibit bands at 241nm, 241nm and 240nm. The [MA] exhibits new bend at lower wavelength in comparison to the spectral bands of metal perchlorate. The appearance of new band indicates that Nicotinic Acid(Nia) capable of coordinating with metal.

The absorption spectrum of free pyridoxine (Pyri) exhibits bands at 236.9nm and 289.1nm [121]. On coordination with the metal ion, the complex of the type [MA] e.g. [Cu(Pyri)], [Ni(Pyri)] and [Zn(Pyri)] shows two bands individually. These absorption bands are 241nm & 291nm; 241nm & 297nm; 242nm & 294nm respectively. The appearance of new band and shift in $\pi \rightarrow \pi^*$ transition shows that there is interaction between π orbital of metal ion and those of Pyridoxine molecule.

It is normally expected that in mixed ligand complex [MAL], the ligand field created is average of the ligand field in the binary complexes $[MA_2]$ and $[ML_2]$. However, in the complexes [MAL], the d-d transition band is at higher energy than in [MA] or [ML]. The ligands A(Nicotinic Acid and Pyridoxine) and L(gly) create stronger field in [MAL] than in [MA] or [ML]. This leads of greater splitting of d orbitals in [MAL] and d-d transition band shifts of higher energy region.

CYCLIC VOLTAMMETRY

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 madcup 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 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 inicro 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 [125] have carried a piece of research work on reduction of 0_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 solution 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.

W.R Heineman et al.[127] prepared a cyclic voltammogram of the agricultural insecticide parathion in 0.5 M pH 5 sodium acetate buffer in 50% ethanol.

H. Kabir M.phil research, BUET [123] have studied the cyclic voltammograms of the complex of [MAL] type where M = Cu (II) & Ni (II) ; A = Folic acid L = Tryptophane, glutamic acid and malonic acid. The cyclic voltammograms indicate the formation of ternary complex.

Cyclic voltammograms of $B_{10}H_{14}$ and $B_{10}H_{12}^{-2}$ solutions have been observed by Donald E. Smith et al [128]. Those voltammograms showed an irreversible oxidation wave at about –1.4V and a reversible couple 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 molecules) is indicative of complex formation. J. J. Lingane [129] 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.

Table-2.4.1: 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
$Cu(ClO_4)_2$	150	-40	190	55
[Cu(Ph-ala)]	180	-685	865	252.5
[Cu(Pyri)]	300	-700	1000	200
[Cu(Pyri)(ph-ala)]	450	-495	945	22.5

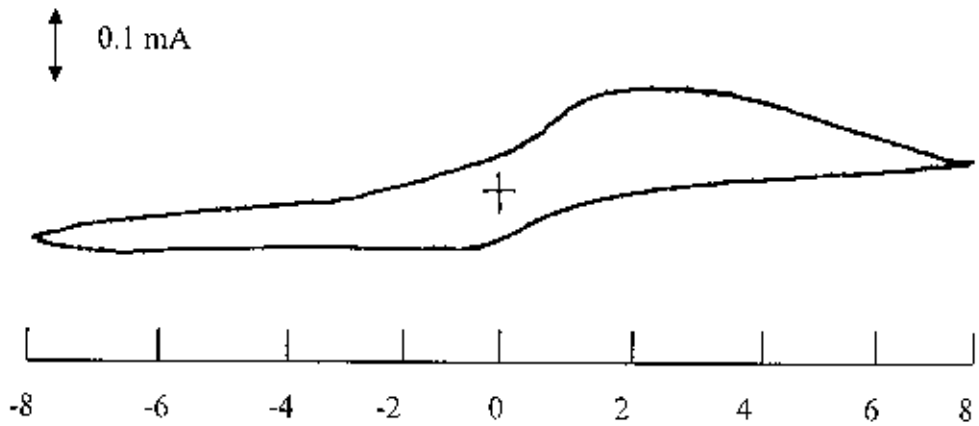


Fig. 2.4.1: Cyclic Voltammogram of $[Cu(ClO_4)_2]$ system in aqueous media at platinum electrode.

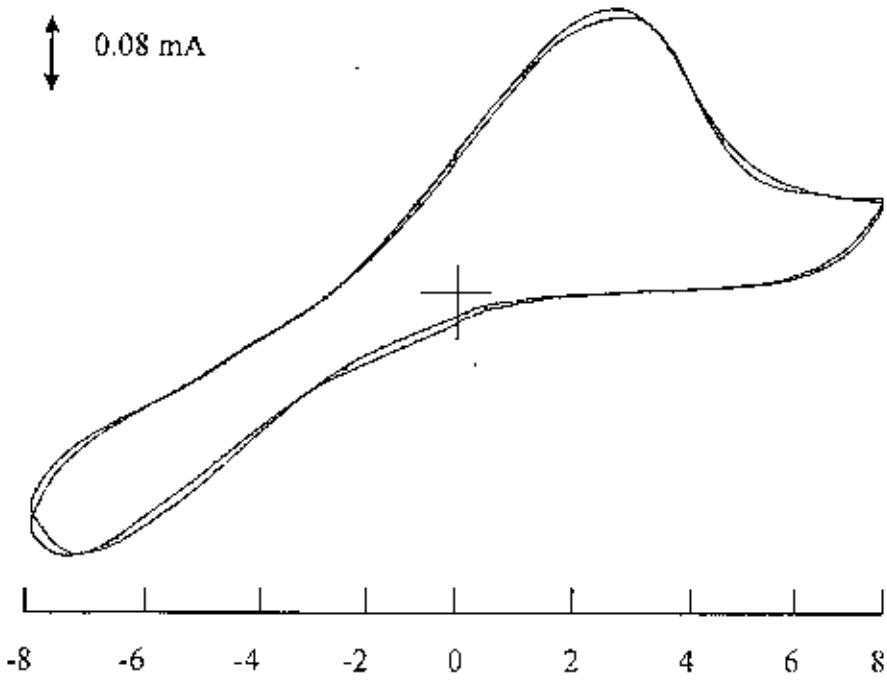


Fig. 2.4.2: Cyclic Voltammogram of [Cu(Ph-ala)] system in aqueous media at platinum electrode.

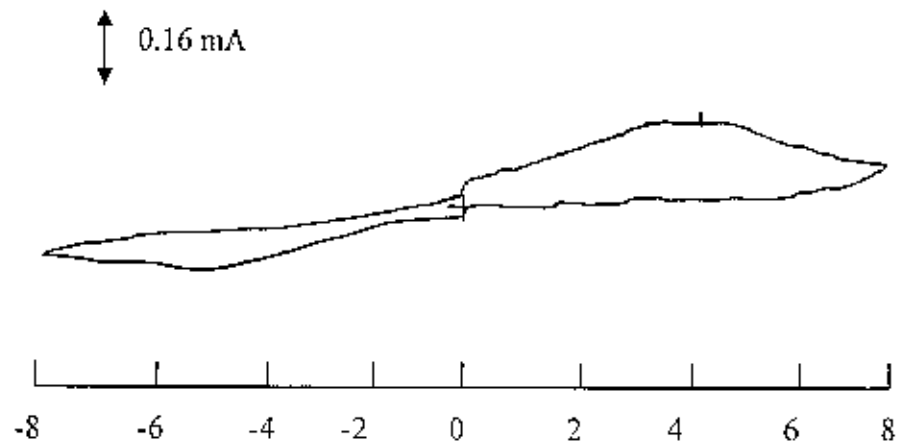


Fig. 2.4.3: Cyclic Voltammogram of [Cu(Pyri)] system in aqueous media at platinum electrode.

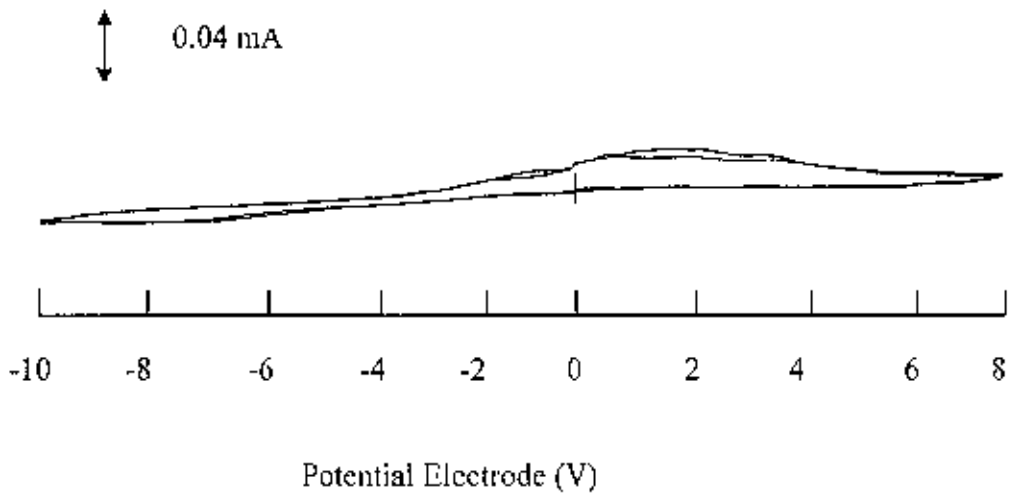


Fig. 2.4.4: Cyclic Voltammogram of [Cu(Pyri)(Ph-ala)] system in aqueous media at platinum electrode.

RESULTS AND DISSCUSSION

In the present investigation cyclic voltammograms of complexes of M(II), [MA], [ML] and [MAL] type have been studied where M=Cu(II); A=Pyridoxine and L= Phenylalanine. Cyclic voltammograms of the Cu(II) complexes were recorded at Pt electrode in aqueous media. Typical voltammograms are given in fig-2.4.1 to 2.4.4. The voltammograms were obtained at a scan rate of 100mV/S for all the voltammetric experiments studied in this work. Solution of [MA], [ML] and [MAL] were prepared by mixing of M(II), A and L in 1:1 and 1:1:1 ratio respectively. 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 voltammetric characteristics are presented in Table-2.4.1. The voltammograms exhibits one oxidation and one reduction peak for all the complex compounds and copper 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 [123]. On the other hand, the cathodic peak potential of the formed complexes shifted towards the more negative potential indicate 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 ΔE^0 $[(E_{pa}+E_{pc})/2]$ is the mean potential indicate the transition potential between the oxidation and reduction process.

POSSIBLE STRUCTURE

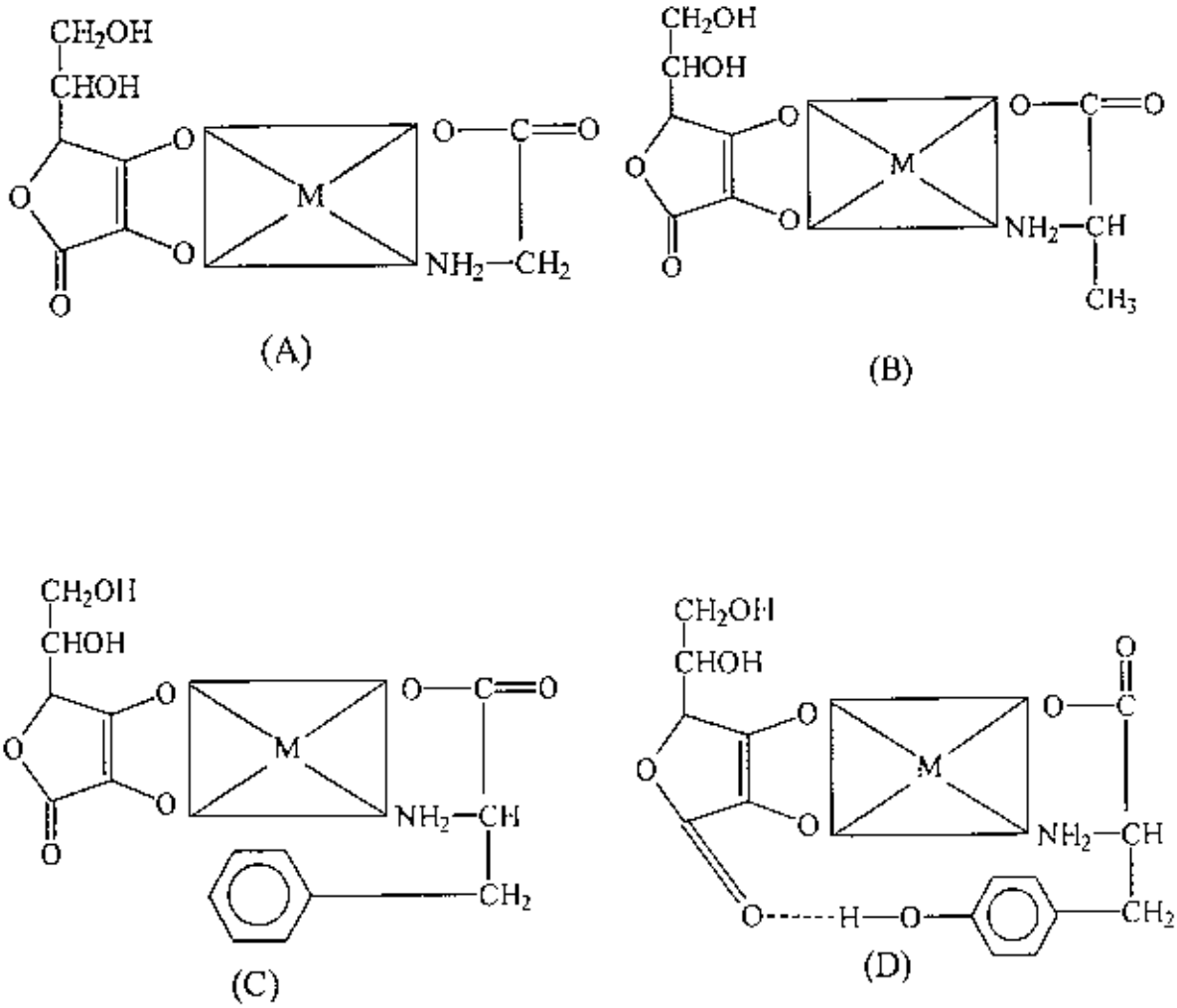


Fig. 2.5.1: Structure of (A) [M(AsA)(Gly)]
(B) [M(AsA)(α-ala)]
(C) [M(AsA)(ph-ala)]
(D) [M(AsA)(Tyr)]

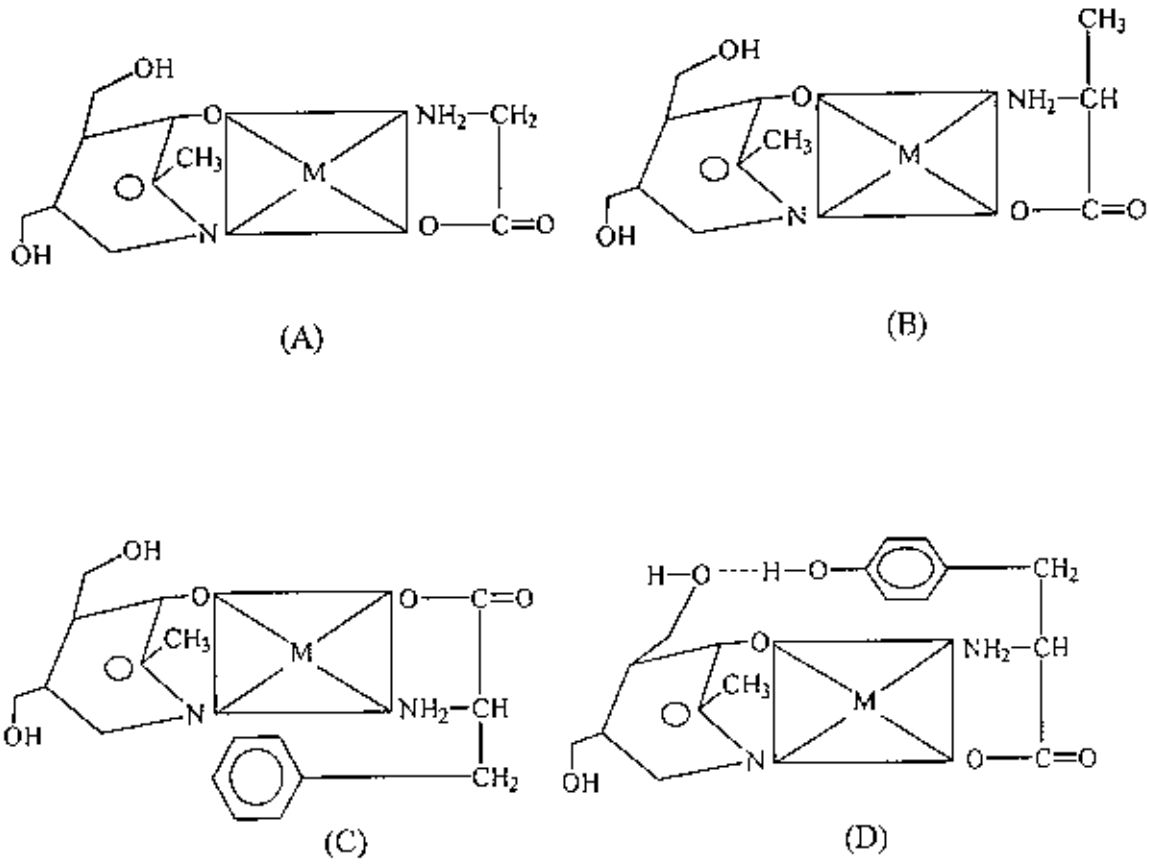
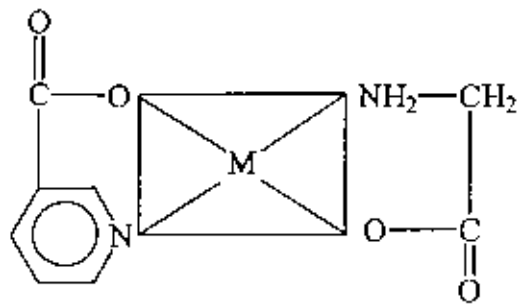
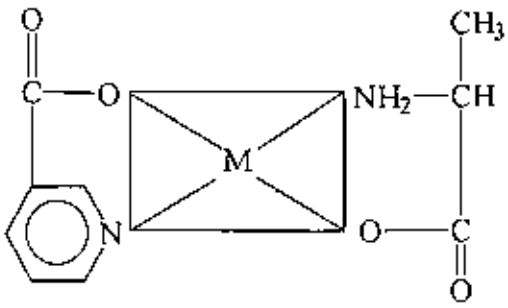


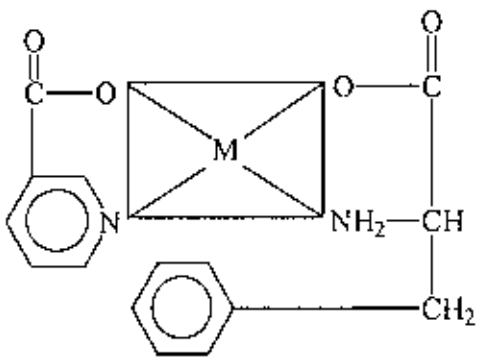
Fig. 2.5.2: Structure of (A) [M(Pyri)(Gly)]
(B) [M(Pyri)(α-ala)]
(C) [M(Pyri)(ph-ala)]
(D) [M(Pyri)(Tyr)]



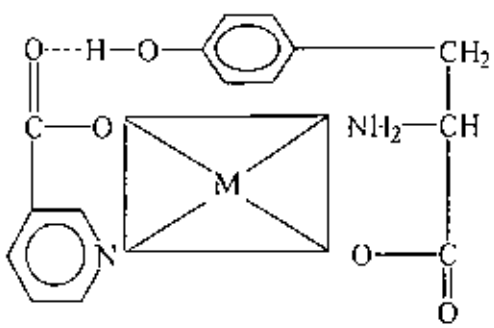
(A)



(B)



(C)



(D)

Fig. 2.5.3: Structure of (A) [M(Nia)(Gly)]
(B) [M(Nia)(α-ala)]
(C) [M(Nia)(ph-ala)]
(D) [M(Nia)(Tyr)]

CONCLUSION

Conclusions

Present studies involved an investigation of the coordination behavior of the complex type [MAL] where A, L are biologically important ligands. Some amino acid (L) and three different vitamins (A) Ascorbic acid, Pyridoxine, Nicotinic acid were used as ligands. The metal ions used were Cu^{2+}, Ni^{2+}, and Zn^{2+}. The protonation constant, Binary constant and Ternary constant have been determined potentiometrically by using SCOGS computer program. The formation of the complexes has been confirmed by UV spectral studies and Cyclic Voltammogram. From the results obtained in this study following conclusion can be drown:

- Ternary complexes [MAL], where L=Trosine are more stable than other natural ligands.
- Ternary complexes of Zn and Cu are more stable than Ni complex.
- Pyridoxine form more stable ternary complexes than ascorbic acid.
- Ascorbic acid form more stable ternary complexes than Nicotinic acid.

A single crystal of the complex [Cu(Pyri)(α-ala)] is obtained. Attempt has been made to determine the structure of this complex. For this X-ray diffraction analysis is essential which is under process.

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