

**STABILITY STUDIES ON  
METAL NITRILOTRIACETATE COMPLEXES  
AND ITS  
APPLICATION IN ELECTROLESS DEPOSITION OF  
Fe-Ni ALLOYS**

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*Of*

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*by*



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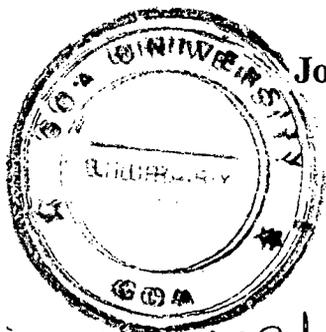
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**AND**  
**Dr. J. S. BUDKULEY.**

## DECLARATION

I hereby declare that the matter embodied in the thesis entitled **"STABILITY STUDIES ON METAL NITRILOTRIACETATE COMPLEXES AND ITS APPLICATION IN ELECTROLESS DEPOSITION OF Fe-Ni ALLOYS"** is based on the investigation carried out by me in the Department of Chemistry of the Goa University, Goa, under the supervision of Dr. Jayant S. Budkuley.

In keeping with general practice of reporting scientific observation, due acknowledgements has been made wherever the work described is based on the finding of other investigators.

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Thesis examined and viva voce examination held on Jan. 29, 2002; Based on the reports and the satisfactory performance in the Viva-voce examination, Mr. J.P.P. Pacheco's thesis is recommended for the award of Ph.D. degree in Chemistry of Goa University.

## CERTIFICATE

Certified that the work "**STABILITY STUDIES ON METAL NITRILOTRIACETATE COMPLEXES AND ITS APPLICATION IN ELECTROLESS DEPOSITION OF Fe-Ni ALLOYS**" presented in the thesis has been carried out by Shri Joaozinho Patricio Perpetuo Pacheco under my supervision and the same has not been submitted for a degree of other university.



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## SYNOPSIS

The knowledge of stability constants of metal complexes plays an important role in the selection of a metal complex for specific applications. In some cases it is desirable to have the metal complex which is highly stable so that the metal ions remain in solution in complex form whereas in some cases it is preferable to have the metal complex which has less stability such that the metal can be easily extracted or deposited by suitable reducing agents. Less stability is imparted to the metal complexes when the ligands are bulky, for example nitrilotriacetic acid (NTA), and such complexes can be best utilized, in electroless deposition either of metal or alloy, using suitable reducing agents like sodium hypophosphite, hydrazine etc. The present investigation is aimed at finding stability constants of metal nitrilotriacetate complexes using  $\text{Fe}^{+2}$  and  $\text{Ni}^{+2}$  as metal ions and their possible application in the electroless deposition of Ni-Fe alloy using hydrazine and hypophosphite as reducing agents. These studies include the use of ternary system involving metal ions and two ligands viz NTA and hydrazidocarboxylic acid.

The work is presented in the thesis in five chapters.

## CHAPTER I

The literature survey is centered on two aspects, namely, (i) the determination of stability constants of metal complexes in single and ternary systems and (ii) the application of the stability studies in electroless plating.

This chapter gives introduction to the chemistry of complex salts and highlights their importance. The knowledge of Werner's theory [1] as is used in the study of complex compounds is highlighted. The earlier studies on the role of the two main complexing agents used in the present investigation, viz. nitrilotriacetic acid (NTA)[2][L<sub>1</sub>] and hydrazido carboxylic acid [L<sub>2</sub>], are illustrated along with the stability [3] of their metal chelates. The role of hydrazine both as a reducing agent as well as complexing agent [4] is discussed in this chapter. The reaction between NTA and hydrazine hydrate has been studied by earlier workers [5]. The carboxylates which are in ionic form can act as ligands and form chelates with metal ions. The well known mathematical approach of Jannik Bjerrum [6] widely used to study stability constants [7-8] of metal complexes is adopted in the present investigation and is duly elaborated in this chapter.

The theory and the methodology of the electroless plating technique are described in the later part of this chapter. In addition, the work done by various workers in the field of electroless plating [9] method is highlighted here. Various components generally used in electroless plating are listed along with their functions. Emphasis is laid on function of two main components of the electroless bath viz complexing agents [10] and the reducing agents. The scope of the present investigation is also defined at the end of this chapter.

## CHAPTER II

This chapter describes various chemical and instrumental methods used during the course of the investigation. It includes the synthesis of hydrazido carboxylic acid ( $L_2$ ) and its utility as complexing agent in pH metry titration either single or along with NTA, forming ternary system with  $Ni^{2+} / Co^{2+} / Mn^{2+} / Zn^{2+} / Mg^{2+}$  as metal ions. The preparative conditions [11] for various experimental work are described here.

Calvin-Bjerrum pH metry titration method is also described in this chapter. This method was adopted to determine stability constants of metal nitrilotriacetate complexes. Basically this involves three titrations:

- i ) Titration of the solution containing mineral acid, the ligand (NTA/  $L_2$ ) and the metal salt ( $Ni^{2+} / Co^{2+} / Mn^{2+} / Zn^{2+} / Mg^{2+}$ ) against standard alkali.
- ii ) Titration of the same quantity of mineral acid and ligand solution without metal salt against the same standard alkali and
- iii ) Titration of the mineral acid alone against the same standard alkali

Apart from this, the pretreatment [10,13] of plastic and copper plates (substrate material) for electroless the plating, the preparation of various electroless bath solutions, the monitoring and control of various bath parameters, and also the characterization of plated materials are described in detail here. Further, the physico-chemical principles involved in the instrumental techniques used in the characterization of  $L_2$  as well as Ni-Fe deposit are also discussed in this chapter. The techniques used are XRD, Atomic Absorption Spectroscopy [14]. Besides, the surface morphology was studied by high resolution photographs.

### CHAPTER III

This chapter presents the experimental data obtained in the pH- metry studies on the complex formation of metal ions with the hydrazido carboxylic acid and nitrilotriacetic acid separately as single ligand system as well as ternary system with these two acids together. The dissociation constants, degree of formation and other physical quantities are evaluated graphically.

Bjerrum's method for stability studies involves calculations based on the graphs of pH v/s volume of NaOH added for systems involving various metal ions. Such graphs obtained for metal ions  $\text{Ni}^{2+}$  /  $\text{Co}^{2+}$  /  $\text{Mn}^{2+}$  /  $\text{Zn}^{2+}$  /  $\text{Mg}^{2+}$  and ligands ( NTA /  $\text{N}_2\text{H}_3\text{COOH}$  ) forming both binary and ternary system, are given in this Chapter. Based on this graphical data the calculated  $\bar{\eta}_A$  values [12] are tabulated here. The acid dissociation constants of the two ligands used in the present investigation viz. NTA (for  $\text{pK}_{a1}$  and  $\text{pK}_{a2}$  ) and  $\text{N}_2\text{H}_3\text{COOH}$  ( for  $\text{pK}_{a1}$  ) are also determined from the graphical data.

The degree of formation ( $\bar{\eta}$ ) in NTA / metal ions;  $\text{N}_2\text{H}_3\text{COOH}$  / metal ions and ternary system involving NTA /  $\text{N}_2\text{H}_3\text{COOH}$  / metal ions systems is calculated for various metal ions listed above as also the pL values. The stability constants of complexes which are evaluated graphically for various metal ions both in binary and ternary system are reported at the end of this Chapter.

## CHAPTER IV

Result obtained in the stability studies of metal nitrilotriacetate complexes as well as metal hydrazido carboxylates are discussed in this Chapter. The graphs of pH [6,12] v/s volume of standard alkali shows the shifting of the plots for metal ion / NTA /  $N_2H_3COOH$  ternary system as compared to metal ion / NTA or metal ion /  $N_2H_3COOH$  binary system which clearly proves the involvement of both the ligands viz NTA and  $N_2H_3COOH$  in complex formation. Using the graph of  $\bar{\eta}_A$  v/s pH for NTA to find the  $pK_{a1}$  at  $\bar{\eta}_A = 0.5$  and  $pK_{a2}$  at  $\bar{\eta}_A = 1.5$ , the  $pK_{a1}$  and  $pK_{a2}$  values are found to be 8.75 and 8.07692 respectively which are in agreement with the reported values. For  $N_2H_3COOH$  at  $\bar{\eta}_A = 0.5$  the  $pK_{a1}$  is found to be 9.35294. Greater accuracy is obtained in  $pK_{a1}$  values by plotting  $\log \bar{\eta}_A / 1 - \bar{\eta}_A$  v/s pH.

For NTA and  $N_2H_3COOH$ , the  $pK_{a1}$  values are found to be 8.406 and 9.2 respectively. There are no reports on the  $pK_{a1}$  values for  $N_2H_3COOH$ . In this investigation,  $pK_{a1}$  value of this acid is determined at temperature between 0 to 4 °C so as to prevent decomposition of  $N_2H_3COOH$ . The calculated values of  $\bar{\eta}$  for  $N_2H_3COOH$  in ternary system are found to be negative, whereas it is found to be positive for NTA in the system for all metal ions used in present investigation. This indicates the dominant role of NTA as compared to  $N_2H_3COOH$  in complex formation.

## CHAPTER V

It was observed that metal nitrilotriacetate complexes have appreciable stability and hence could be used in the electroless deposition of metal or alloys, by using suitable reducing agents. In the present study two reducing agents viz hydrazine hydrate and sodium hypophosphite were used. Experimental work was also carried out by using sodium hypophosphite alone as reducing agent so as to find the condition to get better quality of deposit.

Iron has tendency to pass from Fe (II) oxidation to Fe (III) oxidation state. So it was a necessary to keep Fe in Fe (II) oxidation state during the electroless plating. The same was achieved by first complexing iron with NTA /  $N_2H_3COOH$  and then bringing about reduction of metal ion to metal by using powerful reducing agents such as sodium hypophosphite / hydrazine. Alloy deposition with Fe as one of the component can take place under stringent conditions. In the present study an attempt has been made to get the alloy where bath shows maximum stability.

The present chapter elucidates this attempt at length, bringing the setting up of electroless [10] bath for Ni- Fe alloy deposition. This involves pre-treatment of plates, selection of right bath composition, bath temperature and pH. Calculated values of the area of deposition, rate of deposition, thickness of plating are also given in this chapter. The results obtained can be summarised with respect to various factors as under:

### **1. Temperature:**

Electroless plating was carried out at temperatures of 75<sup>0</sup>C, 80<sup>0</sup>C, and 85<sup>0</sup>C. It was observed that best silvery deposit was obtained at 80<sup>0</sup>C, whereas at 75<sup>0</sup>C and 85<sup>0</sup>C rusty brown deposit was obtained at most of the times. Hence 80<sup>0</sup>C was chosen as right working temperature of the bath.

### **2. pH:**

Electroless plating was carried out from bath maintained at pH 7.5, 8.0, 8.5, and 9.0. It was observed that a good deposition is obtained at pH of 8.0. At a pH more than 8.0, the copper plates were found to be rusty and at times there was loss in weight of copper plates, whereas the bath is unstable at pH less than 8.0.

### **3. Rate of deposition:**

The rate of deposition on the substrate at selected temperature of 80<sup>0</sup>C and pH = 8.0 was studied. It was found that the rate of deposition was slightly more on thin plastic plates as compared to thin copper plates. Similarly, it was observed that the rate of deposition was much less on thick acrylic plates as compared to thin plates. The rate of deposition increases marginally with time perhaps due to the catalytic effect of deposited material. Presence of two complexing agents (viz. NTA and N<sub>2</sub>H<sub>3</sub>COOH), forming ternary system with metal ions reduces the rate of deposition as compared to a system where single complexing agent is used (viz. NTA or N<sub>2</sub>H<sub>3</sub>COOH), irrespective whether

one or two reducing agents are used (viz. sodium hypophosphite / hydrazine). This shows that ternary system involving metal ions ( $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$ ) and two complexing agents reduces the rate of deposition and gives a non-porous deposit due to slow rate of deposition.

#### **4. Thickness of plating:**

Thickness of the deposit increases with time on both plastic and copper substrate. The rate of deposition is found to be more on non-conducting acrylic plates.

Selected plates were subjected to various analytical studies. The deposit on leaching with dil  $\text{HNO}_3$  was analyzed by Atomic Absorption Spectroscopy [14] for Ni and Fe. These analysis as well as X-ray diffraction studies indicate Ni-Fe alloy deposition. The surface morphology was studied by subjecting the deposit to high resolution photography was found to be fairly uniform.

## REFERENCES

1. G. R. Chatwal and M. S. Yadav, *Coordination Chemistry*, Himalaya Publishing House, Bombay -400 004, (1992).
2. R.M. Krishnan, S. R. Natarajan, V. S. Murlidharan and G. Singh, " *Bull Electrchem*", 4(12) (1988) 1010.
3. B.K. Agarwal, M Chandra, B. V. Agarwala and A. K. Dey, *Indian J of Chem*, 15A (1977) 633.
4. J P. Candlin, K. A. Taylor and D. I. Thompson, *Reactions of Transition Metal Complexes*, Elsevier, Amsterdam, (1968) 363.
5. J. S. Budkuley and A. V. Vernekar, *Thermochemica Acta*, 176 (1991) 339-343.
6. J. Bjerrum, *Metal Amine Formation in Aqueous Solution*, Copenhagen, Publisher P. Haase and son, (1957) 17-22.
7. S. Ramamoorthy and M. Santappa, *Stability constants in Aqueous Solution of Complexes of uranyl ion with mixed dibasic acids -II*, 1<sup>st</sup> July 1970.
8. P. K. Datta, A. K. Dey, *Transition Met. Chem*, 5 (1980) 1-3.
9. A. Brenner, and G. E. Riddell, *J. Res. Nat. Bur. Stand.*, 39 (1946) Nov, 385/395 and *Proc American Electroplaters Soc.*, 34 (1947) 156/170.
10. G. G. Gawrilov, " *Chemical (Electroless) Nickel-plating*" Portcullis Press, Redhill (1979).
11. A. Vogel's *Textbook of Quantitative Chemical Analysis* (1989).

12. S. C. Galagali , *Stability of some bivalent Metal complexes of Amino acid Schiff bases*. Ph. D thesis Karnatak University (1981).
13. W. Riedel , “ *Electroless Nickel Plating*” , A. S. M. International , Ohio (1991).
14. H. Willard , L. Merritt, J. Dean, *Instrumental Method of Analysis* , CBS Publishers and Distributers, Sixth Edition 140–145, 199-201.

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**CHAPTER I**  
**LITERATURE SURVEY**

# CHAPTER I

## LITERATURE SURVEY

### INTRODUCTION

The knowledge of stability constants of metal complexes plays an important role in the selection of a metal complex for a specific application. In some cases, it is desirable that the metal complex should be highly stable such that the metal ions remain in the solution in complex form, whereas in other cases, it is desirable that the metal complex should have less stability such that the metal can be easily extracted or deposited by a suitable process. Whenever there are two metal ions in solution, sometimes it is important that the stability constant of one of the metal complex should be high enough to retain it in solution where as the stability constant of the other metal complex should be low so that this metal will be easily precipitated out from solution. This type of technique is used in the separation and identification of metal ions from solution, as is done in qualitative analysis. Chemistry of metal complexes is well established. One of the major factor in such complexes in solution is their stability.

Less stability is imparted to the metal complexes when the ligands are bulky as in nitrilotriacetic acid(NTA) and such complexes can be best utilised in electroless plating either of metal or of alloy, on a suitable base material.

In electroless plating, the metal ion in aqueous solution of complex salt is reduced to metal by using a suitable reducing agent. In this process, it is essential that the metal complex should be moderately stable so that it can be conveniently reduced to metal. For the deposition of an alloy, two or more metal ions that form the complex are essential. Further, these metal ions are reduced to metals depending on their standard reduction potential. The composition of metals thus deposited in the alloy depends on their standard reduction potential, concentration of metal ions and the stability constants of the complexes formed by the metal ions. Since metal ions in the complexes are reduced to metal at a slow pace, the alloy deposited is in crystalline form. The choice of the alloy depends on its desired application. For instance, in recent times the alloys of Fe-Ni, Mg-Ni have been found to be industrially important especially in electronic industry. As such, the thrust of major research is directed towards their production in the form of thin layer deposition of metal/alloy by electroless plating either on metal surface or on non conducting surfaces like plastic.

## 1.1 INORGANIC COMPLEX SALTS

The importance of the molecular complexes in various branches of the theoretical and applied chemistry has been realised since quite some time. In the past, substances which could be prepared from stoichiometric mixtures of two or more compounds, each having independent existence, were known.

Some of these were termed as double salts viz.  $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$  (Potash Alum),  $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$  (Mohrs salt),  $KCl \cdot MgCl_2 \cdot 6H_2O$  (Carnallite) etc, while others were called as molecular compounds or addition compounds, in which one metal salt combined with one or more neutral molecules e.g.  $K_4[Fe(CN)_6]$  ;  $K_3[Fe(CN)_6]$ ;  $[Cu(NH_3)_4]SO_4$ ;  $[Ag(NH_3)_2]Cl$ . copper, nickel and cobalt amines were some of the earliest known compounds of the latter class.

### 1.1.1 WERNER'S CO-ORDINATION THEORY

The understanding of the nature of such addition compounds i.e. metal complexes came mainly because of the efforts of Alfred Werner, Professor of Chemistry in Zurich. In fact, it was Werners's theory, which laid the foundation of our present day knowledge of Co-ordination Chemistry. In 1893, at the age of 26, Werner [1] after studying a number

of such compounds put forth his famous theory of co-ordination, commonly known as Werner's Co-ordination Theory, to explain the formation and the structure of complex compounds. For this work, he was awarded the Nobel Prize for Chemistry in 1913.

Werner's Theory includes the following postulates:

- Each metal exhibits two types of valency-
  - (i) primary or ionisable valency,
  - (ii) secondary (auxiliary) or non-ionisable valency.

For example, in  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ , the primary valency of copper is 2, while its secondary valency is 4.

- The primary valency is satisfied by negative ions while the secondary valency may be satisfied by negative ions or neutral molecules or even positive ions.

For example, in  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ , the primary valency of Co is satisfied by the negative chloride ions while the secondary valency is satisfied by the neutral ammonia molecules. Sometimes a negative ion may satisfy both the types of valences. For example in  $[\text{Co}(\text{NH}_3)_3]\text{Cl}_6$  the three chloride ions satisfy the primary valency as well as secondary valency of cobalt.

- A metal possesses a fixed number of secondary valencies called co-ordination numbers.
- Secondary valences are directed in space around the central metal ion. This postulate predicts the stereo-isomerism of complex compounds.
- The combining power of the metal ion is divided into two spheres of attraction: the “inner” or the “coordination sphere” and the “outer” or the “ionization sphere”. Neutral molecules or oppositely charged ions which satisfy the secondary valency of the metal ions are co-ordinated to the central ion in the coordination sphere, while the outer sphere contains the loosely held ionizable ion. To distinguish the two spheres of attraction, Werner enclosed the coordination sphere in the square bracket.

### **1.1.2 APPLICATIONS OF CO-ORDINATION COMPOUNDS**

Special type of coordination compounds which are cyclic in structure, where the metal is joined to two or more donor groups of a single molecule or ion are referred to as chelate compounds. These compounds are important because of their exceptional stabilities and other remarkable properties. Several of these metal chelates are extensively used in qualitative and quantitative analysis. Chelates are also used in analytical chemistry, water softening, solvent extraction, food preservation etc.

Dimethyl glyoxime, 8 hydroxy quinoline, cupferron, o-phenanthroline are some examples of complexing agents that give metal chelates which are of importance in analytical separations and precipitations. In the presence of excess of complexing agent such as sodium metaphosphate and polydentate amino acids, soap gives no precipitate with hard water, thereby softening the hard water.

EDTA is used for estimation of many cations like  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Zn^{2+}$  and  $Al^{3+}$  by volumetric titrations. The noble metals like Au and Ag are extracted from their ores through the formation of cyanide complexes like  $[Ag(CN)_2]^-$  and  $[Au(CN)_4]^-$  respectively. Schweitzer's reagent like tetramine copper (II) hydroxide  $[Cu(NH_3)_4(OH)_2]$  is used as a solvent for cellulose during the manufacture of artificial silk. A number of metal complexes are of biological importance. Haemoglobin in the red blood cells contains an iron-prophyrin complex. Chlorophyll in green plants contains magnesium prophyrin complex. Vitamin  $B_{12}$  is a cobalt complex. Lead poisoning and copper poisoning can be treated by injecting EDTA, so that metal-EDTA complex is excreted through urine. Another major application of complexing agent is in the plating industry, both in the electroplating and electroless plating processes, wherein metal ion/s are used with a suitable complexing agent for controlled reduction with a suitable reducing agent to metal/s.

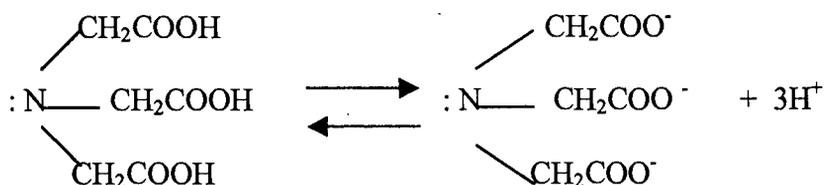
### 1.1.3 VARIOUS COMPLEXING AGENTS

The ligands, which have a lone pair of electrons, can act as complexing agents. These ligands can be monodentate (ammonia), bidentate (ethylene diamine), or polydentate (nitrilotriacetic acid) depending upon their point of attachment to central metal ion. Polydentate ligands form chelates and sometimes completely surround the central metal ion. Selectivity in the use of complexing agent for a specific purpose is important as it decides the degree of stability of the complex. In electroless plating of alloys, the proportion of metals depends on the concentration of complexing agent. Electroless bath solution becomes stable due to the presence of strong complexing agent.

However, higher the concentration of complexing agent, slower will be the speed of separation. The complexing agent forms the complex and prevents the existence of free metal ion in higher concentration, thereby stabilising the bath solution and preventing metal precipitation in the plating process. Table 1.4 and 1.5 gives a list of some of the complexing agents used in electroless plating.

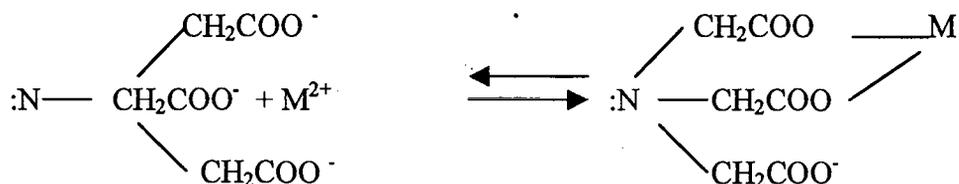
### 1.1.4.1 NITRILOTRIACETIC ACID (NTA) AS COMPLEXING AGENT

Nitrilotriacetic acid (NTA) [2-3] is known to form a variety of complex salts with many metal ions. It has chelate-forming behaviour with metal ions largely due to a lone electron pair on N and three carboxylate ions.



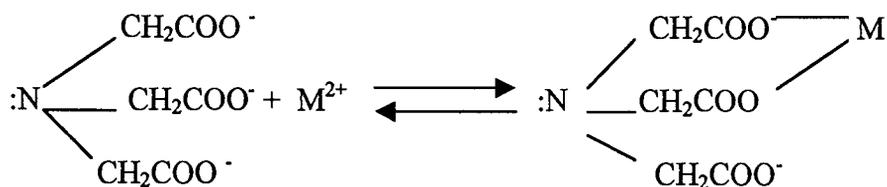
The reaction of this tribasic acid with metal ions has been well investigated [4-6]. Nitrilotriacetic acid,  $\text{H}_3[\text{N}(\text{CH}_2\text{COO})_3]$ , is sparingly soluble in water with solubility [7] equal to 1.28 g in 1 litre at 298 K though most of its salts are highly soluble. Being triprotic acid, it has three dissociation constants [8]. This acid is used in detergents [9], dyes [10], softening of boiler water, electro-deposition process etc.

The complexing of NTA with divalent metal ion can be represented as follows:

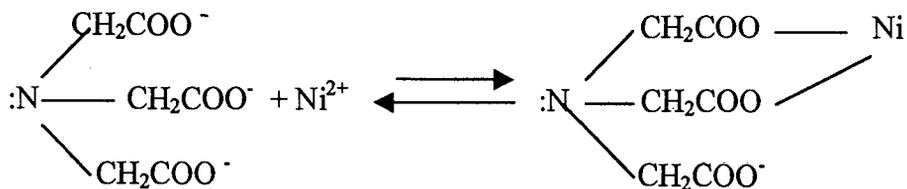


Where  $\text{M}^{2+}$  represent  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mg}^{2+}$  etc.

Nitrilotriacetate can be used as a complexing agent. The complexing of NTA with a divalent metal ion can be represented as under



Where  $\text{M}^{2+}$  represent  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mg}^{2+}$  etc. For example

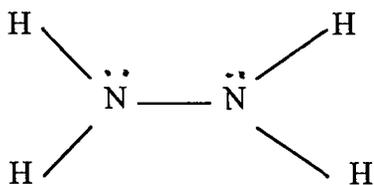


Nitrioltriacetate salts are extensively [11-34] used in the electro-deposition processes. This has been reviewed in detail by Krishnan et al [12]. NTA is used as a constituent in electro cleaners [35-36], in the pre-plate treatments.

Nickel ions form nitrioltriacetate salts with nitrioltriacetic acid. The equilibrium constant value [37-38](with  $\log K=11.26$ ) of these metal chelate indicates that the complex salt is very stable and it can be therefore be used as a complexing agent.

#### 1.1.4.2 HYDRAZINE ( $N_2H_4$ ) AS COMPLEXING AGENT

Hydrazine [39] can also act as a complexing agent. The two lone electron pairs on two nitrogen atoms make hydrazine a preferred ligand for co-ordination studies.



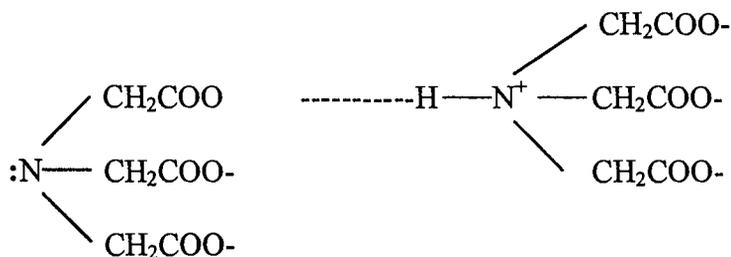
Hydrazine that is bound in complexes is called “hydrazino” in analogy to complex – bound ammonia, which is called “ammino”. Extensive work has been reported , with metal ions as the electrophilic constituents. Several monographs on metal complexes and complex chemistry include

information on hydrazine and hydrazine derivatives as complex salts [40-42]. Alkyl or aryl substitution of hydrazine effectively prevents its functioning as a bridging ligand. A very thorough review, of the reactions of hydrazine with transition metal complexes, was published by Bottomley [43]. It is acknowledged therein that despite the recent work this subject is still in its somewhat prolonged infancy. Hydrazine and its alkyl and aryl derivatives can theoretically act as unidentate, bidentate or bridging ligands. The entire field is literally very "complex". In many cases, the stability of metal hydrazino complexes is limited by interaction between the metal ion and hydrazine leading to lower oxidation state of the metal ion or reduction of the metal itself. In particular, the noble metal salts and complexes are easily reduced by hydrazine and the stability of the complexes is limited to the solution or to the short-lived intermediates [44]. Addition of hydrazine to copper (II) fluoride results in the reduction of copper to the metal, whereas the same reaction with zinc (II) fluorides gives a stable complex[45].

Infrared spectra show that the hydrazine behaves as a monodentate ligand in its complexes with metal ( $M = Ni^{2+}, Co^{2+}, Mn^{2+}, Zn^{2+}, Fe^{2+}$ ) picramates and as a bidentate bridging ligand in all complexes with metal picrates [46]. The reaction of hydrazine with Cu (II) chloride in acidic solution leads to at least 4 different complexes [47], because hydrazine is

not only a ligand but also a reducing agent. Some of the copper (II) is reduced to copper (I). Thus one obtains a white diamagnetic  $[(N_2H_4)Cu]Cl$  and a black paramagnetic, mixed valence copper (I,II) complex  $[(N_2H_5)_2Cu^{I} Cu^{II}]Cl_6$ . Blue and green copper complexes  $[(N_2H_5)_2CuCl_4] \cdot 2H_2O$  and  $[(N_2H_5)Cu] Cl_3$  are also formed.

Budkuley and Vernekar [48] studied the reaction between NTA and hydrazine hydrate and identified the nature of the reaction product. They have reported that NTA and hydrazine hydrate react to form dihydrazinium nitrilotriacetate, a water soluble compound in which there are only two of the three carboxylate as  $-COO^-$ , and that the third is a hydrogen bonded carboxylate. Besides this, there is also the acquisition of a positive charge by the nitrogen in NTA. The two carboxylates which are in ionic form (negative) can also act as donors of a lone pair of the electrons on oxygen and hence can act as ligand and form chelates with metal ion like  $Ni^{2+}$ ,  $Co^{2+}$ ,  $Mn^{2+}$ ,  $Zn^{2+}$ , etc.

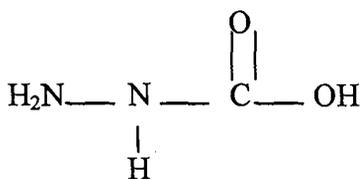


### 1.1.4.3 HYDRAZIDO CARBOXYLIC ACID (N<sub>2</sub>H<sub>3</sub>COOH) AS COMPLEXING AGENT

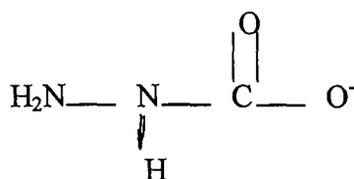
When excess of carbon dioxide is passed into hydrazine hydrate, a sparingly soluble precipitate of hydrazino carboxylic acid, also known as carbozoic acid [49], is obtained. This acid is now called as hydrazido carboxylic acid.



Hydrazino carboxylic acid, N<sub>2</sub>H<sub>3</sub>COOH is more corrosive than either hydrazine or carbon dioxide taken separately. However, due to the lone pair of electrons on nitrogen as well as oxygen of the --COO<sup>-</sup> ion, hydrazido carboxylate or N<sub>2</sub>H<sub>3</sub>COO<sup>-</sup> ion can act as a potent complexing agent.



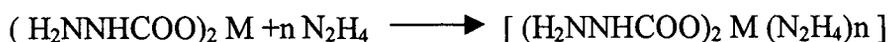
Hydrazido Carboxylic Acid



Hydrazido Carboxylate ion

The salts and chelates of hydrazido carboxylic acid with transition metals are of particular interest because these compounds are sometimes

found as corrosion products when hydrazine is inadvertently allowed to absorb carbon dioxide from air in the presence of metals. The general scheme of reactions that cause numerous contamination incidents is as follows:



where M is a bivalent metal. The Hydrazido carboxylate complexes of the type  $\text{M} (\text{N}_2\text{H}_4)_2(\text{H}_2\text{NNHCOOH})_2$  were obtained simply by allowing aqueous solution of zinc, nickel, manganese, or cobalt salts with hydrazine hydrate added, to stand in the open. The three types of hydrazido carboxylate complexes of bivalent metals [50] are reported

1.  $\text{M} (\text{H}_3\text{N}_2\text{COO})_2 (\text{N}_2\text{H}_4)_2$  where M = Mn, Co, Ni, Zn
2.  $(\text{N}_2\text{H}_5)[\text{M} (\text{H}_3\text{N}_2\text{COO})_3] \cdot \text{H}_2\text{O}$  where M = Fe, Co, Ni, Zn
3.  $\text{K} [\text{M} (\text{H}_3\text{N}_2\text{COO})_3]$  where M = Fe, Co, Ni, Zn

In conclusion, it can be said that the complexing nature of hydrazido carboxylic acid is very well established. The hydrazino carboxylic acid can easily be synthesised and it can be characterised by IR spectroscopy[51-53]. The characteristic IR absorption of N-N stretching in  $\text{N}_2\text{H}_3\text{COO}^-$  is observed around  $980 \text{ cm}^{-1}$ .

### 1.1.5 STABILITY OF METAL ION COMPLEXES IN SOLUTION

Most of the early work in the field of co-ordination compounds was confined to the preparation of chelates and elucidation of their structures. The method [54] available to Werner for investigation of complexes were the study of chemical reactivity, electrical conductivity and isomerism. The study of ionic complexes by Laden followed by the work of Jannik Bjerrum on the complex formation between a metal ion and the organic ligands, especially on the study of metal amines in aqueous solution [55], was of great importance. His concept of stepwise formation of complexes and their mathematical treatment helped to exploit the whole field of metal-ligand equilibria in solution and determination of stability constant of such complexes. The observation of Irving and Williams [56], that the stability constants of bivalent transition metal ions increase monotonically from  $Mn^{2+}$  to  $Cu^{2+}$  irrespective of the nature of the ligand with a drop in stability going from  $Cu^{2+}$  to  $Zn^{2+}$  was a great contribution in the study of co-ordinate complexes in general and transition metal complexes in particular.

The knowledge of the stability constant is essential for the qualitative treatment of several analytical and biological processes. For example  $Cu^{2+}$  can be detected in presence of  $Cd^{2+}$  by qualitative analysis

by addition of KCN, as  $\text{Cu}^{2+}$  forms a stable complex with  $\text{CN}^-$  as compared to  $\text{Cd}^{2+}$ . 2,3 – dimercapto propanol was used to protect the –SH group in enzymes from the attack of arsenical compounds used as poisonous gases during wartime. This was possible because –SH groups of the above compound would co-ordinate strongly with arsenic, rendering the latter harmless. Nowadays metal complexes, which are appreciably stable, could be used in plating of metal by reduction even on insulators.

The equilibrium constant (K) of any reaction is related to the corresponding free energy change ( $\Delta G$ ), hence the entropy changes of the complex formation could be evaluated. These thermodynamic quantities are essential for understanding the properties and stability of complexes. Substituent groups in the molecules of organic reagents affect the physical and chemical properties of the latter. For example, introduction of hydrophilic groups like-  $\text{SO}_3\text{H}$ ,  $-\text{OH}$ ,  $-\text{COOH}$ , etc. in the reagent molecule increases the solubility of metal complexes while introduction of hydrophobic groups such as  $-\text{CH}_3$ ,  $-\text{C}_2\text{H}_5$  lowered the solubility of the complex in water. Perkin [57] observed that the substitution of hydrogen in the amino group of glycine produces hardly any effect on the glycine complexes of group IIB metals. He noticed, however that an increase in the chain length of the amino acid caused a decrease in the stability of metal complex.

There exist a parallelism between a metal ion and a hydrogen ion in forming complexes of the type ML and HL (proton-ligand complex)[58]. This fact enables one to deduce a relationship between metal-ligand stability constant [K] and the pKa of HL, Ka being the dissociation constant of the reagent, HL.

#### 1.1.5.1 STABILITY STUDIES ON METAL ION -NTA SYSTEM

Recently several studies on complexes using acids rather than amines as ligands have been reported. S. Ramamurthy and M. Santappa [59] determined stability constants in aqueous solution of complexes of uranyl ion with mixed dibasic acids. Their inference was that the attainment of maximum co-ordination number of eight around U (VI) is actually more dependent upon the nature of ligand than on the geometry of uranyl ion. S. Ramamoorthy et al [60] have done equilibrium studies of  $\text{Cu}^{2+}$  nitrilotriacetic acid with a solid state cupric ion – selective electrode. They observed that  $\text{Cu}_2$  NTA is not formed in solution even with an excess of  $\text{Cu}^{++}$ . They inferred that in the presence of free  $\text{Cu}^{++}$  in the  $10^{-4}$ -  $10^{-5}$  M range, only a mononuclear proton complex  $[\text{CuHL}]$  is formed. S. N. Dubey, et al [61] studied the complex formation of iminodiacetic acid and nitrilotriacetic acid with aluminium, chromium and beryllium ions and determined stepwise stability constants of the metal complexes with the help of formation curves. They also determined thermodynamic stability constants from the formation constants by extrapolating it to zero ionic strengths.

### 1.1.5.2 TERNARY SYSTEM WITH NTA

Pradyot Kumar Datta, et al [62] have reported studies on the ternary complexes of copper(II), Nickel(II), and Zinc (II), with nitrilotriacetic acid as a primary ligand and some phenolic acids as secondary ligands. They observed that the formation curves of the ligands are wavelike suggesting two distinct steps corresponding to protonation of the carboxylate groups and the phenolic oxygen of the ligands for the proton-ligand system. For binary system the stabilities of the metal complexes follow the trend  $Ni^{2+} < Cu^{2+} > Zn^{2+}$ . For ternary system, it is noteworthy that, NTA complexes usually possess lower stability due to steric hindrance caused by the bulky NTA molecule, and the stereochemical effects are more significant than is electrostatic repulsion. They found that stability order, for mixed ligand complexes with respect to the metal as well as the ligands, is of the same order as in the corresponding binary ML system.

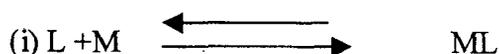
If the stability  $\beta_N$  (defined later) is found to be appreciably greater than zero, then it provides a convincing evidence for the existence of the complex  $ML_N$  in solution [63].

It is desirable to choose a bulk electrolyte which forms only very weak complexes with species under investigation. Salts of the alkali metals with

singly charged anion (often perchlorate ion) have been most widely used. However, medium ions should not form insoluble complexes. Complexes of metal ions with inorganic ligands may conveniently be studied in solutions in which the concentration of sodium ion and metal ions are kept constant and the ratio of perchlorate to ligand ions is varied. Since many inorganic ligands form weak complexes, high concentration of ligand ion may be required. Solutions which are 3 M or 4 M with respect to Na<sup>+</sup> or perchlorate ions are often used for investigations of this type. NaClO<sub>4</sub> is used as a background salt as it forms only very weak complex with species under investigation. However ClO<sub>4</sub><sup>-</sup> cannot be used with metal ions that are powerful reducing agent. In the present case NaClO<sub>4</sub> is used to maintain ionic strength constant [64].

### 1.1.5.3 MATHEMATICAL APPROACH IN STABILITY STUDIES

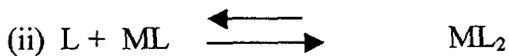
The mathematical approach to study the stability constant is as follows



with L as ligand, M as metal ion and ML as primary complex salt.

$$K_1 = [ML] / [M][L] \text{ OR } K_1 = a_{ML} / a_M \cdot a_L$$

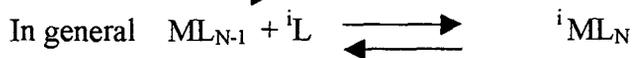
$$a_{ML} = K_1 \cdot a_M \cdot a_L \text{ -----(1)}$$



$$K_2 = [ML_2]/[ML][L] \text{ OR } K_2 = a_{ML_2} / a_M a_L$$

$$a_{ML_2} = K_2 \cdot a_{ML} \cdot a_L \text{ -----(2)}$$

Similarly



Substituting the values of  $a_{ML}$  from (1) and (2) we get

$$a_{ML_2} = K_1 \cdot K_2 \cdot a_M \cdot a_L^2$$

In general

$$a_{ML_N} = K_1 \cdot K_2 \cdot K_3 \cdot \dots \cdot K_N \cdot a_M \cdot a_L^N$$

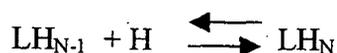
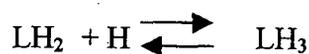
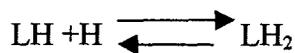
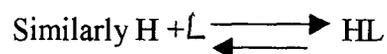
$$\text{or } K_1 \cdot K_2 \cdot K_3 \cdot \dots \cdot K_N = a_{ML_N} / a_M \cdot a_L^N = \beta_N$$

Where  $\beta_N$  is the stoichiometric stability constant

$$\beta_N = [ML_N] / [M][L]^N$$

$$\beta_N = \prod_{i=1}^N K_i \text{ where } \beta_2 = K_1 \cdot K_2$$

$$\beta_3 = K_1 \cdot K_2 \cdot K_3$$



$$\beta_N^H = [LH_N] / [LH_{N-1}][H]$$

**Degree of formation  $\bar{n}$ , as given by Bjerrum is**

$$\bar{n} = \frac{\text{Concentration of the ligand bound to the metal ion}}{\text{Total concentration of the metal ions}}$$

$$= \frac{[ML] + 2[ML_2] + 3[ML_3] + \dots + N[ML_N]}{[M] + [ML] + [ML_2] + [ML_3] + \dots + [ML_N]}$$

$$= \frac{K_1 [M][L] + 2K_1 K_2 [M][L]^2 + 3K_1 K_2 K_3 [M][L]^3 + \dots + N[M][L]^N}{[M] + K_1 [M][L] + K_1 K_2 [M][L]^2 + K_1 K_2 K_3 [M][L]^3 + \dots + K_1 K_2 K_N [M][L]^N}$$

$$= \frac{[M] K_1 [L] + 2K_1 K_2 [L]^2 + 3K_1 K_2 K_3 [L]^3 + \dots + N K_1 K_2 K_N [L]^N}{[M] [1 + K_1 [L] + K_1 K_2 [L]^2 + K_1 K_2 K_3 [L]^3 + \dots + K_1 K_2 K_N [L]^N]}$$

$$= \frac{K_1 [L] + 2K_1 K_2 [L]^2 + 3K_1 K_2 K_3 [L]^3 + \dots}{1 + K_1 [L] + K_1 K_2 [L]^2 + K_1 K_2 K_3 [L]^3 + \dots}$$

$$= \frac{\beta_1 [L] + 2\beta_2 [L]^2 + 3\beta_3 [L]^3 + \dots}{1 + \beta_1 [L] + \beta_2 [L]^2 + \beta_3 [L]^3 + \dots}$$

In general

$$\bar{n} = \frac{\sum_{i=0}^N i \beta_i [L]^i}{\sum_{i=0}^N \beta_i [L]^i}$$

In specific cases

$$\frac{n}{A} = \frac{\sum_{i=0}^N \beta_i^H [L]^i}{\sum_{i=0}^N \beta_i^H [L]^i}$$

Total metal ion concentration  $T^0 M$

$$T^0 M = [M] + [ML] + [ML_2] + \dots$$

$$K = [ML] / [M] [L]$$

$$[ML] = K [M] [L]$$

$$T^0 M = [M] \sum_{i=0}^N \beta_i [L]^i$$

Total ligand concentration  $T^0 L$

$$T^0 L = [L] + [ML] + [ML_2] + [ML_3]$$

$$T^0 L = [L] \sum_{i=0}^N [L]^i$$

Calculation , graphs involved are

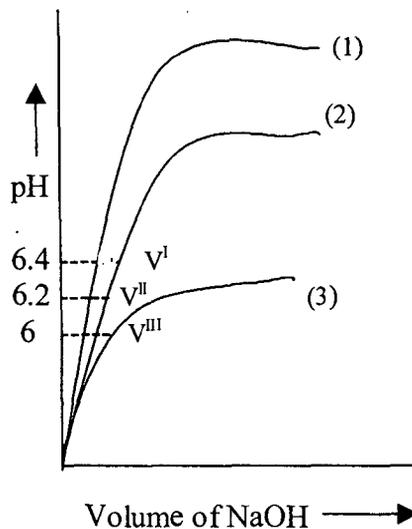


Fig.1.1 Plot of volume of NaOH against pH of solution

(1) and (2) ~~are~~ to be taken to calculate  $\bar{n}_A$

$$\bar{n}_A = \left\{ y T_L^0 + \left( \frac{V^I - V^{II}}{V^0 + V^I} \right) (N + E^0) \right\} / T_L^0$$

where  $E^0$  is the Concentration of the acid after dilution of the mixture.

$Y$ =basicity of the acid

$N$ =concentration of the base

$$\bar{n}_A = \left\{ y T_L^0 - \left( \frac{V^{II} - V^I}{V^0 + V^I} \right) (N - E^0) \right\} / T_L^0$$

$$\bar{n}_A = y - \left( \frac{V^{II} - V^I}{V^0 + V^I} \right) \left\{ \frac{(N - E^0)}{T_L^0} \right\}$$

$T^{\circ}L$  is the initial concentration of ligand after dilution.  $\bar{n}_A$  at pH 6, 6.2, 6.4, 6.6, 6.8, 7,----- is found out or wherever possible. Then  $\bar{n}$  at the same pH value is calculated where  $\bar{n}_A$  is known.

$$\bar{n} = \left( \frac{V^{II} - V^{I}}{V^0 + V^I} \right) \left[ N + E^0 + T^{\circ}L \left( \frac{y - \bar{n}_A}{\bar{n}_A} \right) T^{\circ}M \right]$$

$T^{\circ}M$  is the initial concentration of metal ion after dilution.

$N + E^0 / \bar{n}_A T^{\circ}M$  is same for all.

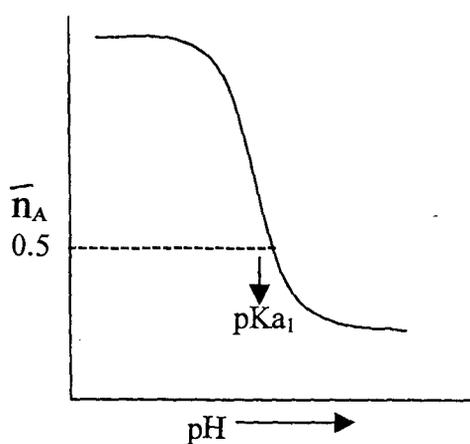


Fig.1.2 Plot of  $\bar{n}_A$  against pH of solution for monobasic acid ligand.

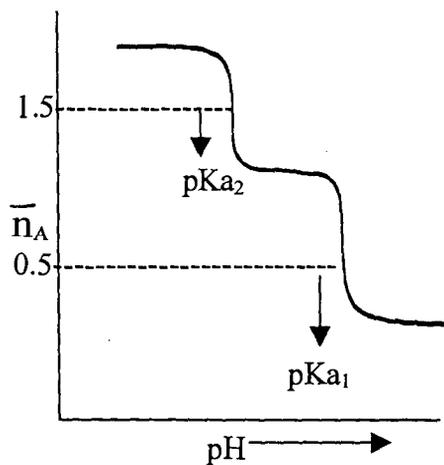


Fig.1.3 Plot of  $\bar{n}_A$  against pH of solution for dibasic acid ligand.

For more accuracy

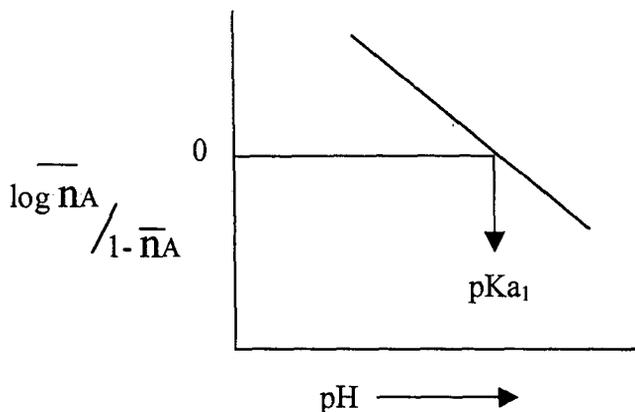


Fig.1.4 Plot of  $\log \bar{n}_A / 1 - \bar{n}_A$  against pH for acid ligand

If basicity is not one, then 1 is replaced by  $\beta$  in the formula  $\log \bar{n}_A / 1 - \bar{n}_A$   
 i.e.  $\log \bar{n}_A / \beta - \bar{n}_A$

$$pL = \log_{10} \left\{ \sum_{i=0}^N \beta_i^H (1 / \text{antilog}[H]) / T_L^0 - \bar{n} T_M^0 (V^{0+} V^{III} / V^0) \right\}$$

$$pL = \log_{10} \left\{ 1 + \log (pKa / pH) / T_L^0 - \bar{n} T_M^0 \right\} \times (V^{0+} V^M / V^0)$$

If 50% of dioxane is used

$$V^M = 2V^{III}$$

From  $\bar{n}$  values at different pH, calculate pL.

Plot  $\bar{n}$  against  $pL$

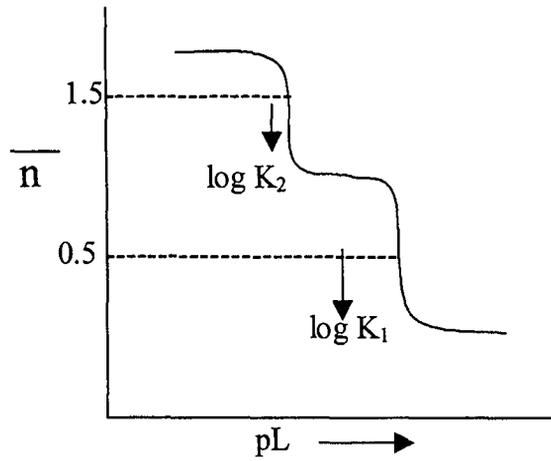


Fig1.5 Plot of  $\bar{n}$  against  $pL$

Where  $pL = -\log L$

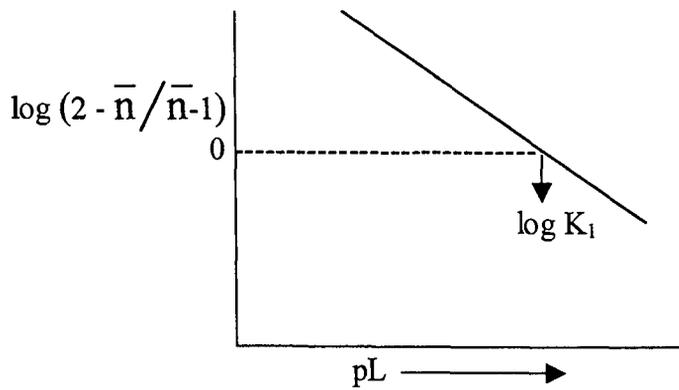


Fig 1.6 Plot of  $\text{Log}[(2 - \bar{n}) / (\bar{n} - 1)]$  against  $pL$

This can be studied at various ionic strength.

Further, the free energy change and the change in entropy during complexation can also be calculated from the equation:

$$\Delta G = -RT \ln K_1$$
$$\Delta G = \Delta H - T \Delta S$$

Thus knowing  $K_1$  at different T, free energy change,  $\Delta G$  can be calculated.

There are various methods of evaluating the stability constants out of which potentiometric method is widely used.

## 1.2 ELECTROLESS PLATING: METAL AND METAL ALLOYS

The deposition of a metal on the surface of metallic / non metallic substrate can be

achieved by two processes:

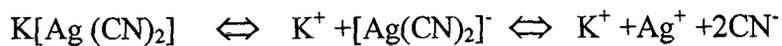
(i) the electrolytic process and (ii) the non –electrolytic process.

In the electrolytic process the reduction of metal ions to metal takes place at the cathode under the influence of electric current.



Where M is the metal. This process is called electroplating, in which noble metal / superior metal is made the anode and the substrate to be plated is made the cathode. The electrolytic solution generally contains complex salt of the metal to be plated. For example, in silver deposition [65], the electrolyte used is potassium argentocyanide.

To obtain a coherent deposit of silver, the silver ion concentration must be low, and this is achieved by using potassium argentocyanide which furnishes relatively controlled amount of silver ions.



During eletrolysis  $\text{Ag}^+$  ions travel to the cathode where they are reduced to metallic silver. Silver at the anode ionises and the  $\text{Ag}^+$  ions associate with  $\text{CN}^-$  ions to form  $[\text{Ag}(\text{CN})_2]^-$  thus keeping the composition of the electrolyte unaltered. The ultimate change being disappearance of silver from the anode and its deposition on the cathode.

Electroplating or galvanic metal plating [66] has certain disadvantages in that the coating for components subjected to great wear are not sufficiently hard. They exhibit unevenness in the thickness and there are difficulties in metal plating of parts of complicated shape i.e. throwing power is poor in electrolytic deposition. This required shaped anodes there by making refining process more difficult and more expensive. Besides, electroplating could not be done on semiconductors or non conductors like plastic. To over come this difficulty A. Brenner and G. Riddell [66] in 1946 invented the non-electrolytic process in which no current is used.

Nowadays the non-electrolytic or electroless plating or chemical plating methods are gaining importance for repair purposes as well as for

protection against corrosion and wear of new parts of machines and apparatus. They offer particular advantages for coating of inner surfaces of vessels, pipes, etc.

Where galvanic process fails completely. The electroless plating or chemical plating can be used for metallisation of various insulators (plastics, glass, and ceramics) as well as semiconductors (germanium, silicon, etc.). With the help of this technique deposition of ternary and even quaternary coating of alloys with magnetic, electrical and protective properties have become feasible.

A brief historical overview of electroless plating will be in place here. In 1844 Wurtz[66] observed that metallic nickel powder is obtained from an aqueous solution of its salts by reduction with hypophosphite. Bretau [68] and Roux [69] obtained bright coatings of metal deposit when reducing agents were added. Fredenici, in a dissertation, described the reaction of nickel salts in alkaline medium with hypophosphite in the presence of a palladium activator. But none of these studies led to practical application.

The discovery of electroless nickel technology as is used today has been made in 1946, when after some two years of work, Brenner and Riddell [70-71] developed a practical system. They studied the electro-deposition of nickel-tungsten alloys from a citrate bath at a higher temperature. The deposits showed a high degree of internal stress, which

they attributed to the presence of oxidation products of citrate used. To solve this problem they used a range of reducing agents including hypophosphite.

General American Transportation Corporation (G.A.T.C.) [72] showed interest in the above method, as means of coating the interiors of tankers used to transport concentrated caustic soda . After five years of development programme G.A.T.C. built their first pilot line in 1955, thereby making the first commercial use of electroless nickel plating. The electroless nickel solution was sold under the trade name “Kanigen” [73,74,75]. The “Kanigen” process (catalytic nickel generation) involved the development of the work of Brenner and Riddell by Gutzeit, the Research Director of G.A.T.C. and his publications. Apart from Kanigen process, in the mid to end of the 70s ,the “ Durni coat” process, also based on sodium hypophosphite reduction was developed [76].

While using sodium borohydride as reducing agent, the “Nibodur” process was made available . Electroless baths based on boron reducing compounds like  $\text{NaBH}_4$  go back to the work of H. Schlesinger [77]. In 1954, for the first time the nickel-boron alloys were proposed for use as alloy coating for steel [77]. For this purpose alcohol or ammine solutions of both components viz. nickel salt and boronhydride were used.

Table 1.1 : The functions of various component in electroless plating, bath solution

Component $s$	Function
1) Metal salt	Provides metal ions to be plated
2) Reducing agent	Provides reducing power at a catalytic heterogeneous interface
3) Complexing agent	Complexing of metal ions and prevents bulk decomposition
4) Stabilizer	Ensure homogeneous stability against bulk decomposition
5) pH adjuster	Ensure optimum pH for plating rate and deposit composition
6) Wetting agents	Increase the wetting properties of the surface to be plated
7) Exaultants	Accelerates the rate of deposition

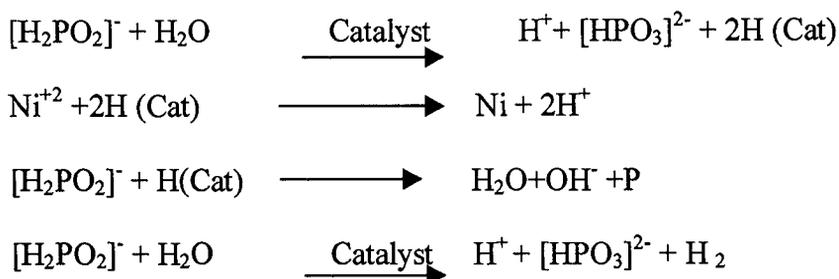
Table 1.2 : The components of electroless nickel bath and their functions

Components	Function	Examples
1) Nickel ions	Source of metal	Nickel chloride Nickel sulphates Nickel Acetate
2) Hypophosphite ions	Reducing agent	Sodium hypophosphite Sodium borohydride, Hydrazine
3) Complexing agents	Form nickel complexes, Prevent free Ni ion concentration there by stabilizing the solution and preventing Ni phosphite precipitation, Also acts as pH buffers.	Monocarboxylic Acids Dicarboxylic Acids Hydroxy Carboxylic Acids. Ammonia, Alkanolamines
4) Accelerators	Activate hypophosphite ions and accelerate deposition. Mode of action opposes stabiliser and Complexants	Anions of some mono- and di-carboxylic Acids, fluorides, borates.
5) Stabilisers	Prevent solution breakdown by shielding catalytically active nuclei	Lead, tin, Arsenic, Molybdenum, Cadmiumon Thallium ions, thiourea, etc.
6) Buffers	Keep the pH value constant over an extended working period	Sodium salts of some complexing agents (choice depends on the pH range used)
7) pH regulators	For accurate adjustment of pH value	H <sub>2</sub> SO <sub>4</sub> and HCl, Na <sub>2</sub> CO <sub>3</sub> , NaOH, NH <sub>3</sub>
8) Wetting agents	Increases wettability of surfaces to be coated	Ionic and Non-ionic Surfactants

## 1.2.1 REDUCING AGENTS IN ELECTROLESS DEPOSITION

Reducing media used for the chemical separation of nickel and cobalt from aqueous solution are hypophosphite, boron hydride, amino borane and hydrazine.

The hypophosphite solutions used are either acidic or alkaline in electroless plating. In acid solution, various chemical reactions taking place can be represented as:



In the presence of catalytic surfaces (example Pd), the hypophosphite ions are oxidised to orthophosphite ions. The hydrogen atoms which are given out during this reaction are partly adsorbed on the surface of the catalyst. The nickel ions are then reduced to metallic nickel by active hydrogen atoms whereby they are oxidised to  $\text{H}^+$  ions. At the same time, a small part of the hypophosphite ions is reduced to  $\text{OH}^-$  ions, water and phosphorous by the adsorbed active hydrogen on the catalytically active surface. Also a

part of the hypophosphite ions are oxidised catalytically to orthophosphite ions and hydrogen is given off. The speed of the separation of Ni depends on the pH value of the solution. The phosphorous content of deposit depends mainly on the pH control of the bath during plating and it is also affected by complexing and buffering agent, the plating temperature and the molar ratio of nickel to hypophosphite [78]. Generally, phosphorous deposit is in the range of 0.5 to 2%.

The reaction of nickel ions in alkaline solutions takes place in the same manner as those in acid solution. It is accompanied by the liberation of hydrogen and oxidation of hypophosphite to phosphorous.

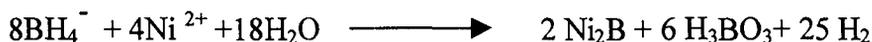
The alkaline solutions have a lower speed of separation and the coating obtained are more porous and less resistant to corrosion but often more lustrous. The investigated solutions are relatively more stable by the presence of strong complexing agents and better solubility of phosphite in alkaline medium even without special additives. The quantity of phosphorous formed is smaller than the nickel- phosphorous coatings produced from acid solutions.

## 1.2.2 BORON HYDRIDE AS REDUCING AGENT

Another possibility of achieving non-electrolytic coatings of metal/alloy is by the use of alkali boronhydrides and their derivatives as reducing media. They have better reducing ability than hypophosphite and can be worked even at lower temperature. All these technically interesting boron hydride processes are marketed under the name "Nibodur". The hydrolysis of boron hydride ions in neutral or acid medium takes place very fast. It can be shown by equation (1) and (2).



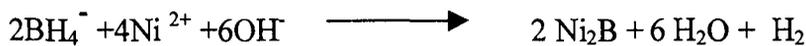
In presence of nickel ions in the solution one obtains boride.



When the pH value of the solution is regulated between 12-14 the main product of the reaction is pure nickel.



One can also assume that the reaction takes place as follows:

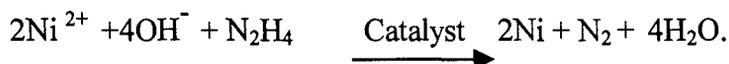


High temperatures accelerate the unwanted decomposition reactions (1) and (2) while they are suppressed by the addition of alkali. Working range of pH is between 12 -14 with complexing agents.

### 1.2.3 HYDRAZINE AS REDUCING AGENT

As long ago as 1947 L. Pessel [79] proposed the use of hydrazine as reducing additive for non electrolytic substitute to hypophosphite solutions. The method of nickel coating by electroless plating in alkaline solution in presence of nickel salts hydrazine and complexing agents was investigated in detail by D. J. Levy [80]. The author asserts that the speed of the process is directly proportional to the concentration of  $\text{Ni}^{2+}$  and hydrazine, the pH and temperature.

The formation of layers can be represented as:



### 1.2.4 ELECTROLESS PLATING: MERITS AND DEMERITS

The advantages of the electroless [81] coating include,

- good throwing power
- uniform coating thickness on complex objects
- no levelling required
- coatings are harder than electrodeposited metal because phosphorus is incorporated in the structure (in hypophosphites)
- deposits can be further harden by heat treatment at 673 K.
- good wear resistance.

- low ductility
- low porosity, which leads to good corrosion resistance
- low labour cost.
- excellent solderability and brazability characteristics .

However, the main disadvantages of electroless method are

- solutions are expensive
- deposit rates are slow
- welding characteristics are poor
- careful analytical control of the bath is required.

### **1.2.5 ELECTROLESS DEPOSITION OF ALLOYS**

With the assistance of hypophosphites, boron hydride, hydrazine (or formaldehyde) deposits are obtained by simultaneous reduction of various metal ternary Nickel alloys of the type such as Ni-M-P and Ni-M-B , where M represents another metal. The main metal Ni or Co must be capable of being catalytically deposited. The reduction of the second metal which participates in the alloy is determined by its electrochemical standard potential, as well as by its catalytic properties in relation to the reduction process. When the metal is difficult to reduce, its share in the alloy cannot reach high value. eg Ni-Cr-P.

The contents of the metal which are catalytic poisons and which slow down the reduction of the main metal (Ni, Co) is limited to a small quantity which can be incorporated in the coating without interrupting the deposition. For example Ni-Sn-P and some ternary alloys like Ni-Co-P, Ni-Fe-P, Ni-Cu-P have important practical uses while other alloys are only of scientific interest. The most important alloy in practical terms is Ni-Co-P, which is used for magnetic data storage. A lot of literature, which is available for the various alloy depositions, is given in the Table 1.3.

A.K. Sharma and co-workers have done electroless nickel plating on magnesium alloys, which are used in aerospace applications. It was found that such alloys has adequate mechanical properties, corrosion resistance, solderability, and environmental stability for stringent space requirements.

Ferromagnetic Ni-Fe layers can be non-electrolytically separated from ammonical solution of nickel and iron chloride, and sulphate respectively, with tartarate as complexing agent and using hypophosphite as reducing medium, the coatings are suitable as accumulator elements in electronic calculating machines. The carrier substance is usually aluminium-copper alloy and glass or polyethylene terephthalate as substrate.

Table 1.3 : Some alloys deposited by electroless deposition process

Alloy deposit	References
Ni-Co-P	82-85
Ni-Fe-P	86-88
Ni-Cr-P	89
Ni-Cu-P	90
Ni-W-P	91-92
Ni-Mo-P	93-95
Ni-Sn-P	92 , 95-100
Ni-Co-B	101-104
Ni-Fe-B	101-108
Ni-Sn-B	109-110
Ni-W-B	107 , 111
Ni-Mo-B	107 , 112
Ni-Re-B	107

The participation of iron in the alloy coatings is determined by the proportion of  $\text{Fe}^{2+} / \text{Ni}^{2+}$ , as well as by the concentration of the complexing agent. There are a number of patent specification which have as their subject, the separation of Ni-Fe-P coatings [113-117].

### 1.2.6 COMPLEXING AGENT IN ELECTROLESS PLATING

The common complexing agents used are monocarboxylic acids, dicarboxylic acids, ammonia, alkanolamines. The various types of the complexing agents used in electroless plating are shown in Table 1.4 and the complexing agents used with hydrazine as reducing agent are shown in Table 1.5.

In 1953, G. Gutzeit and E.J. Ramirez (155) patented the use of dicarboxylic acid e.g. succinic acid, malonic acid and glutaric acid as complexing agent in electroless plating. It was shown that the speed of the separation is maximum at certain concentration of the acid and for succinic acid it was at pH of 5.8. Together with the simplest hydroxy carboxylic acid, the glycolic acid (oxy-acetic acid) [156], lactic acid became very popular [157-160] as it prevented deterioration in the quality of the coating. Lactic acid acts as a complexing agent as well as a buffer and at optimum concentrations (0.4M / L) it also has an accelerating effect.

Table 1.4 : Complexing agents used in various electroless plating baths

Complexing agent	Reducing agent	Reference
Lactic acid / Lactate Propionate	NaH <sub>2</sub> PO <sub>4</sub> (A)	122 , 123
Glycolic acid	NaH <sub>2</sub> PO <sub>2</sub> (A)	119
Acetic acid	NaH <sub>2</sub> PO <sub>3</sub> (A)	124
Sodium acetate	NaH <sub>2</sub> PO <sub>2</sub> (A)	124
Ammonium acetate	NaH <sub>2</sub> PO <sub>2</sub> (A)	124
Fluoroboric acid	NaH <sub>2</sub> PO <sub>2</sub> (A)	126
Fluoride	NaH <sub>2</sub> PO <sub>3</sub> (A)	125
Tartaric acid	NaH <sub>2</sub> PO <sub>2</sub> (A)	128
Succinic acid	NaH <sub>2</sub> PO <sub>2</sub> (A)	128
Salicylic acid	NaH <sub>2</sub> PO <sub>2</sub> (A)	127
Phthalic acid	NaH <sub>2</sub> PO <sub>3</sub> (A)	127
Glycine	NaH <sub>2</sub> PO <sub>2</sub> (A)	129
Amino acids	NaH <sub>2</sub> PO <sub>2</sub> (A)	130
Sodium citrate	NaH <sub>2</sub> PO <sub>3</sub> (AK)	119
Ammonium citrate	NaH <sub>2</sub> PO <sub>2</sub> (AK)	131
Sodium pyrophosphate	NaH <sub>2</sub> PO <sub>3</sub> (AK)	133
Potassium pyrophosphate	NaH <sub>2</sub> PO <sub>2</sub> (AK)	133
Ammonium chloride	NaH <sub>2</sub> PO <sub>3</sub> (AK)	131
Sodium tetraborate	NaH <sub>2</sub> PO <sub>2</sub> (AK)	132
Ammonium oxalate	NaH <sub>2</sub> PO <sub>3</sub> (AK)	134
Ammonium sulphate	NaH <sub>2</sub> PO <sub>2</sub> (AK)	134
Glycolic acid	NaH <sub>2</sub> PO <sub>2</sub> (AK)	135
EDTA-Sodium salt	NaH <sub>2</sub> PO <sub>2</sub> (AK)	135
Sodium-Potassium tartarate	NaBH <sub>4</sub>	133
EDTA	NaBH <sub>4</sub>	120
Sodium Fluoride	NaBH <sub>4</sub>	136
Sodium citrate	DEAB	120
Sodium succinate	DEAB	118
Sodium acetate	DMAB	139
Sodium pyrophosphate	DMAB	140
Lactic acid	DMAB	137
Boric acid	DMAB	138
Malonate	DMAB	121
Pyrophosphate	DMAB	121

A= Acid bath,            DMAB= Dimethylamino borane,  
 AK = Alkaline bath,    DEAB = Diethyl Amino Borane.

Table 1.5 : Complexing agents used in various electroless plating baths with hydrazine as reducing agent

Complexing agent	References
Tartaric acid	141, 142
Sodium Sulphite	143
Sodium Tartarate	141, 145, 149
Ammonia	144, 146, 147, 150
Amine	146
Disodium salt of EDTA	146
Amylamine	146
Ethanolamine	146
Monoethanolamine	146
Sodium citrate	148, 152
Citric acid	149, 152, 154
Potassium cyanide	147, 151
Glycine	153

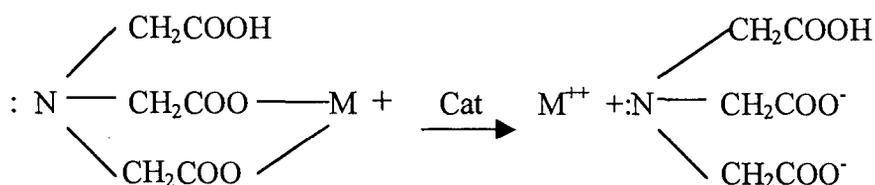
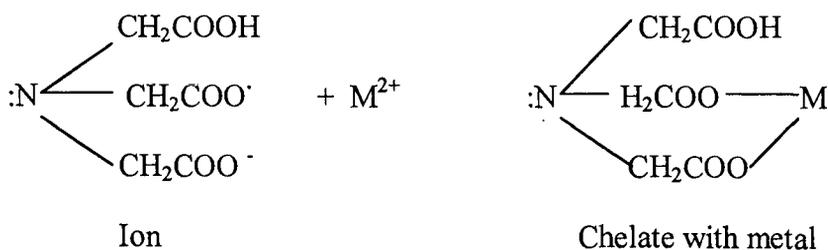
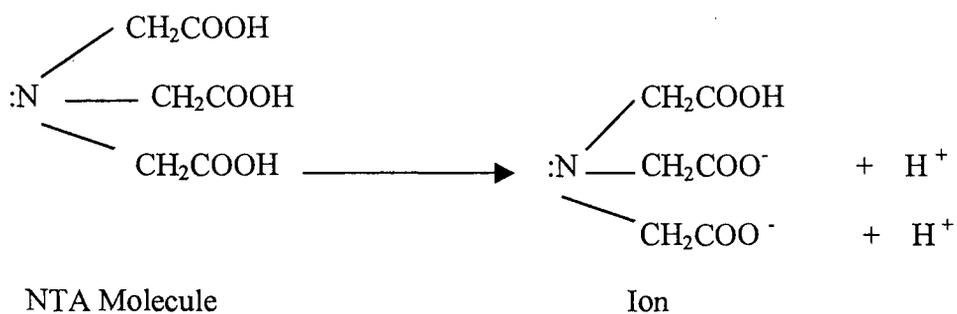
The first members of the homologous series of the saturated carbonic acid (HCOOH and CH<sub>3</sub>COOH) are poor complexing agents. Combinations of carboxylic acids, and hydroxy carboxylic acid e.g. propionic acid /lactic acid are often used [158,161]. The unsaturated carboxylic acids find very limited use as complexing agents.

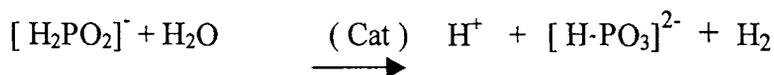
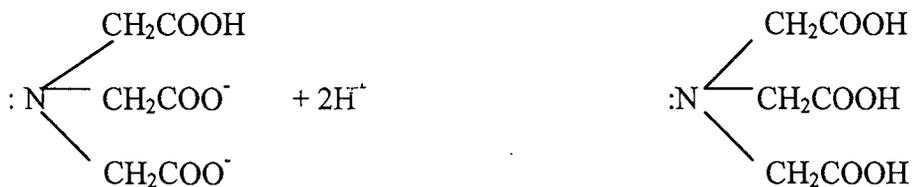
G. Gutzeit [162] has examined the complex forming action of the amino acids namely amino acetic acid; glycine,  $\alpha$ -aminopropionic acid ( $\alpha$ -alanine),  $\beta$ -amino propionic acid ( $\beta$ - alanine),  $\alpha$ - amino butyric acid, amino succinic acid (aspartic acid) and triacetic acid as well as EDTA. These acids prevent the separation of unwanted phosphate and the same time they positively influence the speed of the process.

The formation of complexes are not only limited to the use of organic additives. There are some inorganic salts which are also used, even if only to a limited extent . e.g. ammonium salts [163-164] and fluorine borates [165,166]. There is also possibility of formation of complexes between Ni (II) ions and H<sub>2</sub>PO<sub>2</sub><sup>-</sup> ions [167].

## 1.2.7 NITRILOTRIACETATE AS COMPLEXANT IN ELECTROLESS PLATING

Nitrilotriacetic acid (NTA) can also act as a complexing agent in electroless plating. NTA forms chelates with metal ions in presence of hydrazine. This complex formation prevent free metal ion concentration and thereby stabilizes the solution from which a uniform and smooth deposit of the metal can be obtained.

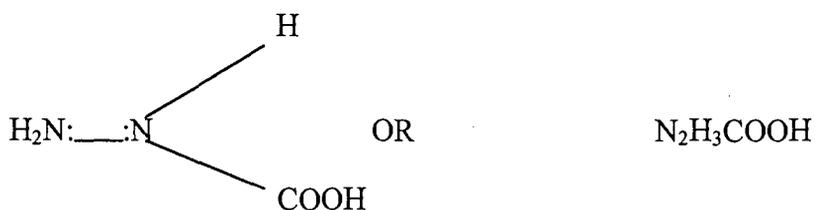




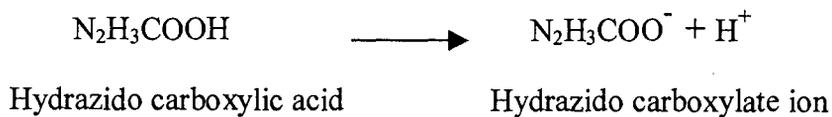
In the presence of Pd, the hypophosphite ions are oxidised to orthophosphite ions. The hydrogen atoms formed are partly adsorbed on the surface of the catalyst. The metal ions are reduced to metal by active hydrogen. 0.5 to 2 % of P forms alloy with metal deposited.

## 1.2.8 HYDRAZIDO CARBOXYLIC ACID AS COMPLEXANT

Hydrazido carboxylic acid, like other carboxylic acids, can also act as a complexing agent which forms metal chelates, and the metal ions are reduced at a uniform speed to metal



Hydrazido carboxylic acid



There are no reports of the use of hydrazido carboxylic acid as complexing agent.

### 1.3 SCOPE OF PRESENT INVESTIGATION

No systematic studies have been reported on the stability of the complex between metal ion and hydrazido carboxylic acid as ligand in solution. One of the reasons could probably be the instability of hydrazido carboxylic acid in acidic medium at room temperature. Similarly, there are no reports on the determination of stability constants of metal-nitrilotriacetate complexes using pH-metry method in the study of ternary system involving nitrilotriacetate, hydrazido carboxylic acid.

Literature survey indicates that these two acids are potent complexing agents. However there are no reports on the use of hydrazido carboxylic acid of being used as complexing agent in plating processes. Though some work in electrolytic deposition with NTA, as complexing agent has been reported, not much work has been carried out in the electroless plating with this acid. Moreover, there are no reports available indicating the use of ternary system with these two acids in plating process.

It was therefore thought interesting to determine the stability constant of hydrazido carboxylic acid salts with various metal ions.

Similarly to carry out investigations in order to understand stability properties of metal ions with this acid in combination with nitrilotriacetic acid in ternary system.

The investigation on the above complexes could be further extended to find out its possible application in deposition process.

It was therefore thought interesting to determine the stability constant of hydrazido carboxylic acid salts with various metal ions. Similarly, to carry out investigation in order to understand stability property of metal ions with this acid in combination with nitrilotriacetic acid in ternary study.

## REFERENCES

1. D Banerjea, "Coordination Chemistry", Tata McGraw Hill, New-Delhi, 1994
2. H. Brintzinger and G. Hesse, *z. An. Org. Allge. Chem*, 249 , (1942) 299.
3. D. T. Sawyer and P.J. Paulsen, *J. Am . Chem.. Soc.*, 81 (1959) 816.
4. W. Heintz, *Ann*, 122 (1862) 260.
5. F.T. J. Rajabalee, *J. Inor. Nuclear Chem*, 36 1974 (557).
6. Y. Tomita and Y. Ueno, "*Bull. Chem Soc., Japan*" 36,[9].1963 (1069).
7. M. Bersworth, "*J. Org. Chem.*," 15 , (1950) 46.
8. G. Schwarzenbach and W. Biedermann, "*Helv. Chem. Acta*" .31, 1945 (331).
9. N.S. Thom, "*Water Research*," 5,(1971),391.
10. Bird, "*J. Soc. Dyers Col*" ,56,(1940)473.
11. R.M. Krishnan, "*Ph.D. Thesis*,"..Dhanbad School of Mines,(1990)
12. R.M. Krishnan,S. R. Natarajan,V.S. Murlidharan and G.Singh "*Bull Electrochem*" 4,12(1988)1010
- 13.Schwarzenbach, "*Chemia*," 3,(1949)1
- 14.B.Kirson and R. Borustein, "*Bull. Soc. Chem.*" France (1961) 1081. *Chem. Abst.*56,1132,I(1962)
15. B.Kirson and R. Borstein , "*Bull. Soc. Chem.*" France(1961) 1101, *Chem .Abstr.*,56(1962)1133b
- 16 Richard L. Gustafson and E. Arthur Martell "*J. Phys. Chem*" 567-82(1963) "*Chem., Abstr.*," 58,8618a (1963).

17. N. F. Kazarinova, N.I. Latosh and I. Ya. Postovs, Kii, Tr, Soveschch, Pa Kompha Ksonam, Abad, Nauk SSR, Ural S. K. Filialsverdlovsk 39-52(1958), "Chem., Abstr.," 58,46449(1963)
18. Technic. Inc. Brit. Patent 921,960(1963), "Chem. Abstr.," 59,224b(1963)
19. Ya. D. Fridman, R. A. Veresova, A. Ya. Fridman, and R.I. Sorochan, Zn., Ne org., Khim 14 ,(5) 11893,(1969), Chem., Abstr., 7,25170j(1969)
20. J. Scherzer and A. M. Weisberg. U.S. Patent, 3,530,049,(1970) Chem., Abstr., 73,136797e(1970)
21. R. E. Luma and P. Gourerh "Rapp Rech Cent., Reg. Etud, Nucl. Kinshasa," 18,35(1972) "Chem., Abstr.," 85,100071x (1976)
22. V. Majer, J. Vesely and K. Stubik, Anal. Letti, 6,(6), 577-84,(1973); "Chem., Abstr.," 79,60842 s ,(1973)
23. H. Hayashida, Hideyasu , Y. Nakamura, Jap. Patent, 7216047(1972) "Chem., Abstr.," 78,143217x ,(1973);
24. R.H. Gibson and P. E. Sturreck, "J. Electrochem. Soc.," 123(8), 1170 – 3 (1976) Chem., Abstr., 85,101211e(1976)
25. V.L. Korner, I. P. Mukanov and M.N. Konyukhov, Zn. Fiz-Khim, 51 (6)1380-3,(1977) "Chem., Abstr.," 87,74275m(1977)
26. T. Juodiene and K. Iodkazis, "Isslad Obl. Electro., Osazhdeniya. Met. Mater. Resp. Kon F Electro Khim, Lit, SSR 14<sup>Th</sup> , 161-5(Russ)(1976), "Chem., Abstr.," 87,31035r (1977)

27. F.I. Darulov, E. R. Popor, V. V. Orlenko and M. A. Loshkorer (USSR)  
Vopr. Khim. Khim. Tekhnol 45,48(1976) (Russ); "Chem. Abstr."  
92535 a(1977)
28. L. B. Lerner and T. F. Davis, U.S. Patent 4706,598(1978) "Chem.,  
Abstr" 88,160733m(1978)
29. I. Valsiunas, A. Bernotas, (USSR) Isslad obl Osazhdeniya, Met.  
Mater, Resp.konf. Elektrokhim Lit SSR 139 (1981) Akad Nauk. Lit.  
SSR Inst. khim. khim Technol Vilnius . USSR "Chem Abstr" 97,  
46484 s (1982)
30. A. B. Bogatyrev, G. K. Burkat and P.M. Vyacheslvov, Izv. Vyssh.  
Uchebn.Zaved. Khim khim Technol, 25 (8), (1982) (Russ); "Chem  
Abstr." 97, 190333j (1982).
31. K. Obata, T. Sonoda, Tsakasa and N. Dohi, Kinzoku Hyomen Gijutsu  
33 (8) 375 (1982) Chem Abstr 97,221127b (1982)
32. V. A. Volkav, L. G. Lukyanovo, L.F. Atyunina, (USSR) "Tekhnol,  
Organ. Protzvod" No 248 (1983) (RUSS) ; Chem. Abstr. 98, 224139  
P(1983).
33. W. T. Matson , D. D. patent , 4,436,596 (1984) : "Chem Abstr. ". 100,  
182238 (1984)
34. T. Juodiene, B. Girauskas, and K. Juodkazis, Issled Obl, 'Electro  
Osazhdenlya, Met. Mater, Resp. Konf. Elektrokhin", Lit. SSR 19<sup>th</sup>  
223-7(RUSS) (1983): Chem. Abstr. 100, 164246 U (1984)
35. K. Yokoyama, Jap. Patent, 7522971; CA 84(1976) 10480 e

36. K.Daiishi, Setyaku Co. Ltd., Kohai, Tokyo Koho, Jap. Patent ,  
5918782 and 8418782 (1984); CA100 (1984), 178682 V
37. I. P. Mavani, C.R. Jejurkar and P.K.Bhattacharya, J.Indian Chem.  
Soc.,49 (1972) 469
38. B.K. Agarwal, M .Chandra, B. V. Agarwal and A.K. Dey, Indian J. of  
Chem., 15A (1977) 633
39. Eckart W. Schmidt. "Hydrazine and its Derivatives". John Wiley &  
Sons , New York (1984) 371-375
40. Candlin J.P. , K.A. Taylor and D.T.Thompson; Reactions of transition  
metal Complexes , Elsevier, Amsterdam, (1968) 363
41. Jorgensen C.K. ; Inorganic Complexes , Academic press, London and  
New York (1963) 61
42. Wilkins R.G. The study of kinetics and mechanism of reactions of  
transition metal complexes , Allyn and Bacon, Boston (1974) , LC74-  
10756
43. Bottomley F. , S. G. Clarkson and S. B. Tong; Electrophilic  
Behaviour of the coordinated nitrosyl Cation ; Rections of  
pentahalogen – nitrosyl- Irridates (1-), J. Chem Soc., Dalton Trans  
(1974), 2344-2346 (1974)
44. Ionov V.P. etal ; Extraction separation of mixtures of platinum and  
common metals , J.Anal. Chem., USSR 30 , 802-806 (1975)
45. Glavic P., J. Slivnik and A. Bole: Reactions of copper (II) and zinc (II)  
fluorides with hydrazine, J. Inorg. Nucl., Chem 42, 617-618 (1980)

46. Agarwal R. C. and N. K. Singh; Hydrzine Complexes of some First row transition metal (II) picrates and picramates, Def, Sci. J. (India) 27 109-114 (1977); CA88,98481
47. Hall and J.W. etal; The interaction of hydrazine with copper (II) chloride in acidic solution. The formation , spectral and magnetic properties and structure of copper (II) Copper (I) and mixed valece species, univ, North Carolina, Tech. Rept. NLU-TR- 6 (and UV- TR- 14 ) (Feb 1979 ) AD –A065103, CA 91, 133307. Some paper by Brown, D.B. etal, Inorg Chem. 18 2635- 2641 (1979)
48. Jayant S. Budkuley and A.V. Vernekar. Thermochemica Acta, 176 (1991) 339-343.Elsevier Sci Pub B. V. , Amsterdam.
49. Stolle,R, and K Hoffman; on hydrazino carbonic acid (In German ) Ber. Deut chem. Ges 37 4523-4524 (1904)
50. Braibanti, A, etal ; transition metal chelates of hydrazine carboxylic acid, Nature 211,1174-1175 (1960)
51. A. Braibanti, F. Dallavalle, H.A. Pellinghelli and E. Leporati. J.Inog Chem Vol 7 No7 1430 (1968)
52. K.C.Patil, R. Soundararajan and E.P. Goldberg Synth . React . Inorg. Met- Org Chem 13(1) (1983) 29 –43
53. B. N. Sivasankar and Govindarajan. Indian Journal of Chem Vol- 33A (1994) 329
54. H. J. Emeleus and A.G. Sharpe. Morden aspects of Inorganic Chemistry. Universal Book Stall , 5, Ansari Road , New Delhi. 110002 (1994)427

55. Jannik Bjerrum . Metal amine formation in aqueous solution.  
Copenhagen. Published by P. Haase and sons (1957) 17-22
56. Irving H. and R.J. P. Williams , J. Chem. Soc., (1953)3192
57. Perkin, D. J. Biochem J. , 51, 487 (1952)
58. Francois M. M Morel., Principles of Aquatic Chemistry  
Massachusetts. Institute of Technology. A. Wiley Interscience  
Publication , John Wiley and sons, 243
59. S. Ramamoorthy and M. Santappa. Dept. of Physical Chemistry, Univ.  
of Madras, Madras-25, India Stability Constants in aqueous solution of  
complexes of Uranyl ion with mixed dibasic acids- II , 1 st July 1970.
60. S. Ramamoorthy, C.Guarnaschelli and D. Fecchio, Inland waters  
Branch, Dept. of Fisheries and Forestry, Ottawa Ontario, Canada.  
Equilibrium studies of Cu(II)-Nitrilotriacetic Acid with a solid state  
cupric ion selective electrode, March, 1971.
61. S. N. Dubey, A. Singh, D.M. Puri. Dept of chemisry, Kurukshetra  
Univ,. Kurukshetra-132 119, India. A study in the complex formation  
of Iminodiacetic acid and nitrilotriacetic acid with aluminium ,  
chromium and Beryllium ions. 3<sup>rd</sup> July 1980.
62. Pradyotkumar Dutta (Chem lab. D. H. S. K. College Dibrugarh  
786001, India ) Madhup Chandra and Arun K. Dey ( Chem lab . Univ.  
of Allahabad, Allahabad, India). Ternary Complexes of copper (II), Ni  
(II) and Zn (II) with nitrilotriacetic acid as a primary ligand and some  
phenolic acids as secondary ligands. Transition metal . Chem . 5,  
(1980) 1-3

63. Francis J. C. Rossoti and Hazel Rassoti. The determination of stability constants and other equilibrium constants in solution.
64. Gordon M. Barrow Physical chemistry 5<sup>th</sup> Edition Mc Garw Hill International Edition (1988) 328-329
65. Fredrick Prescott Intermediate chemistry inorganic and physical. Univ Tutorial press ltd; London, N. W. I (1961) 365
66. G. G. Gawrilov Chemical (Electroless) Nickel – Plating portcullis press Redhill, Surey (1979) 12
67. A. Wurtz , C. R. Hebd. Seances Acad sci 18(1844) P 702 and 21 (1845) P 149
68. A. Breteau, P. Bull. Soc . Chem 9 (1911) 515/518
69. U. S. Pat 1. 207. 218 (1916)
70. A. Brenner. and G. E. Riddell, J. Res. Nat. Bur.,Stand . 37 (1946) P 1,PP 31/34, Proc. American electroplaters soc.33 (1946) P 16
71. A. Brenner and G. E. Riddell, J. Res. Nat. Bur.,Stand . 39 (1946) Nov. PP, 385/395 and Proc. American electroplaters Soc.34 (1947) PP 156/170
72. Wolfgang Riedel. Electroless Nickel plating. ASM International, Ohio, USA, Finishing publication, England (1991) PP 10
73. R. Colin; Galvanotechnik 57 (1966) P 158
74. K.Mayer, Fachb. Oberflächentechnik 5 (1967) I.P 30

75. Chemisch. Nickel Kanigen H. Schnarr.OHG- publication (1975)
76. G. Schmidt Galvanotechnik, 59 (1968) PP 666/669
77. U. S. Pat 2.461.661 (1945 )
78. Standard Guide for Autocatalytic Nickel Phosphorous deposits on metals for Engg Use. ASTM/656-91
79. U. S. Pat 2430581. (1947 )
80. Levy, D. J. Electrochem. Technol, 1(1963) 1-2, 38
81. Kalantary, M. R. et al, Transactions of the Institute for metal finishing , 71 (2),55:1993
82. Lawless G. W. & Fisher R. D. Plating 54 (1967) 709
83. Brit. Pat. 992660 (1965)
84. Tokano O. and Ishibashi S. Jne . Met Finish. Soc., Japan 19 (1968)345
85. Saranov E. I. et al ISW . Wusov chim I. Chim . Technol.10 (1967)403
86. Schmeckenbecher A. F. Jnl Electrochem Soc. 113 (1966)778
87. U. S. Pat 3282723. (1966 )
88. Aoki K. & Ishibasni, S. Jnl. Met. Finish Soc. Japan 21 (1970)11,622
89. Tadashi, H. Trans. Inst. Electron and commun. Eng . Jap (1971)8,778
90. Hirth, F.W. & Speckhardt, H. Galvanotechnik 64 (1973) 6, 452

91. Beljakova, A. F. et al Metalloved, i. Tenm obra. b. Metallorr (1970) 5, 64
92. Ishibashi, S. et al Jnl. Met. Finish. Soc., Japan 21 (1970)10,540
93. Rosenblyum, R. and Dyakov, A. Zashchita Metallov 6 (1970) 1, 76
94. Sovikova Z. etal . Koroze a Ochrana Materialu 2 (1963)46
95. U. S. Pat 3674516. (1972 ); DOS 2148744 (1972)
96. Cavallotti P. and Salvago, G. Electrochem , Metallorum3 (1968)23
97. Pearlstein, F. and Weightman, R. Electrochem Technol , 6 (1968) 11/12,427
98. DOS 1918275 (1971); Brit Pat 1216954 (1971)
99. Ismajilov et al Jnl. Phys. Chimij 45 (1971) 10, 2652;UdSSR Pat 291992 (1969)
100. UdSSR Pat 369182 (1971)
101. Lang K. Galvanotechnik 56 (1965)6,347
102. Lang, K. Metalloberfl.19 (1965)8,257
103. Lang, K. et al Nickel-Ber 23 (1965)10,391
104. DBP 1243493 (1961)
105. U. S. Pat 3483029 (1969 )
106. UdSSR Pat 287490 (1969)
107. Valsyunene J. I. et al . Lietuovos TSR Mokslu Akademijos Darbai, B. Serija 2 (69) 1972, 3.
108. U. S. Pat 3140188(1964 ) : Brit. Pat. 971777 (1964)

109. Zupak, L. E. and Ismajlov, A. V. Zashchita Metallov 5 (1969) 6, 688, UdSSR Pat. 217165 (1970)
110. Zupak, L. E. et al ISW Wusov Chim, i Chim, Technol 14 (1971)3,410
111. UdSSR Pat 298696 (1971)
112. UdSSR Pat 306196 (1972)
113. U. S. Pat 3350210
114. U. S. Pat 3382079
115. U. S. Pat 3496014
116. Brit. Pat. 1194980
117. Brit. Pat. 1198781
118. J. W. Dini "Proc. Electroless nickel confernces III" Garderner publication Inc. Cincinnati (1983)
119. U. S. Pat 2532283 (1950)
120. K. Lang "Galvanotechnik" 56 (1965)6, 347
121. G. O. Mallory "Plating" 58 (1971)4, 319
122. G. Gutzeit "Plating" 46 (1959) 1158, 1275,1377: 49 (1960)63
123. U. S. Pat 2822294 (1958)
124. U. S. Pat 2876116 (1959)
125. N.A. Solowjew "J. Prickl Chimij" 32 (11959)3, 556
126. G. Gawrilov, "Metalloberfi Angew. Electrochemi" 25 (1971)8, 277
127. U. S. Pat 2532283 (1951)
128. U. S. Pat 2822293 (1958)

129. U. S. Pat 287445 (1958)
130. U. S. Pat 2999770 (1961)
131. M. V. Sullivan and J. H. Eigler "J. Electrochem Soc"104 (1957)  
226
132. S. Ishibashi , et al, Jnl. Met. Finish. Soc. Japan" 15 (1964) 4, 135
133. M. Schwartz "Proc. Am. Electroplaters Soc."47 (1960) 176
134. V. Brussenzo and D. Pletnev "Priboestroene" (1963) 2
135. J. W. Dini and P. R. Coronado , "plating" 54 (1967) 4, 385
136. DBP 1247115 (1963)
137. H. Narcus "Plating" 54 (1967)4,381
138. U. S. Pat 2990296(1961)
139. U. S. Pat 3338726(1967)
140. U. S. Pat 3574664(1970)
141. E. W. Schmidt, Ed, "Hydrazine and its derivatives", Wiley  
Interscience (1984)
142. C. Paal and L. Friederici, "Ber." 65, (1932)19, CA26;1870
143. T. H. James, "J. Amm. Chem. Soc." 62 (1940) 1654
144. W. Peacock, Br. Pat,524753; CA35,6755 (1940)
145. J. T. Owen and N. J. Bloomfield. "U. S. Pat 2801935,Merck &Co  
CA;51,15384i (1957)
146. R. N. Rhoda and A. M. Madison, U. S. Pat. 2915406, CA, 54,  
5420a (1959)
147. M. R. Edwards and A. R. Burkin, Hydrometal, Meeting (1973)  
Inst. Min. Metall, London , England, (1975) 84,; CA 84,96027

148. A.V.Izmailov et al , "Izv. Vysch. Ucheb. Zaved. Khim.i Khim Tokh" 16; (2) (1973) 1917, CA, 81; 40523
149. V. M. Gershov, et al . "LitvPSR Zinad- Akad, Vistis, Khim. Ser" (1974) 271 CA. 81, 177135
150. K. Y. Okuno, Yamashita and T. Yukawa "Application of Electroless Ruthenium Plating flim to Electronic Materials" (1974)
151. A. Vaskehis and O. Diemontaite. "Liet. TSR, Mokslu. Akad. Darb. Ser.B" No,5 3-13 (1976); CA86,147810 (1976)
152. V. M. Gershov, and P. I. Dzyubenko, Latv. Psc. Zinat Akad Vestis Khim, "Ser, No1, (1977) 15; CA:86,144109
153. A. P. Ratnikov, A. V. Izmailov and G. Z. Schilova, "Izv, Vyssh, Uchebn, Zaved. Khim i Khim. Tekhnol." 22, (1979) 848-851;CA: 91,161562
154. G. A. Kurnoskin. et al , ""Izv, Vyssh, Uchebn, Zaved. Khim. I. Khim. Tekhnol." 23, (6)(1980) 742;CA: 93,208658
155. U. S. Pat. 2658842 (1953)
156. U. S. Pat. 2532283 (1951)
157. Gutzeit, G. Plating 46 (1959) 1158, 1275,1377; 49 (1960)63
158. U. S. Pat. 2822294(1958)
159. U. S. Pat. 2822293 (1958)
160. U. S. Pat. 2837445(1953)
161. U. S. Pat. 2874073 (1959)
162. U. S. Pat. 2999770 (1961)
163. Solowjew, N. A. Jurnal Priki. Chimi i 32 (1959) 3, 556

164. U. S. Pat. 2819187 (1958)
165. Gawrilov, G. Matalloberfi, Angrew. Elektrochmie 25 (1971) 8,  
277 Bulg Pat. 16114 (1970)
166. U. S. Pat. 3490924 (1970)
167. Medvedkov, V. N. and Erofeev, B. V. Doki. Akad. Nauk. SSSR;  
191 (1970) 5, 1106

**CHAPTER II**  
**EXPERIMENTAL**

# CHAPTER II

## EXPERIMENTAL

### 2. INTRODUCTION

The principles and the experimental procedures for the analytical methods and the physico-chemical techniques employed in the present investigation are described in this chapter. These include the pH metric titration[1] to determine the stability constants of various metal nitrilotriacetate and hydrazido carboxylate[2] complexes, preparation of various electroless bath solutions for the deposition processes, pretreatment of plastic and copper metal plates for electroless plating, monitoring and control of different bath parameters during deposition, characterization of plated materials using different techniques and study of structural properties.

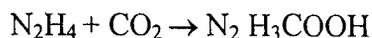
#### 2.1 CHEMICALS USED

Commercially available chemicals, analar or equivalent grades, were used in the investigation. All the solutions were prepared from these reagents or compounds prepared in situ. Chemicals used include, perchloric acid, sodium perchlorate monohydrate, nickel sulphate, ferrous sulphate, cobaltous chloride, zinc chloride, nickel chloride, manganese(II) chloride, magnesium chloride, nitrilotriacetic acid, ascorbic acid, sodium

hypophosphite hydrated, palladium chloride, hydrazine hydrate, Eriochrome black -T indicator, Xylenol orange indicator, Murexide indicator, stannous chloride.

### **2.1.1 PREPARATION OF HYDRAZIDO CARBOXYLIC ACID**

Carbon dioxide gas was slowly and continuously bubbled through 50 mL of hydrazine hydrate taken in a narrow mouthed small reagent bottle (Fig. 2.1) for 48 hours. A syrupy liquid initially formed changes to thick white. It was then diluted with 25 mL of 50% ethanol solution and CO<sub>2</sub> gas again bubbled for another 90 minutes for the remaining hydrazine to react. White crystalline hydrazido carboxylic acid[3] so formed was filtered through Whatman filter paper No 1 in buchner funnel. The residue was first washed with 50% ethanol and subsequently with pure ethanol. Filtrate, which was tested[4] for hydrazine, showed negligible hydrazine content.



The white residue in the buchner funnel was transferred into a petridish and kept for 48 hours in a vacuum dessicator over P<sub>2</sub>O<sub>5</sub> and used as and when required. This compound was characterized chemically and also by IR spectroscopy.

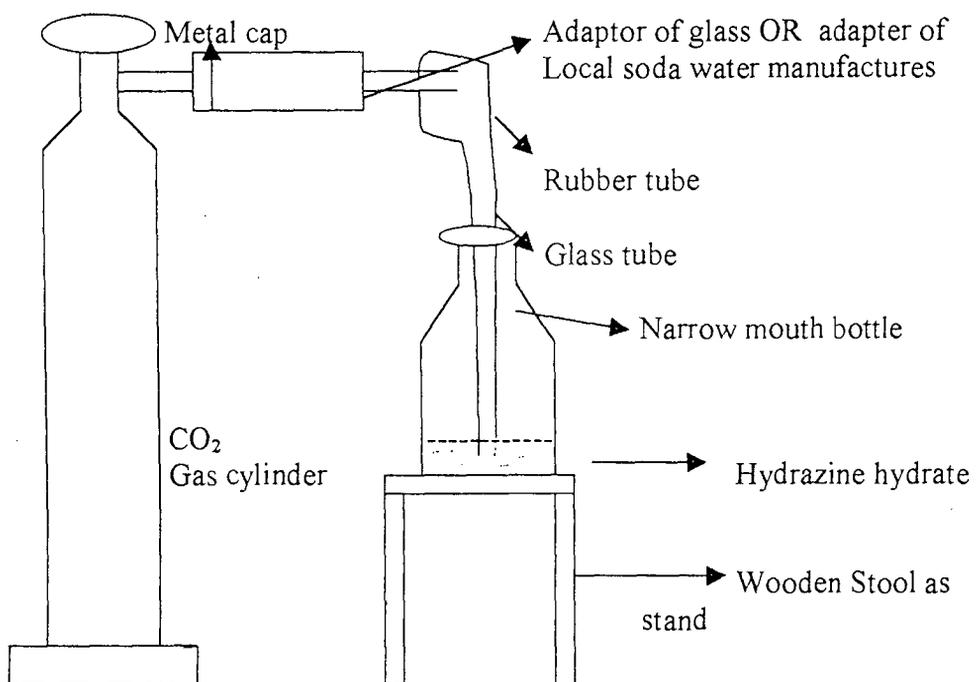


Fig 2.1 Experimental set up for the preparation of hydrazidocarboxylic acid

## 2.1.2 PREPARATION OF SOLUTIONS

Of the several solutions prepared in the course of the study the following are of particular importance:

1.  $2 \times 10^{-2}$  M Perchloric acid,
2. 2M Sodium perchlorate,
3. 0.003 M Nitrilotriacetic acid (NTA),
4. 0.003 M Hydrazido carboxylic acid ( $\text{N}_2\text{H}_3\text{COOH}$ ),
5.  $5 \times 10^{-4}$  M Metal salt solutions.

## **2.2 CHEMICAL ANALYSIS**

Estimation of metal ions in solution was carried out by complexometric titrations using standard EDTA (Na-salt) solution. These solutions of metal salts were used in pH-metric titrations in the stability studies. The thin film deposit, obtained in the electroless plating experiments, was leached out with 0.2 M HNO<sub>3</sub> and further was subjected to volumetric analysis for the nickel metal.

### **2.2.1 ESTIMATION OF Mg, Zn and Mn**

Metal(II) ions like magnesium, manganese and zinc were volumetrically estimated[4] against standard EDTA (0.001) solution using Eriochrome Black-T indicator. The solution was maintained at pH=10 using appropriate buffer solution containing ammonium chloride and ammonia. The end point was the colour change from red to blue.

### **2.2.2 ESTIMATION OF NICKEL**

In a typical experiment, a pinch of freshly prepared Murexide indicator[4] was added to nickel solution, followed by the addition half test tube of 1M NH<sub>4</sub>Cl and liquor NH<sub>3</sub> till solution turns yellow, and then 10 mL of liquor ammonia. The mixture was titrated against standard EDTA. At the end point the colour of the solution changes from yellow to bluish violet.

### **2.2.3 ESTIMATION OF COBALT**

A known volume of the solution containing  $\text{Co}^{+2}$  was pipetted out in a titration flask. The pH of the solution was increased by adding hexamethyl tetramine, which acts as a buffer of pH=6. A few drops of Xylenol orange were added as an indicator. The resultant solution was titrated with EDTA solution[4] until the colour changed from red to yellow.

### **2.3 pH METRY TITRATIONS: APPARATUS**

In this method a number of pH-metry titrations (Fig. 2.2) were carried out using a microburette. The titrations were carried out at 303K. However, in the case of hydrazido carboxylic acid, the titrations were carried out between 273-277K to prevent the decomposition of hydrazido carboxylic acid since this acid is unstable above 277K. Borosil microburette of 1 mL capacity with 0.01 mL accuracy was used for these titrations. A pH meter (ELICO Ioniser Li-126) with 0.0001 unit sensitivity was used for measurements. The pH meter was calibrated before every titration using standard buffer solution of pH 4.01. The temperature was recorded using temperature sensor supplied with the instrument.



Fig. 2.2 Instrumental setup for pH-metry titration

### 2.3.1 pH METRY TITRATIONS

In the Calvin –Bjerrum[1] pH titration method usually a set of three titration are carried out. Titration of the solution containing mineral acid , the ligand and the metal salt against the standard alkali.

- Titration of the same quantity of mineral acid and ligand solution without metal salt against the same standard alkali.
- Titration of the mineral acid alone against the same standard alkali.

The details of titrations carried out are as follows:

#### 2.3.1.1 *Metal titration:*

In a typical experiment, 50mL solution containing, 5 mL of ( $2 \times 10^{-2}$ M) perchloric acid, 5mL of (2M) sodium perchlorate, 5 mL of ( $5 \times 10^{-4}$ M), metal ion solution, 30 mL of double distilled water and 5 mL of the (0.003 M) complexing agent (reagent or ligand solution) were pipetted out in the same order into 100mL-beaker. The solution was titrated against a standard sodium hydroxide (0.4M) solution at constant temperature till the pH of the solution was around 12.

With hydrazido carboxylic acid as ligand / complexing agent, the temperature was maintained between 273-277K to prevent its decomposition in acid medium.

The ternary system, containing two ligands viz. NTA and hydrazido carboxylic acid, along with metal ions, the temperature of the solution was maintained between 273-277K and titrated against 0.4 M NaOH.

Thus the titrations carried out were as follows:

- (a) 5 mL of perchloric acid+5mL NaClO<sub>4</sub> +5mL NTA +5mL solution containing metal ions + 30 mL double distilled water at 303 K. v / s 0.4 M NaOH.
- (b) 5mL HClO<sub>4</sub> +5mL NaClO<sub>4</sub>+5mL L<sub>2</sub> +5mL metal ions solution +30mL water at 273 K to 277 K v / s 0.4 M NaOH
- (c) 5mL HClO<sub>4</sub>+5mL NaClO<sub>4</sub>+5mL NTA(L<sub>1</sub>)+5ml hydrazido carboxylic acid (L<sub>2</sub>) +5mL solution containing metal ions +25 mL double distilled water at 273 K to 277 K v/s 0.4 M NaOH

The metal ion solutions of NiCl<sub>2</sub>, CoCl<sub>2</sub>, ZnCl<sub>2</sub>, MnCl<sub>2</sub>, MgCl<sub>2</sub>, of concentration  $5 \times 10^{-4}$  M each, were used in pH-metry titration.

### **2.3.1.2 Reagent titration (Complexing agent/ ligand)**

The composition of the titrant was almost the same except that additional 5 mL double distilled water was taken instead of 5mL metal salt solution. The mixture used for titration was

- (a) 5mL HClO<sub>4</sub>+5mL NaClO<sub>4</sub>+5mL NTA(L<sub>1</sub>)+ 35 mL double distilled water at 303K v/s 0.4 M NaOH.

(b) 5mL HClO<sub>4</sub> +5mL NaClO<sub>4</sub>+5ml L<sub>2</sub>\* +35 ml double distilled water at 273-277K vs 0.4<sup>M</sup>NaOH.

Where, L<sub>2</sub>\* represent hydrazido carboxylic acid (N<sub>2</sub>H<sub>3</sub>COOH).

**2.3.1.3 Acid titration:** Here, the composition of the titrant was almost the same, as in 2.3.1.2, except an additional amount of 5 mL of double distilled water was used instead of 5mL of the reagent (complexing reagent) solution.

The mixture used for a titration was:

(a) 5mL HClO<sub>4</sub>+5mL NaClO<sub>4</sub>+ 40 ml double distilled water at 303K vs. 0.4M NaOH.

After the completion of titration , the combined electrode was washed thoroughly with distilled water and kept in 0.1 M HCl solution for 15 minutes and again washed with double distilled water and made to stand in distilled water for at least 2 hours before further use.

The experimental data relating to all these measurements with different reagents, metal ions and at different temperatures is given in the next chapter.

## 2.4 ELECTROLESS PLATING

Electroless plating [5,6] involves the deposition of metal or alloy from the bath solution by using suitable reducing agent. The main features of the electroless plating process are (i) pretreatment of the base material (substrate), (ii) preparation of suitable bath solution, and (iii) electroless deposition.

## 2.4.1 PREPARATION OF PLATES

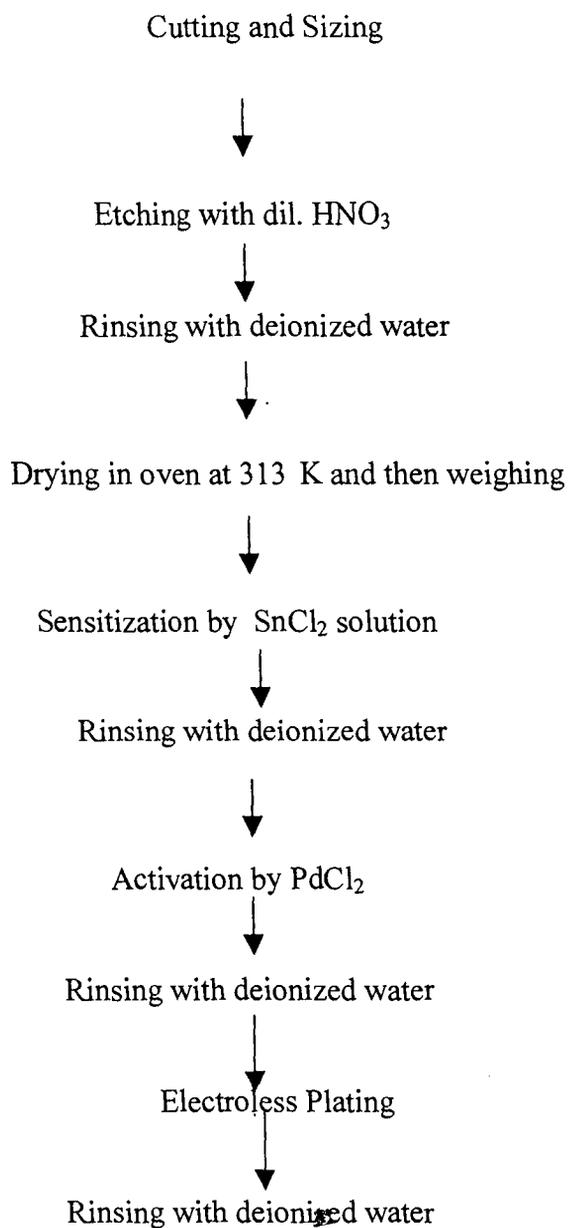
Two types of plates, of 5 x 1.5 cm<sup>2</sup> each, of pure copper metal and plastic were used for the electroless deposition experiments. However, for analysis by XRD and atomic absorption spectroscopy, plates of 2.5 X 6.0 cm<sup>2</sup> were used.

### 2.4.1.1 PREPARATION OF COPPER PLATES

Electroless plating experiments on copper substrate were carried out with novel bath. Thin copper plates, of desired shape and dimensions (1.5x 5 cm), were cut from copper metal foil (99.5% purity). The plates were etched or cleaned by rubbing with cotton dipped in 2N HNO<sub>3</sub>. The plates were then washed with de-ionized water, dried at 313K and weighed.

These plates were then sensitized by dipping in 3% SnCl<sub>2</sub> solution (3 g SnCl<sub>2</sub> +40 mL conc. HCl, diluted to 100 mL) for 10 seconds and then activated by dipping in PdCl<sub>2</sub> solution (0.00625 g PdCl<sub>2</sub> dissolved in the dilute HCl by adding the acid dropwise till the solution is clear) for 5 seconds. The plates were then rinsed in deionized water and thereafter dipped in the bath solution for electroless plating.

**Table 2.1** Pretreatment of copper plates used in the present investigation

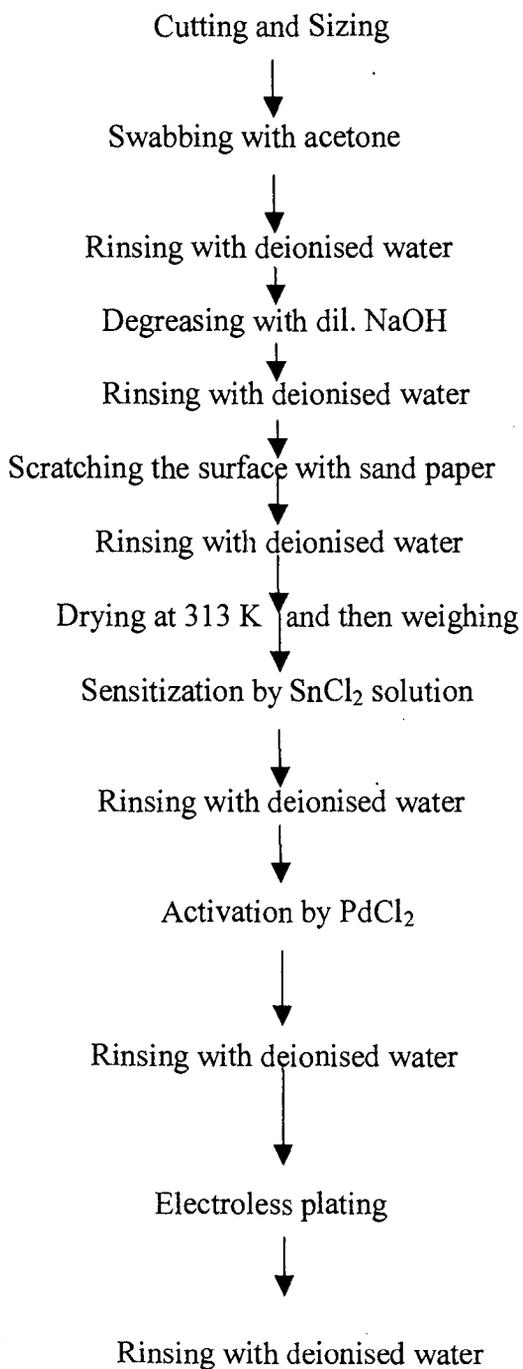


### 2.4.1.2 PRETREATMENT OF PLASTIC PLATES.

Electroless plating experiments on thin and thick plastic substrate were also carried out with a novel bath. Thin and thick plastic plates of desired dimensions (1.5 cmX5cm or 2 cm X 6 cm X 0.5cm) were cut from OHP transparency or thick acrylic plastic. These plates were then washed with dilute NaOH to remove grease and then rinsed with de-ionized water followed by rinsing with dil. HCl and water again. Lastly the plates were cleaned with acetone. The plates were dried and then roughened and again rinsed with deionised water, dried in an oven at 313 K and weighed.

These plates were then sensitized by dipping in 3% SnCl<sub>2</sub> solution (3 g SnCl<sub>2</sub> +40 mL conc. HCl, diluted to 100mL) for 1 minutes, rinsed with water and then activated by dipping in PdCl<sub>2</sub> solution (0.00625 g PdCl<sub>2</sub> dissolved in dil. HCl by adding it dropwise) for 30 seconds. The plates were then quickly rinsed in deionised water and then dipped in the bath solution for electroless plating.

**Table 2.2:** Pretreatment of plastic plates used in the present investigation



## 2.5 MONITORING THE QUALITY OF DEPOSITION

For technical applications it is necessary that the chemically (electroless) deposited metal or alloy should have a good adhesion on the substrate material. A metal-metal bonding between the deposit and the substrate [7] metal is envisaged in electroless plating.

In case of non-metallic substrate (plastic, ceramic) mechanical bonding forces do play an important role. The following simple tests are commonly used for qualitative determination of adhesion in electroless plating.

A strong adhesive tape is fixed on the plated surface and then removed. A good adhesion is indicated [8] by non-removal of plated matter.

In bending test, the coated plate is bent through  $180^{\circ}$ . A good adhesion will not [9] exhibit lifting of the coating on bending

Quenching test is a simple, common and reliable method [5] of qualitative determination of adhesion of coated matter in electroless plating. Here, the coated plate is heated to about 473-500K, and then, quenched by dipping it in water at room temperature. A weak adhesion is indicated, by lifting of the coating. It is very common to use peel-off method after quenching for better assessment. All the three tests mentioned above were used in this study.

## 2.6 MONITORING RATE AND THICKNESS OF THE COATING.

The rate of deposition of metal on substrate material was evaluated periodically by using weight gain method. In this method the weight of dry plate was found out (i) before plating process and (ii) after electroless plating process i.e. at the end of the experiment. The difference in weight or gain in weight or plating, the area of the plated surface and approximate density of metal (s) deposited was then used to calculate [6] the rate of deposition by using the following equation.

$$\text{Rate of deposition} = (W \times 10^4 / A \times d \times t) \mu\text{m} / \text{hr}$$

Where,

W= weight of the alloy deposited in g.

A = area of the coated surface in  $\text{cm}^2$

t = plating time in hours

d= average density of alloy (-----g /  $\text{cm}^3$ )

[density of Ni =8.9 g / c.c., density of Fe=7.87 g / c.c.

Average density was calculated on the basis of percentage composition of the metals and substituted in the above formula.

Thickness of plating = Rate of deposition X time

## **2.7 TESTING THE POROSITY OF DEPOSIT**

The porosity can be tested by (i) the feroxyl test and (ii) the hot water bath. In the feroxyl test, a solution of feroxyl is used [25g / L of  $K_3Fe(CN)_6$  and 15 g / L of NaCl ] in which the plate with deposit is dipped. By the short circuit element of corrosion which is present in the area of the pores, the iron dissolves inside the pores and lead inside the pores and leads to turn blue coloration.

In the hot water test the plates with the deposit are kept in water with pH of about 7 at a temperature of 363 K –368 K, the pores can be identified as red spots.

## **2.8 INSTRUMENTAL TECHNIQUES**

Instrumental techniques play an important role in the characterization or revealing the structural features of the compounds, metals, alloys, etc.

In the present investigation the instrumental techniques used were infrared spectroscopy, X- ray diffraction, atomic absorption spectroscopy and scanning electron microscopy (SEM)

### **2.8.1 X- RAY POWDER DIFFRACTION**

Philips X-ray diffractometer model 1840 with  $Cu K\alpha$  radiation with nickel filter was used to obtain the X-ray diffraction patterns [10] of the plates which were subjected to electroless plating.

## 2.8.2 ATOMIC ABSORPTION SPECTROSCOPY

Atomic absorption spectroscopy (AAS) was employed for the estimation [11] of iron in the film obtained in plating since the chemical method was found to be unsuitable. Estimation showed that the quantity of iron in the alloy was too less. In the atomic absorption spectroscopy (AAS) the absorption is measured by the difference in the transmitted signal in the presence and absence of test element. The main component of the AAS is the lamp. It may be Hollow cathode lamp or the electrode discharge tube. The cathode construction differs for the various metals. These lamps with their narrow band emission provide virtually complete specificity for each element. The instrument GBC 932AA (Fig 2.3) atomic absorption spectroscope was used during the course of this investigation.

In the present study, thin film deposit on plastic plate was leached out in 100mL of 0.2N HNO<sub>3</sub> prepared by using millicure water. The solution was quantitatively analysed for Fe content by using 0.2 N HNO<sub>3</sub> as blank with AAS. The standard solution of Fe was obtained from MERK for AAS. It provides the following standard data to help in finding out the amount of Fe in the unknown solution. This result was further confirmed by carrying out the gravimetric estimation of Fe. For preparation of 100 µg /mL Fe solution, 1.0 g of Fe was dissolved in 20mL of 5 N HCl, and 5 mL of 6N HNO<sub>3</sub> and further diluted to 1 liter to obtain 1000µg /mL Fe.

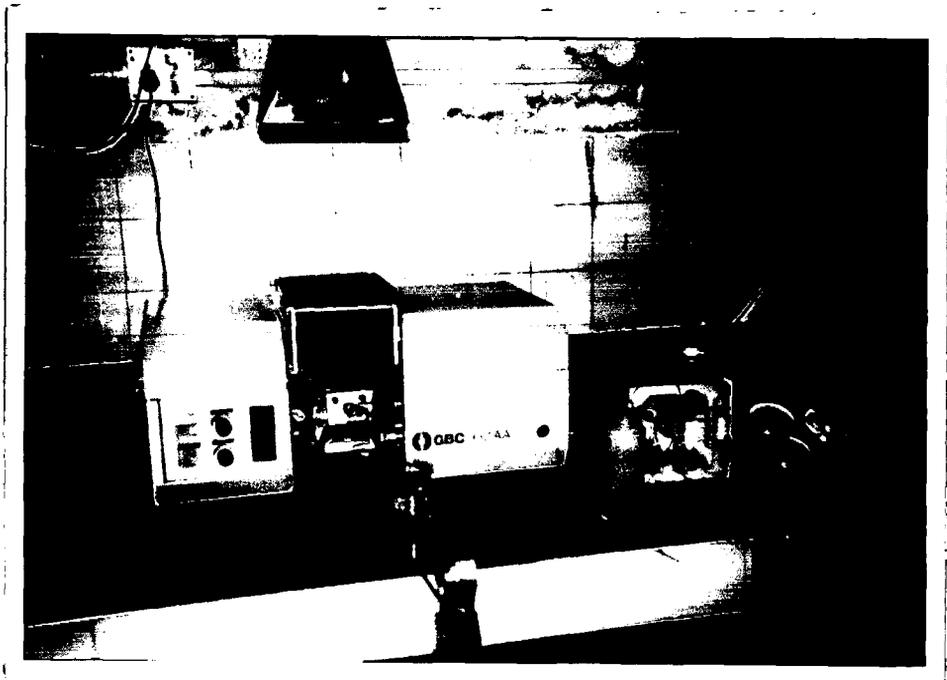


Fig. 2.3 Atomic Absorption Spectrophotometer GBC 932 AA

**Table 2.3** Standard calibration data for estimation of Fe by AAS

Wavelength nm	Slit width nm	Working range $\mu\text{g} / \text{ml}$	$\mu\text{g} / \text{mL}$
248.3	0.2	2-9	0.05
372	0.2	20-80	0.45
386	0.2	36-145	0.80
392	0.2	680-2700	15

### 2.8.3 SURFACE MORPHOLOGY.

Surface morphology of the plated material was investigated by using high resolution photography with Leica-orthoplan Pole Microscope at the magnification of 250 times. This microscope was used to obtain the micrograph of the covered surface to understand the surface morphology of the coating as well as to assess changes occurring due to atmospheric exposure. Scanning electron microscope (SEM) was also used for this purpose to scan some coated surfaces. The SEM uses the secondary electrons produced by the scanning beam to give life like, almost three dimensional image of the surface of the specimen being scanned. The magnification range of the SEM is more than 10,000 times.

Enlarged photographs of the copper and plastic plates were also obtained after exposing these plates to atmosphere for a period of one year.

## 2.8.4 INFRARED SPECTROSCOPY

Every molecule has a number of fundamental vibration frequencies and each fundamental frequency may be associated with absorption of radiation of its own frequency. This absorption of frequencies is obtained in the form of spectrum in the infrared spectroscopy [12-14]. Infrared spectrophotometer was used during the course of this investigation.

The spectra of the solid samples were obtained in the range of 4000 to 400  $\text{cm}^{-1}$  using Fourier Transform Infrared Spectrophotometers (F.T.I.R.). The F.T.I.R. used in the present investigation is shown in Fig.2.4.

The spectrum of the solid sample of hydrazidocarboxylic acid was recorded by dispersing it in Nujol or fluorolobe (Mull technique), and pellet technique using KBr, wherever possible. The observed infrared bands were calibrated with the standard frequencies of polystyrene [15].

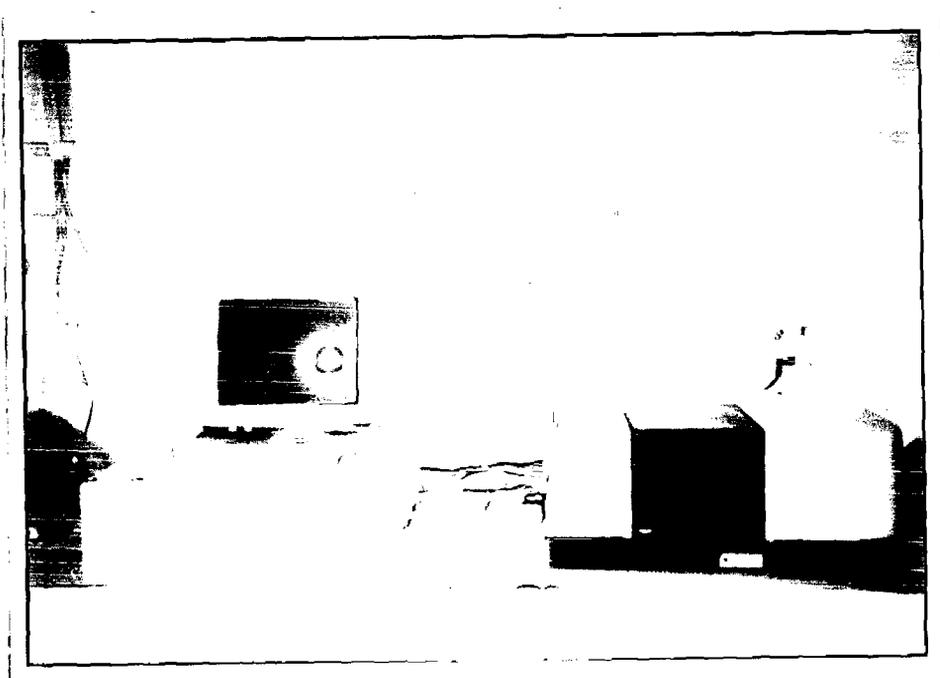


Fig. 2.4 Fourier Transform Infra Red Spectrophotometer SHIMADZU

## SUMMARY

In this chapter, the various chemicals used, the preparation of solution required for the experimental work, preparation of hydrazido carboxylic acid is described. Volumetric methods used for the estimation of Ni , Co , Zn , Mn , Mg during the present investigation are described. The experimental work involves two parts (i) pH-metry titrations to determine the stability constants of complexes and (ii) electroless plating from bath solution containing  $\text{Fe}^{+2}$  and  $\text{Ni}^{+2}$  ions.

In the electroless plating, the pretreatment of plates, preparation of bath solution and monitoring the quality of deposit is described citing the tests involved. The instrumental techniques used for characterization and quantitative estimation are described under IR spectroscopy, XRD and AAS. Lastly the method used to study the surface morphology is described in brief.

## REFERENCES.

1. J. Bjerrum, "Metal Ammine Formation in Aqueous Solution", P. Haase & Son (1957)
2. G.G. Gawrilov. "Chemical (Electroless) Nickel- plating", Portcullis Press. Redhill (1974).
3. E. W. Schmidt, "Hydrazine and its Derivatives, Preparation, Properties, Applications", John Wiley & Sons (1984) 416.
4. A. I. Vogel, "Textbook of Quantitative Chemical Analysis (Revised by G. H. Jeffery, J.. Bassett, J. Mendham, R. C. Denney)" ELBS Low-priced Edition. (1989).
5. G. Gawrilov, Galvanotechnik, 64 (1973).
6. W. Riedel, " Electroless Nickel Plating", A.S.M. International, Ohio,(1991)
7. E. Raub and K. Muller, Handbuch der Galvanotechnik Bdl Teil 1, Hanser Verlag, Munchen [1963],110.
8. W. Riedel, Galvanotechnik, 57 (1996) 9, 583.
9. G. Gutzeit, Metal Progr., 66 (1954) 1, 113; Trans. Inst. Metal Finish., 33 (1956)383.
10. D. P. Shoemaker, C. W. Garland and J. W. Nibler, "Experiments in Physical Chemistry", McGraw-Hill Inter. Editions (1989).

11. Nick Antanasopoulos, "Flame methods manual for atomic absorption", GBC Scientific Equipment PTY Ltd., Victoria, Australia. Analytical data. 9-8.
12. Willard H., Merritt L., Dean J., "Instrumental Methods of Analysis", CBS Publishers and Distributors, Sixth Edition (1995).
13. E. Galen, "Instrumental Methods of Chemical Analysis", Mc Graw-Hill International Edition, Singapore, Fifth Edition, (1993).
14. D. H. Wiffen, "Spectroscopy", Longmans, London, (1966).
15. C. N. R. Rao, "Chemical Applications of Infrared Spectroscopy", Academic, New York (1963).

**CHAPTER III**  
**STABILITY STUDIES**

# CHAPTER III

## STABILITY STUDIES

### INTRODUCTION

The stability studies of metal nitrilotriacetate complexes were carried out by using the pH-metry method. Two strong ligands, namely, nitrilotriacetic acid and hydrazidocarboxylic acid were used as complexing agent in this study. These two ligands, individually and also in combination in ternary system, were used for this purpose. Calvin-Bjerrum [1] pH titration method was adopted during this investigation. This involved three types of titrations : (i) acid titration, (ii) reagent titration and (iii) metal <sup>ion</sup> titration, which help to calculate the various quantities such as practical protonation constants  $\bar{n}_A$ , n and pH and the stoichiometric formation constants of various metal complexes from the experimental data.

### 3.1 CHARACTERIZATION OF HYDRAZIDO CARBOXYLIC ACID

Hydrazidocarboxylic acid ( $N_2H_3COOH$ ), which was synthesized in situ by the action of carbondioxide gas on hydrazine hydrate, was obtained as colourless crystalline compound. The spectrum of the solid sample was

recorded by dispersing it in Nujol using FTIR spectrophotometer. The spectrum shows (Fig. 3.1) the expected values for absorption for water at  $\approx 3300 \text{ cm}^{-1}$  and also for  $\nu_{\text{N-N}}$  stretching in  $\text{N}_2\text{H}_3\text{COOH}$ ,  $\sim 980 \text{ cm}^{-1}$ . The observed values are in agreement with the reported [2,3] values.

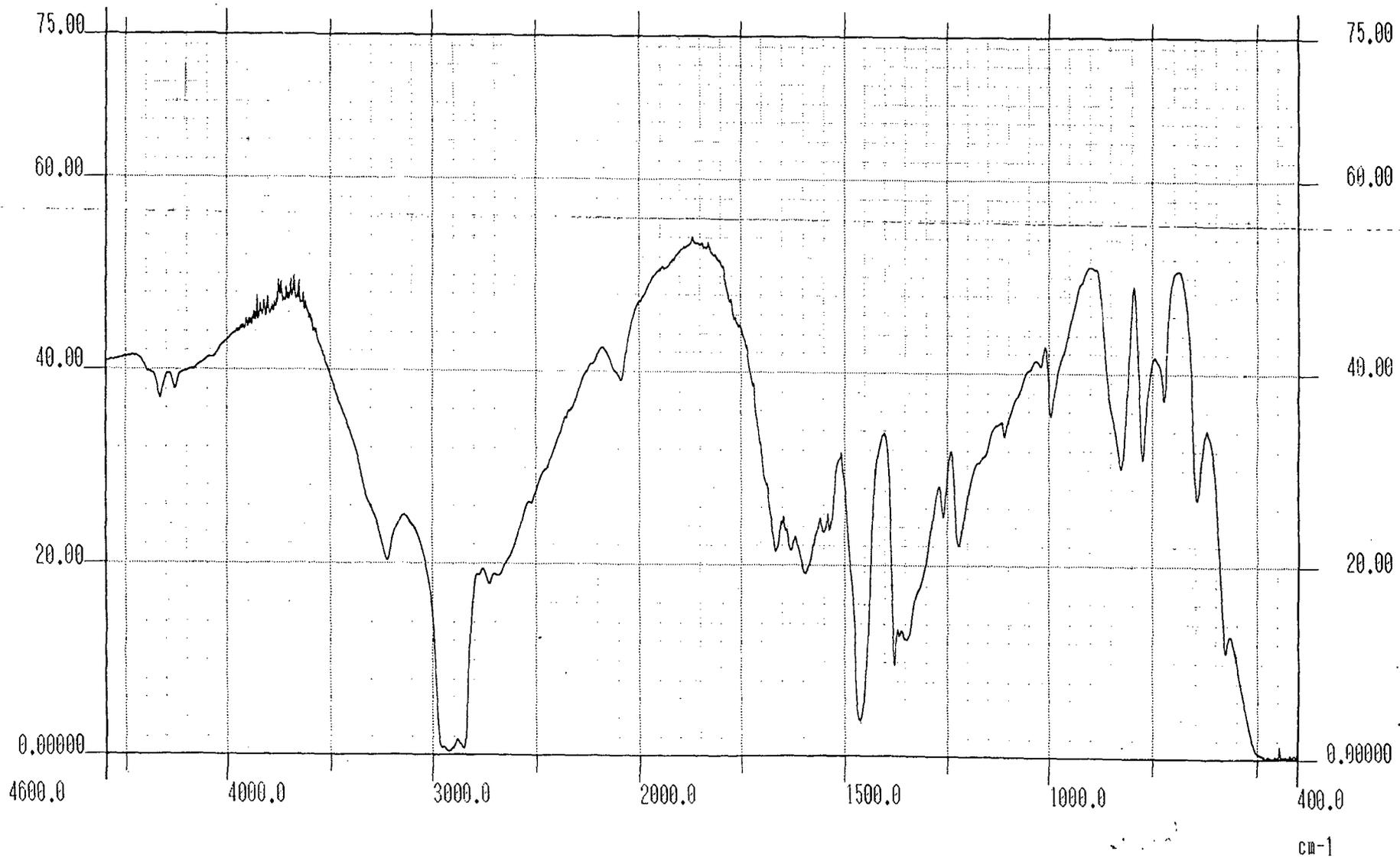
### 3.2 THE pH- METRIC TIRATIONS

This type of method in pH-metric titration was initially proposed by Calvin and Bjerrum and subsequently modified by Irving and Rossotti[4]. They used this method in such a way that the necessity of converting the pH values to stoichiometric  $\text{H}^+$  ion concentrations, is not involved. In this method, the acid dissociation constants of the ligand can be determined under the same experimental conditions as the formation constant.

The pH metric titrations carried out during the course of this study were:

- titration of the mineral acid (of known strength) solution against the standard alkali,
- titration of the mineral acid in the presence of ligand solution of known concentration against the same standard alkali,
- titration of the mineral acid, the ligand and the metal salt against standard alkali, and

%T



- titration was carried out to study the ternary system, i.e. titration of the mineral acid, mixture of two different ligands of equal concentration and the metal salts of known concentration against standard alkali.

Concentration of the mineral acid was kept constant in all four types volumetric methods.

Most of the titrations were carried out at ambient temperature but those involving hydrazidocarboxylic acid were performed by maintaining the temperature between 273-277K, so as to prevent its decomposition in acidic medium. The total volume of solution used for titration was 50 mL and in order to avoid volume correction, concentrated alkali (0.4M NaOH) was used. Since the mineral acid used was more dilute (i.e.  $2 \times 10^{-2}$  M  $\text{HClO}_4$ ), the volume of the titrant was very less, hence microburette was used in the experimental work.

Microburette of 1.0 ml capacity and with 0.01 ml accuracy was used for the titrations. Since very small change in pH occur during the pH-metry titration, the pH meter with 0.0001 unit sensitivity was used for these measurements.

Metal chloride solutions of  $5 \times 10^{-4}$  M concentration were used in these pH-metry titrations (where metal = Zn, Co, Mn, Ni and Mg).  $\text{NaClO}_4$  was used as a neutral electrolyte to keep the ionic strength constant. The observed experimental data of various pH metric titrations

are listed in Tables 3.1 to 3.18. The plot of pH V/s volume of 0.4 M NaOH pertaining to these titrations are given in Figures 3.1 to 3.18.

Graphically, the measured pH values against the volume of the alkali added give a set of three curves (Figs. 3.19 to 3.30). The ligand titration curves are located towards the right and show lower values of pH when compared to the plain acid curve for the same volume of alkali if the ligand is acidic, as in the present case. When the metal complex is formed in the metal ion titration (third header in Section 3.2), the curve is further displaced relative to the previous and indicates still lower pH values for the same volume of alkali. For the ternary system involving two ligands and the metal ion, the expected shift will be towards the right and seen in the case of the pH-metry titration with a metal ion and single ligand. This behaviour is seen in Fig. 3.19 to 3.28. Comparative effects of different type of metal ions on a single ligand, NTA and hydrazidocarboxylic acid, are shown in Figs. 3.29 to 3.30 respectively.

Table 3.1: Observed data in pH – metry titration  
 [ 5mL + HClO<sub>4</sub> + 5mL NaClO<sub>4</sub> + 40 mL H<sub>2</sub>O ] v/s  
 0.4 M NaOH

Volume of NaOH (mL)	pH
0.0	2.4925
0.450	2.5471
0.850	2.6778
0.1300	2.8767
0.1700	3.2424
0.2100	7.2486
0.2500	9.8344
0.2900	10.4900
0.3300	10.7800
0.4200	11.0540
0.5500	11.3080
0.6800	11.4520
0.8500	11.5590
0.9800	11.5950
1.200	11.6500
1.2600	11.7080
1.4800	11.9180

Table 3.2: Observed data in pH – metry titration  
 [ 5mL HClO<sub>4</sub> + 5 mL NaClO<sub>4</sub> + 5mL N.T.A + 35mL H<sub>2</sub>O ]  
 v/s 0.4 M NaOH

Volume of NaOH (mL)	pH
0.0	2.2601
0.04	2.2932
0.70	2.3064
0.10	2.3580
0.1400	2.4296
0.1900	2.5013
0.2250	2.7197
0.2600	3.9098
0.3000	8.3346
0.3400	8.9591
0.3800	9.6398
0.4200	10.1910
0.4600	10.468
0.5500	10.7430
0.6400	10.9260
0.7300	11.0540
0.8500	11.1650
1.300	11.4190
1.2600	11.4520
1.4500	11.5240
1.6800	11.5970
1.8500	11.6320

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Table 3.3: Observed data in pH – metry titration  
 [ 5mL HClO<sub>4</sub> + 5 mL NaClO<sub>4</sub> + 5mL N T A + 5 mL  
 NiCl<sub>2</sub> + 30mL H<sub>2</sub>O ] v/s 0.4 M NaOH

Volume of NaOH (mL)	pH
0.0	2.3348
0.05	2.3714
0.09	2.4778
0.13	2.6041
0.17	2.7291
0.22	2.9655
0.26	3.4769
0.30	8.0193
0.34	9.3573
0.38	10.162
0.42	10.6750
0.500	11.0780
0.600	11.2610
0.6800	11.3870
0.7560	11.4610
0.8900	11.5690
1.0	11.6440
1.1800	11.7320
1.3911	11.8030

Table 3.4: Observed data in pH – metry titration  
 [ 5mL HClO<sub>4</sub> + 5 mL NaClO<sub>4</sub> + 5mL N.T.A + 5 mL L<sub>2</sub> +  
 25mL H<sub>2</sub>O + 5 mL Ni Cl<sub>2</sub> ] v/s 0.4 M NaOH

Volume of NaOH (mL)	pH
0.0	1.9218
0.500	2.0248
0.900	2.1020
0.1200	2.1886
0.1700	2.3508
0.2100	2.6641
0.2500	3.4182
0.3000	7.9154
0.3400	9.0048
0.3800	9.8513
0.4200	10.2590
0.4700	10.4990
0.5450	10.7750
0.6300	11.1660
0.7750	11.1230
0.9450	11.2520
1.300	11.3070
1.2700	11.4550
1.4800	11.5090

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Table 3.5: Observed data in pH – metry titration  
 [ 5mL HClO<sub>4</sub> + 5 mL NaClO<sub>4</sub> + 5mL N T A +  
 5 mL CoCl<sub>2</sub> + 30mL H<sub>2</sub>O ] v/s 0.4 M NaOH

Volume of NaOH	pH
0.0	2.4229
0.500	2.4794
0.850	2.5643
0.1400	2.5677
0.1800	2.1875
0.2200	3.0345
0.2600	3.4351
0.3000	7.8747
0.3400	9.3800
0.3800	10.1880
0.4200	10.7790
0.4700	11.0710
0.5500	11.3480
0.6300	11.5290
0.7100	11.6220
0.8300	11.7660
0.9900	11.8760
1.1700	11.9490

Table 3.6: Observed data in pH – metry titration  
 [ 5mL HClO<sub>4</sub> + 5 mL NaClO<sub>4</sub> + 5mL N T A + 5 mL L<sub>2</sub> +  
 25mL H<sub>2</sub>O + 5 mL CoCl<sub>2</sub> ] v/s 0.4 M NaOH

Volume of NaOH	pH
0.0	2.2836
0.5000	2.2983
0.1000	2.3600
0.1350	2.4960
0.1800	2.6972
0.2100	2.8617
0.25000	3.3384
0.2900	6.8255
0.3300	8.7847
0.4200	10.3940
0.4650	10.7220
0.5000	11.0130
0.5800	11.2330
0.7100	11.4710
0.8350	11.6190
0.9550	11.6900
1.0	11.7650
1.1300	11.8380

Table 3.7: Observed data in pH – metry titration  
 [ 5mL HClO<sub>4</sub> + 5 mL NaClO<sub>4</sub> + 5mL N T.A +  
 5 mL ZnCl<sub>2</sub> + 30mL H<sub>2</sub>O ] v/s 0.4 M NaOH

Volume of NaOH	pH
0.0	2.3594
0.450	2.4380
0.900	2.5082
0.1200	2.6185
0.1600	2.7104
0.2300	3.1191
0.2800	4.8100
0.3200	8.7552
0.3600	9.5983
0.4000	10.0700
0.4800	10.7720
0.5400	11.0140
0.6300	11.2650
0.7800	11.5040
0.94000	11.6350
1.0	11.7080
1.2200	11.8220
1.3900	11.9220

Table 3.8: Observed data in pH – metry titration  
 [ 5mL HClO<sub>4</sub> + 5 mL NaClO<sub>4</sub> + 5mL N T.A + 5 mL L<sub>2</sub> +  
 25mL H<sub>2</sub>O + 5 mL ZnCl<sub>2</sub> ] v/s 0.4 M NaOH

Volume of NaOH	pH
0.0	2.4445
0.5000	2.5160
0.1000	2.6070
0.1900	2.9166
0.2100	3.1908
0.2500	3.8661
0.2900	7.9091
0.3300	9.0267
0.38000	9.9802
0.4100	10.5670
0.4500	10.7860
0.5250	11.1000
0.6000	11.3020
0.7200	11.4670
0.8500	11.5770
0.9500	11.6510
0.200	11.6690
1.2100	11.7960
1.3900	11.8140

Table 3.9: Observed data in pH – metry titration  
 [ 5mL HClO<sub>4</sub> + 5 mL NaClO<sub>4</sub> + 5mL N T A +  
 5 mL MnCl<sub>2</sub> + 30mL H<sub>2</sub>O ] v/s 0.4 M NaOH

Volume of NaOH	pH
0.0	2.3563
0.400	2.3929
0.800	2.4829
0.1200	2.6113
0.1700	2.7381
0.2100	2.9567
0.2450	3.3581
0.2900	6.3502
0.3350	9.2011
0.3700	9.9554
0.4100	10.5780
0.4550	10.8760
0.4900	11.0390
0.5750	11.2780
0.6550	11.4600
0.7750	11.5690
0.9900	11.6960
1.1100	11.7330
1.2300	11.8230

Table 3.10: Observed data in pH – metry titration  
 [ 5mL HClO<sub>4</sub> + 5 mL NaClO<sub>4</sub> + 5mL N T A + 5 mL L<sub>2</sub> +  
 25mL H<sub>2</sub>O + 5 mL MnCl<sub>2</sub> ] v/s 0.4 M NaOH

Volume of NaOH	pH
0.0	2.2869
0.500	2.3596
0.800	2.4096
0.1100	2.4980
0.1450	2.6233
0.1800	2.7671
0.2300	3.0964
0.2800	4.2341
0.3200	7.9325
0.3600	9.0386
0.4000	9.9781
0.4400	10.4210
0.4800	10.7170
0.5800	11.1410
0.7000	11.3790
0.8550	11.5620
0.9700	11.6730
1.1400	11.7650

Table 3.11: Observed data in pH – metry titration  
 [ 5mL HClO<sub>4</sub> + 5 mL NaClO<sub>4</sub> + 5mL N T A +  
 5 mL MgCl<sub>2</sub> + 30mL H<sub>2</sub>O ] v/s 0.4 M NaOH

Volume of NaOH	pH
0.0	2.4063
0.400	2.4611
0.800	2.5493
0.1200	2.6224
0.1600	2.7505
0.2000	2.9136
0.2300	3.1697
0.2700	4.3051
0.3000	8.6037
0.3400	9.3538
0.3700	9.9393
0.4150	10.5060
0.4600	10.8180
0.4950	10.9830
0.5900	11.2200
0.7000	11.4190
0.8450	11.5470
0.9700	11.6350
1.100	11.6740
1.1900	11.7620

Table 3.12: Observed data in pH – metry titration  
 [ 5mL HClO<sub>4</sub> + 5 mL NaClO<sub>4</sub> + 5mL N.T.A + 5 mL L<sub>2</sub> +  
 25mL H<sub>2</sub>O + 5 mL MgCl<sub>2</sub> ] v/s 0.4 M NaOH

Volume of NaOH	pH
0.0	2.0372
0.400	2.1086
0.800	2.2549
0.1200	2.3796
0.1500	2.4496
0.1900	2.7229
0.2200	3.1247
0.2500	5.0676
0.2800	7.3791
0.3300	8.3897
0.3800	9.1612
0.4100	9.7684
0.4550	10.2290
0.5000	10.4680
0.5400	10.6160
0.5800	10.7460
0.6600	11.0400
0.7500	11.0390
0.8700	11.1690
1.500	11.3150
1.2400	11.4070
1.4500	11.4790
1.6200	11.5540
1.8500	11.6260

Table 3.13: Observed data in pH – metry titration  
 [ 5mL HClO<sub>4</sub> + 5 mL NaClO<sub>4</sub> + 5mL L<sub>2</sub> + 35 mL H<sub>2</sub>O ]  
 v/s 0.4 M NaOH

Volume of NaOH	pH
0.0	2.4709
0.06	2.6527
0.1050	3.4272
0.1600	7.3490
0.2000	8.1213
0.2500	9.1331
0.2900	9.7778
0.3500	10.5650
0.3850	10.7540
0.4350	10.9380
0.4830	11.0840
0.5400	11.2310
0.5900	11.3040
0.6300	11.3580
0.6850	11.4510
0.7350	11.4900
0.7800	11.5430
0.8300	11.5820
0.9100	11.6370
0.9800	11.6920
1.1050	11.7660
1.2300	11.8210

Table 3.14: Observed data in pH – metry titration  
 [ 5mL HClO<sub>4</sub> + 5 mL NaClO<sub>4</sub> + 5 mL L<sub>2</sub> + 5mL NiCl<sub>2</sub> +  
 30mL H<sub>2</sub>O ] v/s 0.4 M NaOH

Volume of NaOH (ml)	pH
0.0	2.3592
0.700	2.6695
0.1550	5.2371
0.2080	7.5496
0.2500	9.0611
0.2850	9.9639
0.3350	10.5170
0.3800	10.7750
0.4700	11.0500
0.5500	11.3260
0.6380	11.4630
0.9000	11.5550
0.9900	11.6100
1.1800	11.7810
1.36	11.781
1.5000	11.8360

Table 3.15: Observed data in pH – metry titration  
 [ 5mL HClO<sub>4</sub> + 5 mL NaClO<sub>4</sub> + 5mL L<sub>2</sub> + 5 mL CoCl<sub>2</sub> +  
 30 mL H<sub>2</sub>O ] v/s 0.4 M NaOH

Volume of NaOH	pH
0.0	2.4243
0.05000	2.5874
0.1000	2.8605
0.1400	3.4807
0.1900	7.2934
0.2300	8.4281
0.2700	9.4606
0.3120	10.2890
0.3600	10.6760
0.4750	11.1560
0.5650	11.3040
0.7000	11.4700
0.8250	11.6000
0.9100	11.6760
1.50	11.7330
1.1650	11.8080
1.3100	11.8800

Table 3.16: Observed data in pH – metry titration  
 [ 5mL HClO<sub>4</sub> + 5 mL NaClO<sub>4</sub> + 5 mL L<sub>2</sub> + 5mL ZnCl<sub>2</sub> +  
 30mL H<sub>2</sub>O ] v/s 0.4 M NaOH

Volume of NaOH	pH
0.0	2.4558
0.05	2.6002
0.1200	3.2026
0.1700	6.5434
0.2050	7.9134
0.2550	9.1025
0.3000	9.9811
0.3400	10.5490
0.4250	11.0060
0.5200	11.2270
0.6400	11.4290
0.7600	11.5390
0.8950	11.6470
1.300	11.7180
1.1800	11.7910
1.3900	11.8610

Table 3.17: Observed data in pH – metry titration

[ 5mL HClO<sub>4</sub> + 5 mL NaClO<sub>4</sub> + 5mL L<sub>2</sub> + 5 mL MnCl<sub>2</sub> + 30 mL H<sub>2</sub>O ] v/s 0.4 M NaOH

Volume of NaOH	pH
0.0	2.4425
0.05	2.5883
0.09	2.8253
0.13	3.3162
0.18	7.3283
0.2250	8.3139
0.2700	9.5002
0.3150	10.2480
0.3700	10.7620
0.4700	11.0740
0.5520	11.2560
0.6450	11.3840
0.7200	11.4790
0.8600	11.5890
0.9850	11.6820
1.1600	11.7750
1.3100	11.8300

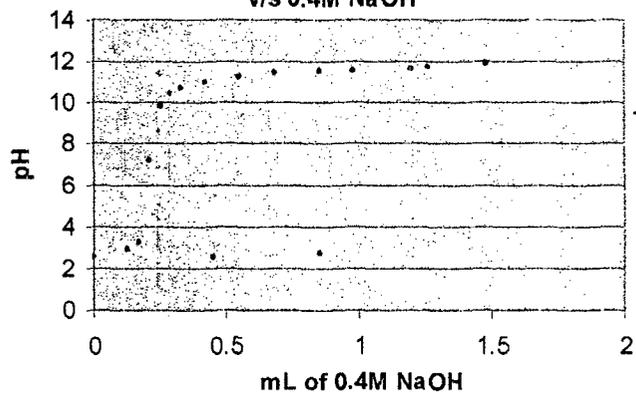
Table 3.18: Observed data in pH – metry titration

[ 5mL HClO<sub>4</sub> + 5 mL NaClO<sub>4</sub> + 5 mL L<sub>2</sub> + 5mL MgCl<sub>2</sub> + 30mL H<sub>2</sub>O ] v/s 0.4 M NaOH

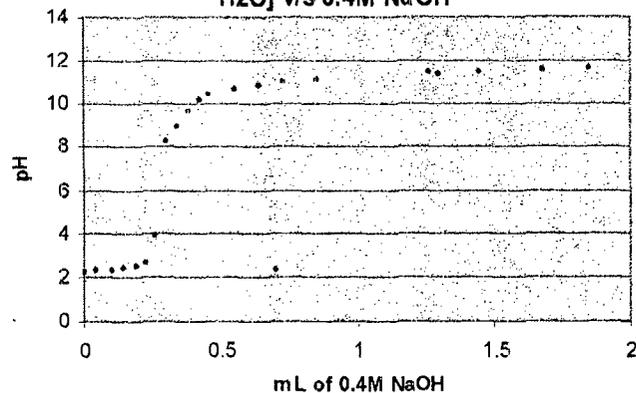
Volume of NaOH	pH
0.0	2.4060
0.05	2.5491
0.820	2.7499
0.1300	3.1635
0.1720	7.1102
0.2180	8.4522
0.2600	9.6674
0.300	10.3840
0.342	10.754
0.388	10.9580
0.438	11.088
0.52	11.2720
0.600	11.3990
0.7000	11.512
0.795	11.585
0.92	11.677
1.02	11.733
1.135	11.786
1.26	11.84
1.39	11.895

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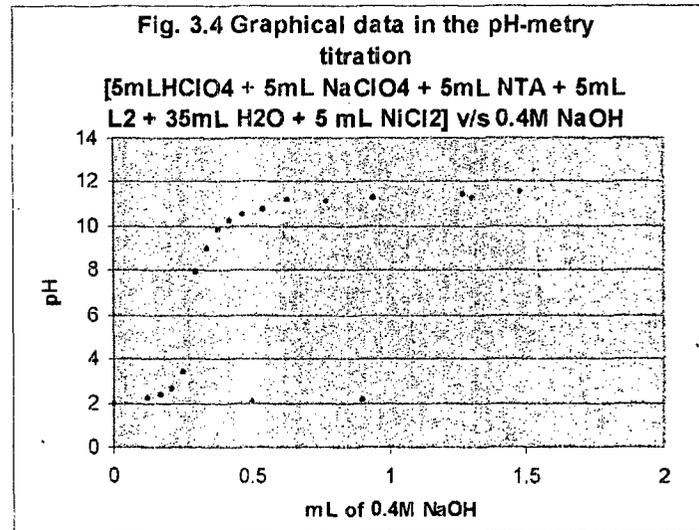
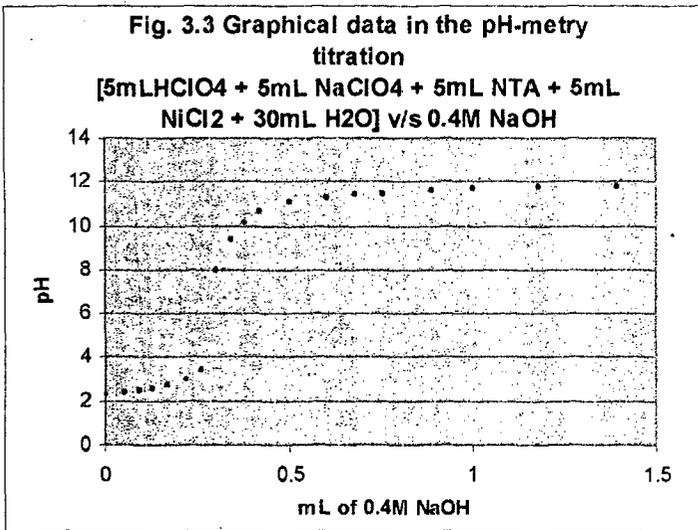
**Fig. 3.1 Graphical data in the pH-metry titration  
[5mLHClO4 + 5mL NaClO4 + 40mL H2O]  
v/s 0.4M NaOH**

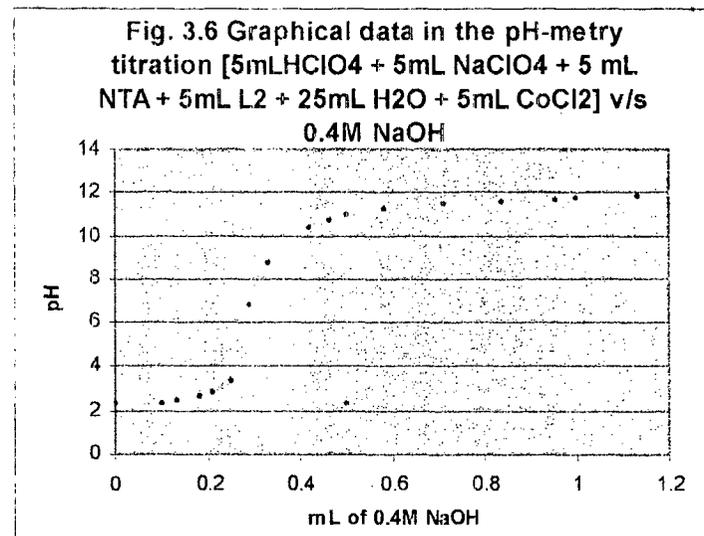
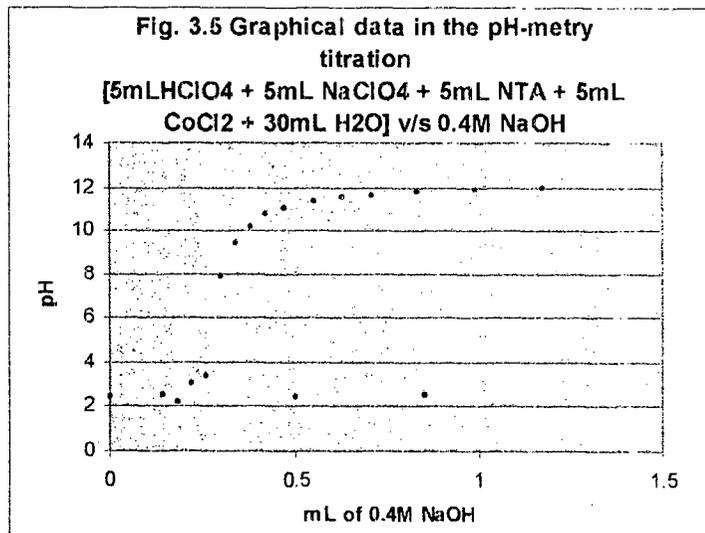


**Fig. 3.2 Graphical data in the pH-metry titration  
[5mLHClO4 + 5mL NaClO4 + 5mL NTA + 35mL  
H2O] v/s 0.4M NaOH**

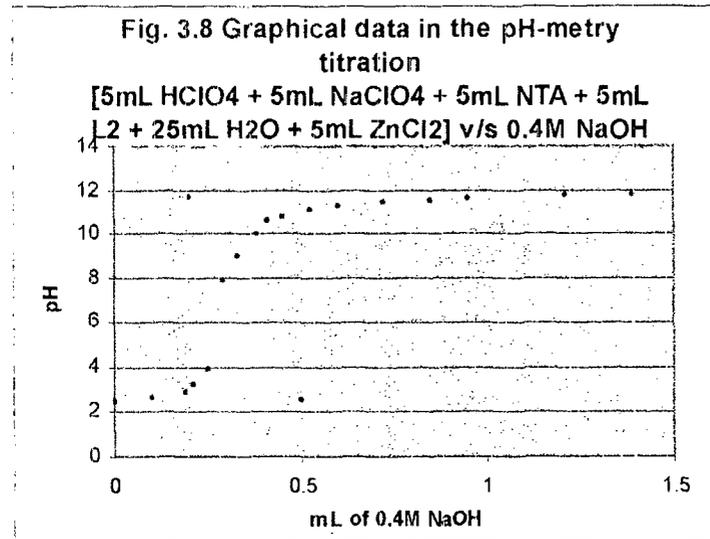
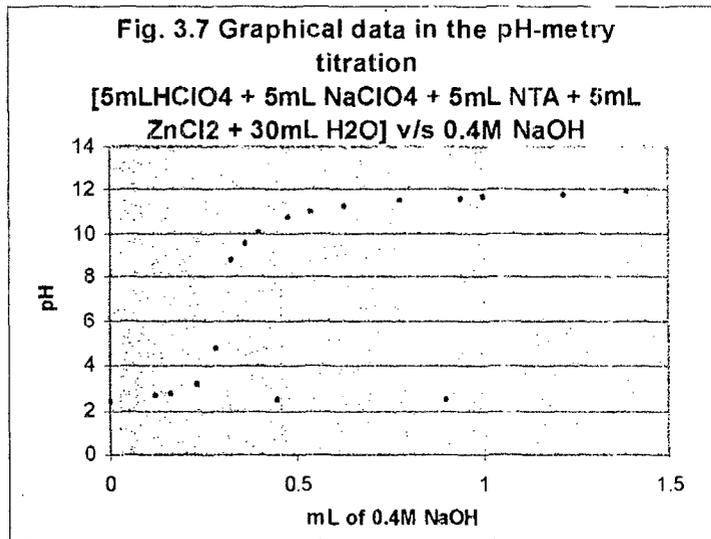


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Fig. 3.9 Graphical data in the pH-metry titration

[5mL HClO<sub>4</sub> + 5mL NaClO<sub>4</sub> + 5mL NTA + 5mL MnCl<sub>2</sub> + 30mL H<sub>2</sub>O] v/s 0.4M NaOH

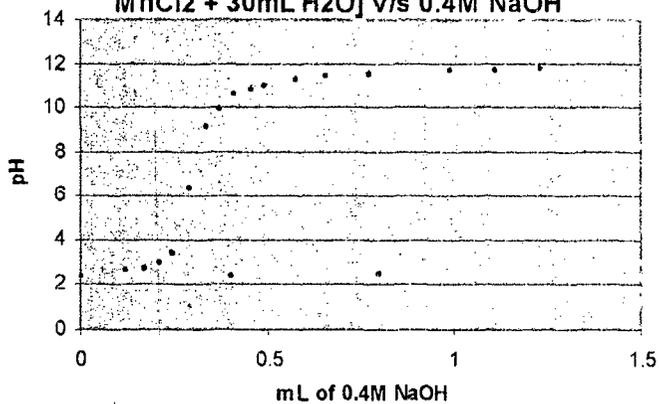


Fig. 3.10 Graphical data in the pH-metry titration

[5mL HClO<sub>4</sub> + 5mL NaClO<sub>4</sub> + 5mL NTA + 5mL L<sub>2</sub> + 25mL H<sub>2</sub>O + 5mL MnCl<sub>2</sub>]v/s 0.4M NaOH

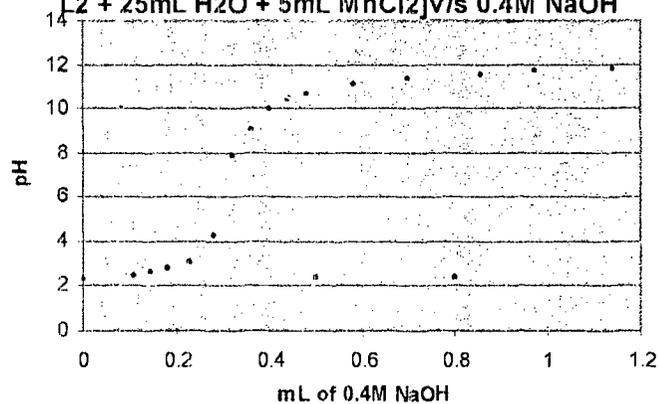


Fig. 3.11 Graphical data in the pH-metry titration

[5mL HClO<sub>4</sub> + 5mL NaClO<sub>4</sub> + 5mL NTA + 5mL MgCl<sub>2</sub> + 30mL H<sub>2</sub>O] v/s 0.4M NaOH

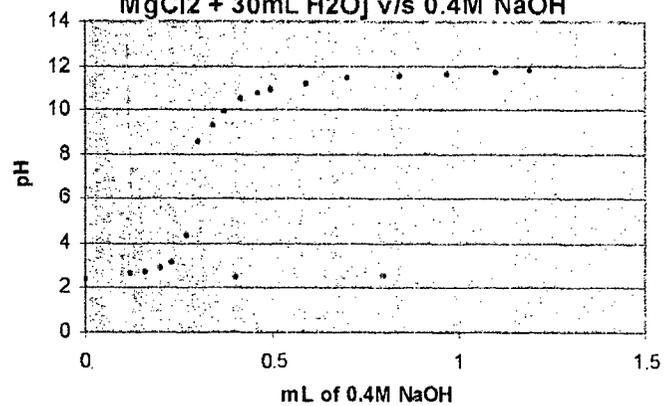
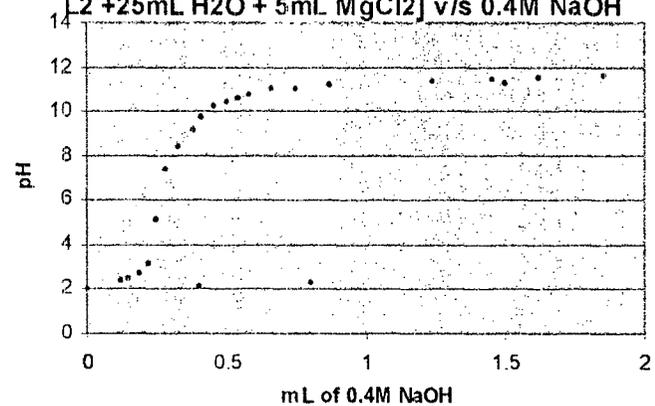
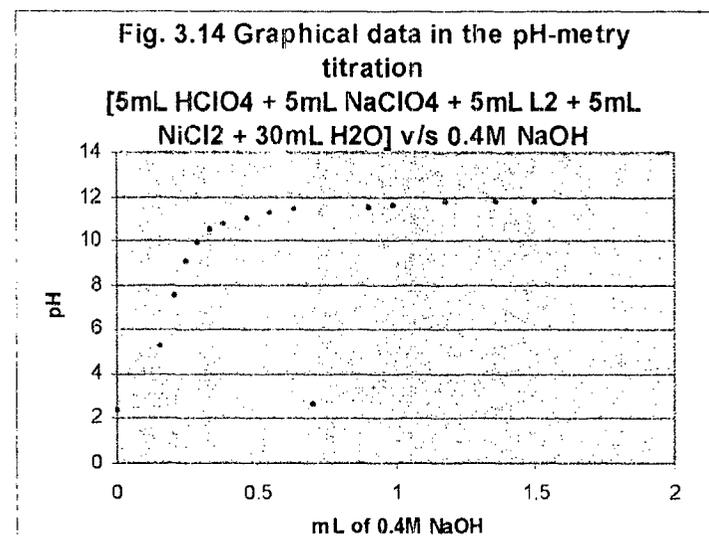
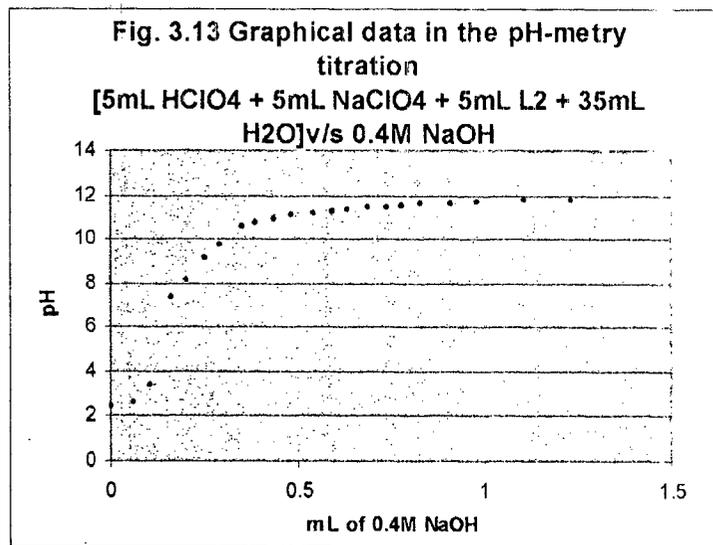
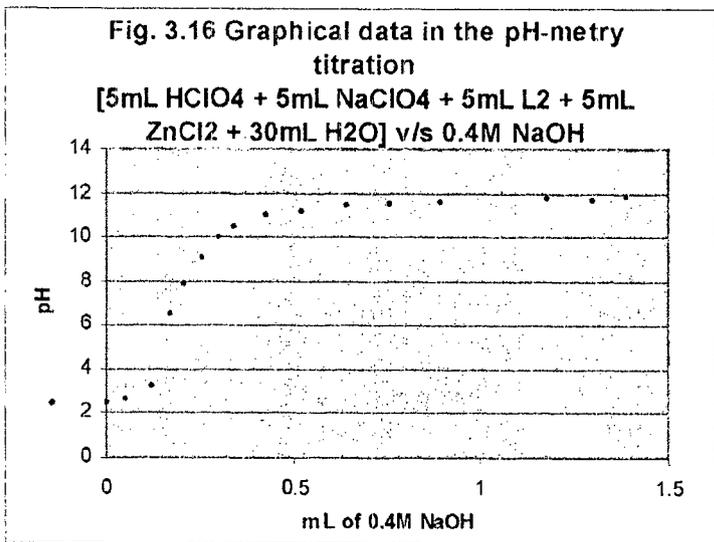
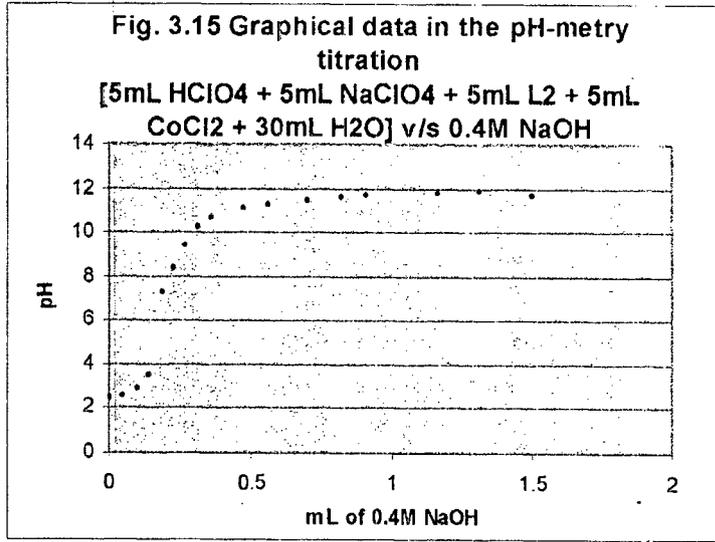


Fig. 3.12 Graphical data in the pH-metry titration

[5mL HClO<sub>4</sub> + 5mL NaClO<sub>4</sub> + 5mL NTA + 5mL L<sub>2</sub> + 25mL H<sub>2</sub>O + 5mL MgCl<sub>2</sub>] v/s 0.4M NaOH







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Fig. 3.17 Graphical data in the pH-metry titration  
[5mL HClO<sub>4</sub> + 5mL NaClO<sub>4</sub> + 5mL L2 + 5mL  
MnCl<sub>2</sub> + 30mL H<sub>2</sub>O] v/s 0.4M NaOH

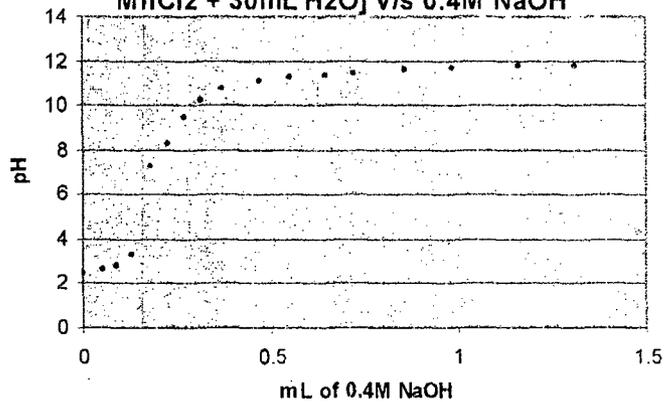
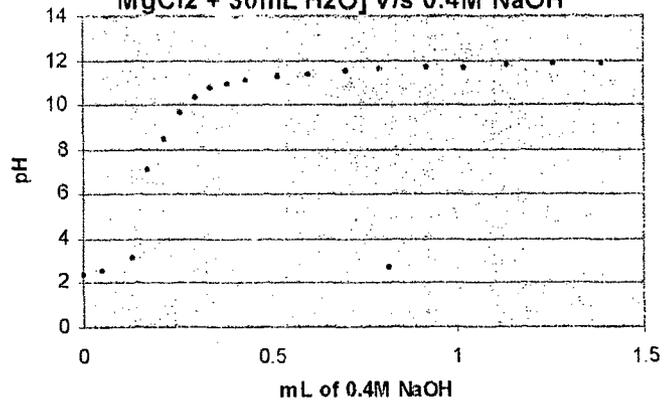
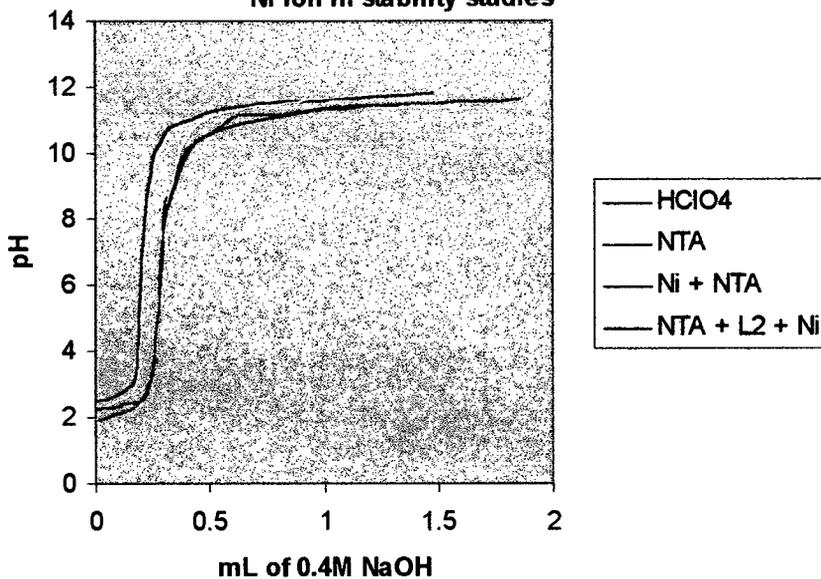


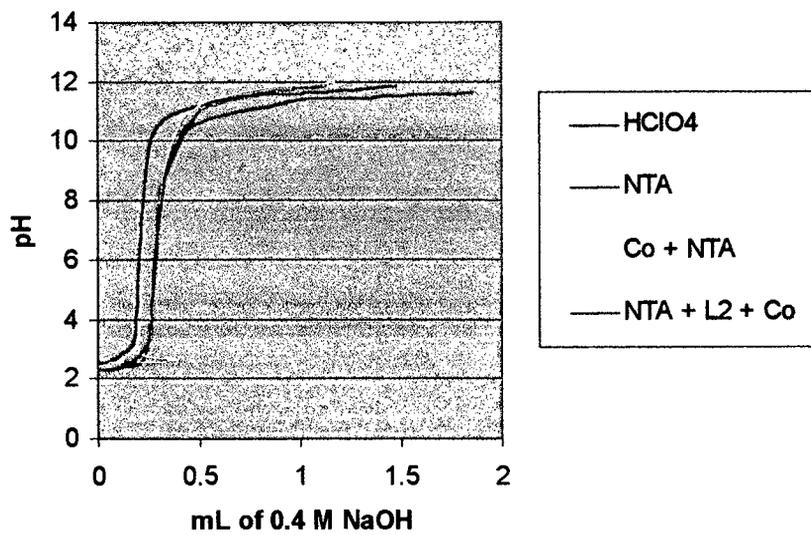
Fig. 3.18 Graphical data in the pH-metry titration  
[5mL HClO<sub>4</sub> + 5mL NaClO<sub>4</sub> + 5mL L2 + 5mL  
MgCl<sub>2</sub> + 30mL H<sub>2</sub>O] v/s 0.4M NaOH



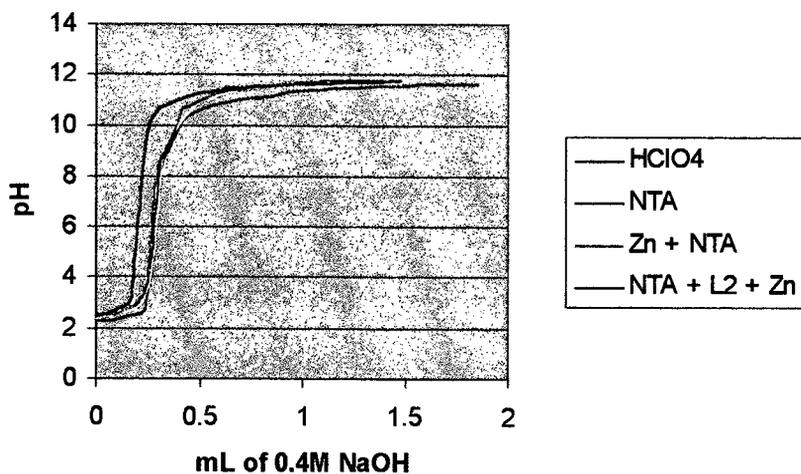
**Fig. 3.19 Graphical representation of pH-metry data for Ni ion in stability studies**



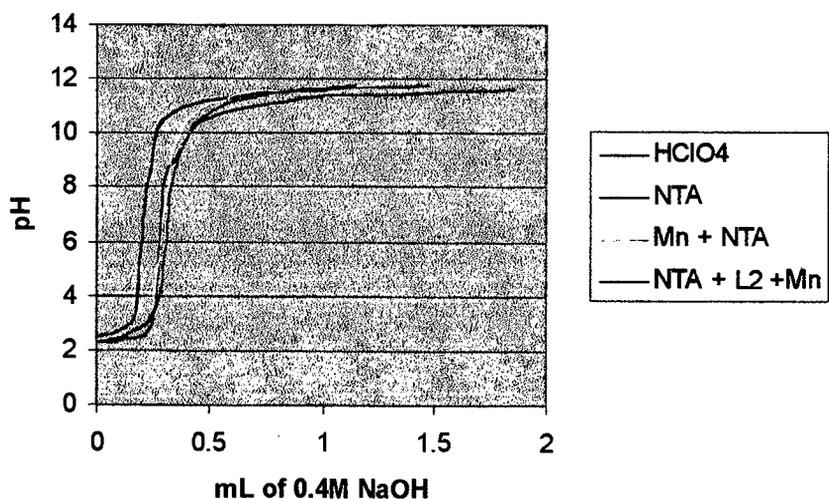
**Fig. 3.20 Graphical representation of pH-metry data for Co ion in stability studies**



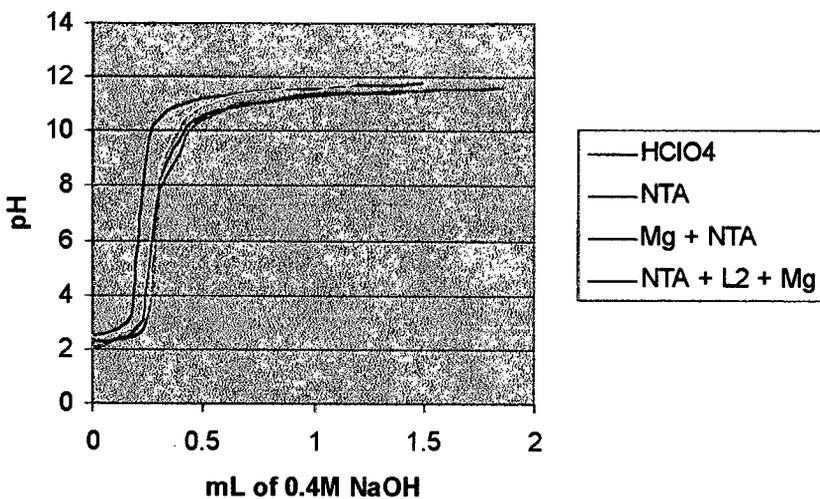
**Fig. 3.21 Graphical representation of pH-metry data for Zn ion in stability studies**



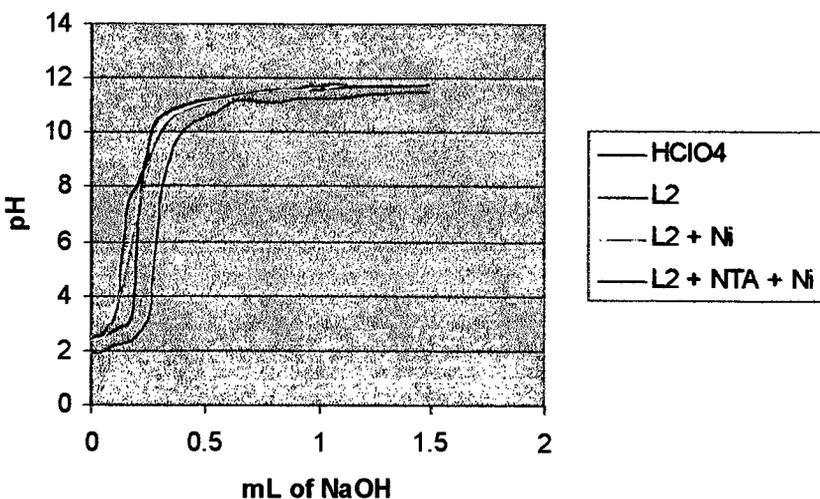
**Fig. 3.22 Graphical representation of pH-metry data for Mn ion in stability studies**



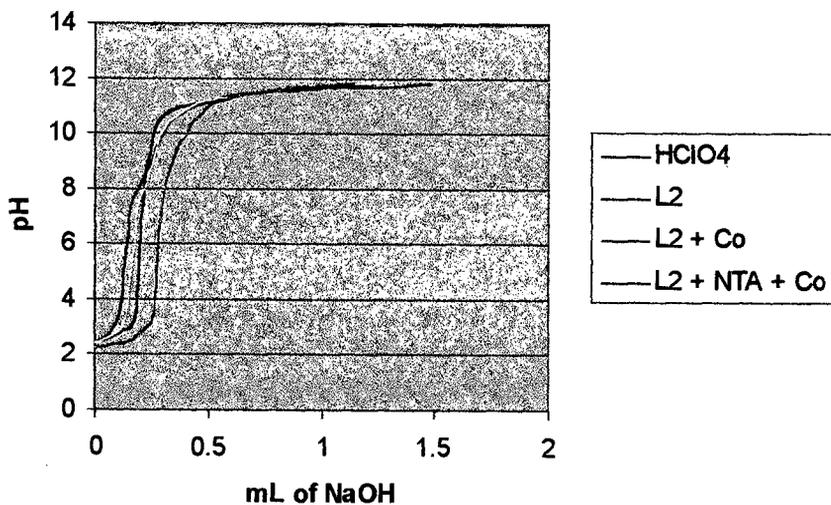
**Fig. 3.23 Graphical representation of pH-metry data for Mg ion in stability studies**



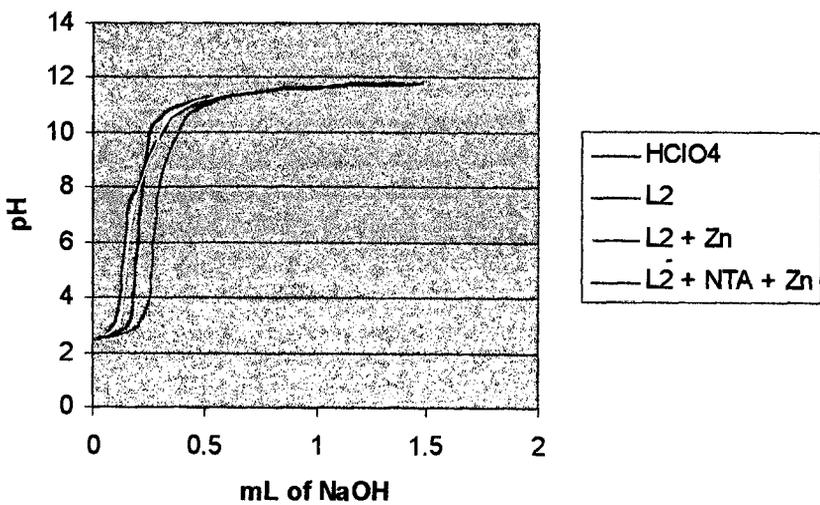
**Fig. 3.24 Graphical representation of pH-metry data for Ni ion in stability studies**



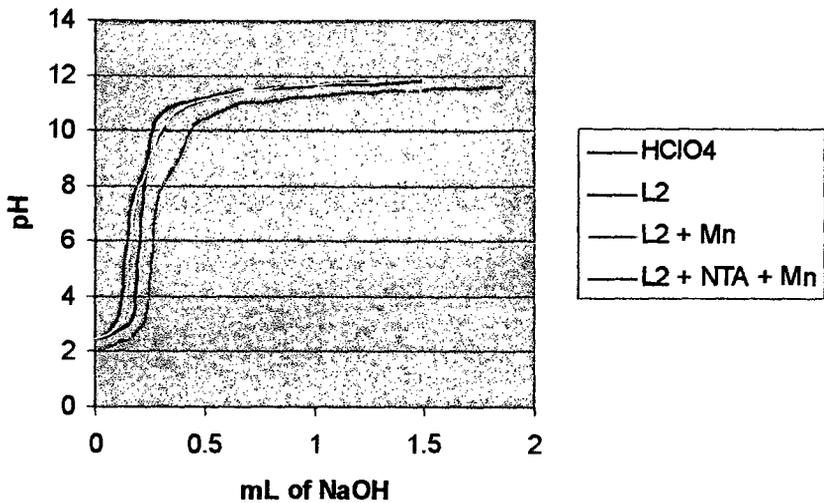
**Fig. 3.25 Graphical representation of pH-metry data for Co ion in stability studies**



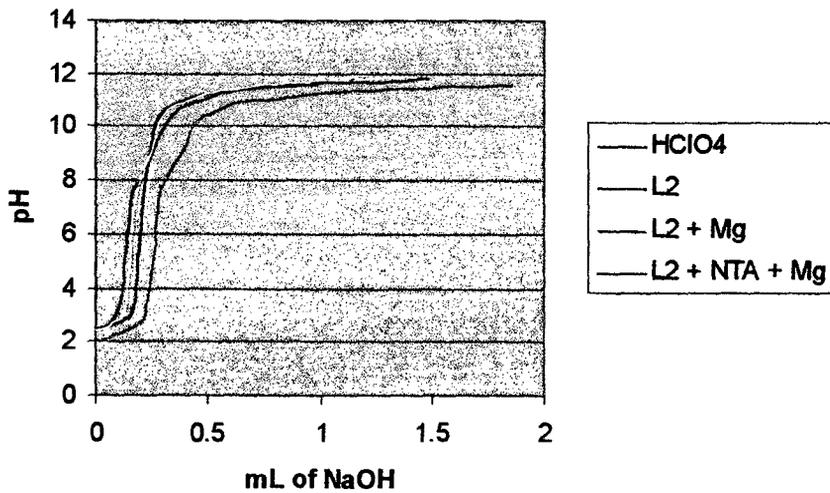
**Fig. 3.26 Graphical representation of pH-metry data for Zn ion in stability studies**



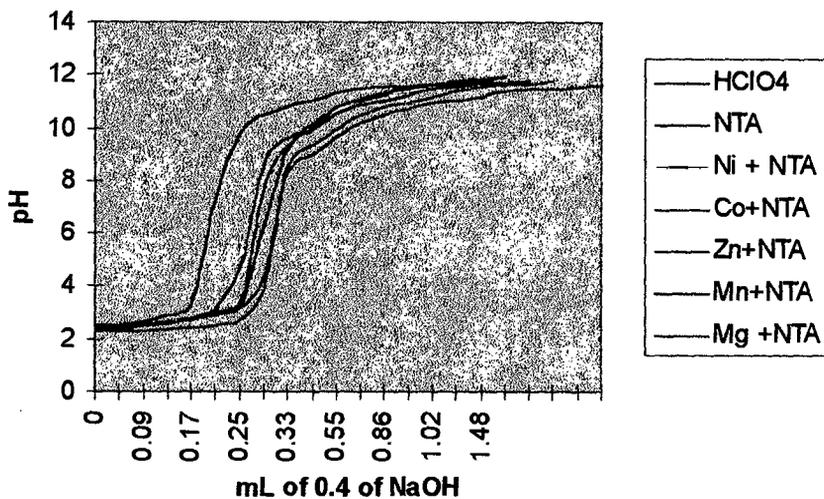
**Fig. 3.27 Graphical representation of pH-metry data for Mn ion in stability studies**



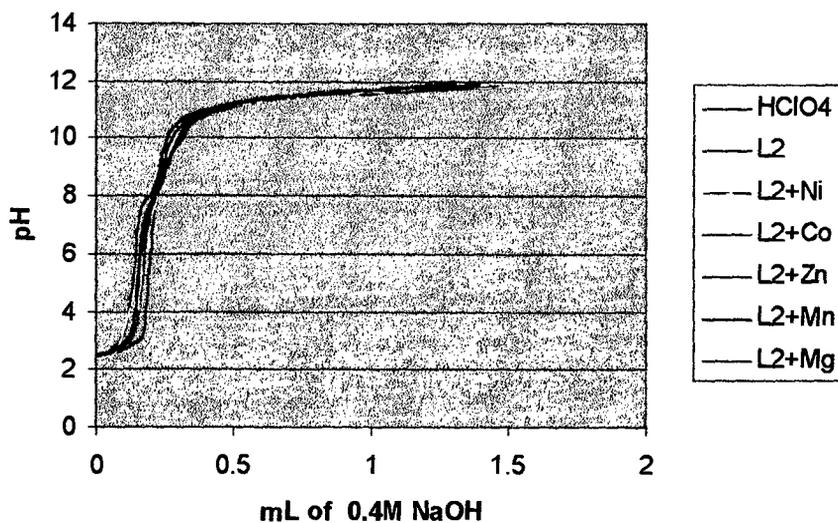
**Fig. 3.28 Graphical representation of pH-metry data for Mg ion in stability studies**



**Fig. 3.29 Graphical comparison of pH-metry data for different metal ions with NTA**



**Fig. 3.30 Graphical comparison of pH-metry data for different metal ions with hydrazido carboxylic acid**



### 3.3 CALCULATION OF $\bar{n}_A$ AND ACID DISSOCIATION CONSTANT

In order to calculate the formation constant of the metal complexes, it is necessary to know the acid dissociation constant of the reagents ( ligands ) accurately, since the values of, n, pL and also the formation constants depends on these constants. The formation constant of metal complexes is mainly dependent on the acid dissociation constants of these reagents. The values of  $\bar{n}_A$  for the reagents is calculated at various pH values and the formation constants are deduced from the plots of  $\bar{n}_A$  verses pH.  $\bar{n}_A$  is the ratio of total concentration of protons bound to the ligand to the total concentration of ligand not bound to metal i.e.

$$\bar{n}_A = \frac{\text{(Total concentration of protons bound to the ligand)}}{\text{(Total concentration of protons not bound to the metal)}}$$

It can be calculated by using the formula,

$$\bar{n}_A = \frac{[Y - (V^{\text{II}} - V^{\text{I}})]}{V_0 + V^{\text{I}} \{(N - E^0) T_L^0\}} \dots \text{equation 3.1}$$

Where,

Y = basicity of acid (ligand),

For NTA, Y=3

For  $\text{N}_2\text{H}_2\text{COOH}$ , Y=1.

$T_L^0$  = initial concentration of the ligand after dilution,

Since 5 ml of 0.003 M solution of ligand NTA or hydrazidocarboxylic acid ( $L_2$ ) was diluted to 50 ml, the concentration of ligand after dilution was taken as 0.0003 M.

$T_M^0$  = initial concentration of the metal ion, after dilution,

since 5ml of 0.0005 M metal ion solution was diluted to 50 ml, the concentration of the metal ions was taken as 0.00005 M.

$N$  = concentration of the base. (= 0.4 M NaOH),

$E^0$  = concentration of the acid after dilution,

since 5 ml of 0.002M acid was diluted to 50 ml, the concentration of the acid was taken as 0.002 M.

$V_0$  = initial volume of the mixture,  $V_0 = 250$ ml.

$V^I$  = volume of the NaOH corresponding to definite pH (in Fig. 3.1 for  $Ni^{+2}$ ), the values of  $V^I$  are obtained from Fig. 3.1 and these are listed in Table 3.19 as well as in the Table 3.20, for  $Ni^{+2}$ .

$V^{II}$  = volume of the NaOH corresponding to the same pH (in Fig. 3.2/3.13 for  $Ni^{+2}$ ), the values of  $V^{II}$  are obtained from Fig. 3.2 for the system  $HClO_4 + NTA$ . These are listed in Table 3.19. The values of  $v''$  for the ternary system  $HClO_4 + N_2H_2COOH(L_2)$  are obtained from Fig. 3.13 and these are listed in Fig. 3.20, for  $Ni^{+2}$ .  $\bar{n}_A$  for the system  $HClO_4 + N_2H_2COOH(L_2)$  was calculated by using the formula given in equation 3.1. These values are listed in Tables 3.19 and 3.20.

Table 3.19

pH	V <sup>1</sup> HClO <sub>4</sub> (From fig 3.1)	V <sup>11</sup> for HClO <sub>4</sub> + NTA (from Fig3.2)	$\bar{n}_A$
2.6	0.052	0.2	-0.898
2.8	0.112	0.223	0.053
3.0	0.147	0.246	0.378
3.2	0.162	0.254	0.580
3.4	0.165	0.262	0.439
3.6	0.171	0.263	0.550
3.8	0.174	0.265	0.598
4.0	0.176	0.267	0.615
4.2	0.182	0.268	0.726
4.4	0.183	0.270	0.703
4.6	0.184	0.272	0.680
4.8	0.185	0.274	0.657
5.0	0.186	0.275	0.634
5.2	0.187	0.277	0.611
5.4	0.187	0.278	0.600
5.6	0.188	0.279	0.588
5.8	0.191	0.281	0.616
6.0	0.193	0.282	0.645
6.2	0.192	0.283	0.673
6.4	0.198	0.285	0.702
6.6	0.2	0.285	0.741
6.8	0.206	0.286	0.874
7.0	0.212	0.287	1.007
7.2	0.214	0.288	1.047
7.4	0.216	0.289	1.087
7.6	0.219	0.290	1.126
7.8	0.221	0.291	1.166
8.0	0.224	0.291	1.206
8.2	0.224	0.292	1.199
8.4	0.225	0.308	0.808
8.6	0.225	0.315	0.620
8.8	0.229	0.323	0.433
9.0	0.229	0.385	0.120
9.2	0.231	0.354	-0.240
9.4	0.233	0.369	-0.599
9.6	0.235	0.377	-0.740
9.8	0.241	0.4	-1.194
10.0	0.253	0.415	-1.288
10.2	0.259	0.238	-1.542
10.4	0.280	0.446	-1.384
10.6	0.282	0.492	-2.540
10.8	0.335	0.554	-2.760
11.0	0.388	0.638	-3.588
11.2	0.459	0.746	-4.555
11.4	0.594	0.931	-5.828
11.6	0.912	1.169	-3.709

Table 3.20

pH	V <sup>1</sup> HClO <sub>4</sub> (from fig. 3.1)	V <sup>11</sup> HClO <sub>4</sub> +L <sub>2</sub> (from fig. 3.13)	$\bar{n}_A$
2.6	0.053	0.037	1.439
2.8	0.112	0.064	2.274
3.0	0.147	0.077	3.251
3.2	0.162	0.086	3.010
3.4	0.165	0.100	2.711
3.6	0.171	0.105	2.746
3.8	0.174	0.109	2.719
4.0	0.176	0.111	2.741
4.2	0.182	0.112	2.857
4.4	0.183	0.114	2.839
4.6	0.184	0.118	2.741
4.8	0.185	0.120	2.703
5.0	0.186	0.227	2.665
5.2	0.187	0.124	2.647
5.4	0.187	0.126	2.629
5.6	0.188	0.127	2.611
5.8	0.191	0.132	2.553
6.0	0.193	0.133	2.576
6.2	0.195	0.135	2.598
6.4	0.198	0.364	2.620
6.6	0.2	0.141	2.562
6.8	0.206	0.435	2.597
7.0	0.212	0.150	2.631
7.2	0.214	0.152	2.634
7.4	0.216	0.155	2.636
7.6	0.219	0.168	2.338
7.8	0.221	0.177	2.155
8.0	0.224	0.186	1.982
8.2	0.224	0.195	1.757
8.4	0.225	0.265	1.533
8.6	0.225	0.214	1.308
8.8	0.226	0.223	1.083
9.0	0.229	0.236	0.816
9.2	0.231	0.245	0.623
9.4	0.233	0.255	0.429
9.6	0.235	0.264	0.252
9.8	0.241	0.282	0.073
10.0	0.253	0.291	-0.002
10.2	0.253	0.310	-0.327
10.4	0.280	0.323	-0.127
10.6	0.282	0.341	-0.545
10.8	0.335	0.382	-0.226
11.0	0.388	0.455	-0.746
11.2	0.459	0.518	-0.561
11.4	0.594	0.627	0.131
11.6	0.912	0.809	3.675

The graphical representation of  $\bar{n}_A$  v/s pH, for the above two systems using data from Table 3.19 and 3.20 ~~are~~ shown in Fig. 3.31 and 3.32. These plots are useful in the evaluation of the pK values. For the system involving di or tri-basic acid, for the first dissociation, the pK<sub>1</sub> value is found at  $\bar{n}_A = 0.5$  and for the second dissociation, the pK<sub>2</sub> value at  $\bar{n}_A = 1.5$ . pK<sub>3</sub> values are not found as the third carboxylic acid group in NTA remains acidic and does not take part in complex formation. For the system involving monobasic acid, pK<sub>1</sub> value is found at  $\bar{n}_A = 0.5$ .

Greater accuracy in the pK values can be achieved by plotting the  $\log [\bar{n}_A / (y - \bar{n}_A)]$  vs pH, where y is the basicity. For NTA, the basicity is three, and for N<sub>2</sub>H<sub>3</sub>COOH, the basicity is one. And hence, the graph of  $\log [\bar{n}_A / (3 - \bar{n}_A)]$  vs pH was plotted for NTA system and  $\log [\bar{n}_A / (1 - \bar{n}_A)]$  vs pH was plotted for N<sub>2</sub>H<sub>3</sub>COOH system. The pK<sub>1</sub> values can be found, when  $\log [\bar{n}_A / (3 - \bar{n}_A)] = 0$  for NTA and  $\log [\bar{n}_A / (1 - \bar{n}_A)] = 0$  for N<sub>2</sub>H<sub>3</sub>COOH. The plots are shown in Fig. 3.33 and 3.34 based on data shown in Table 3.21 and 3.22 respectively.

Fig 331 Graph of  $\bar{nA}$  v/s pH for  $HClO_4$   
+  $NaClO_4$  + N T A

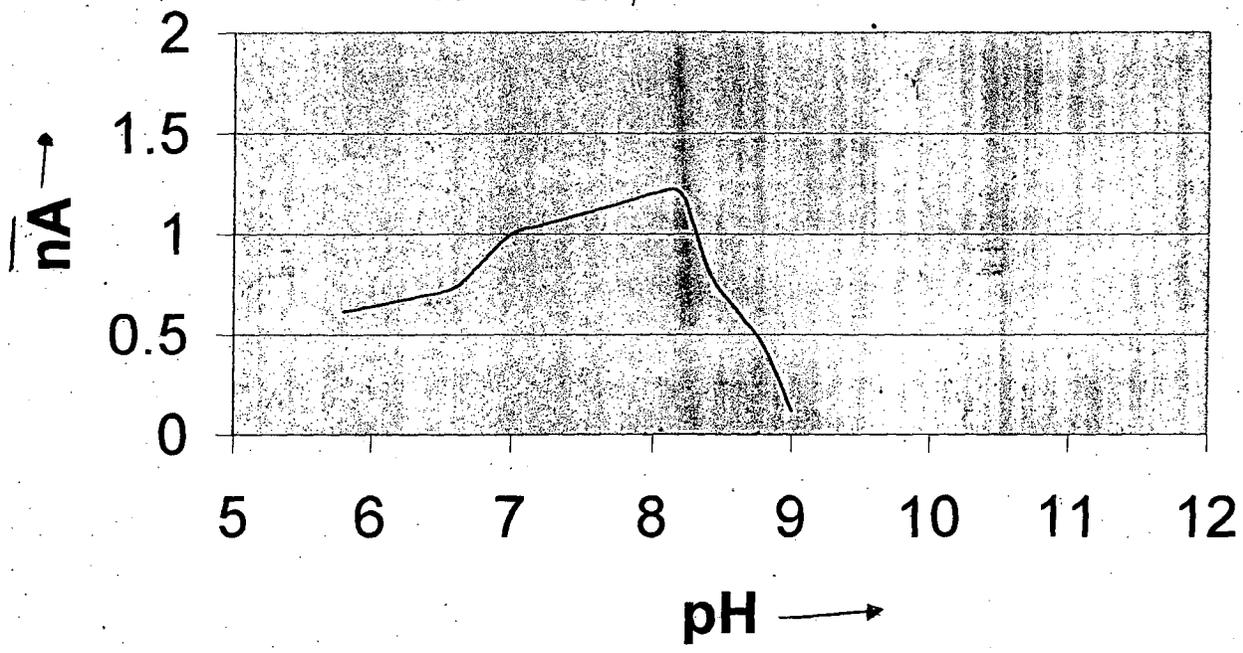


Fig 332 Graph of  $\bar{nA}$  v/s pH for  $\text{HClO}_4$   
 $+\text{NaClO}_4 + \text{N}_2\text{H}_3\text{COOH}$

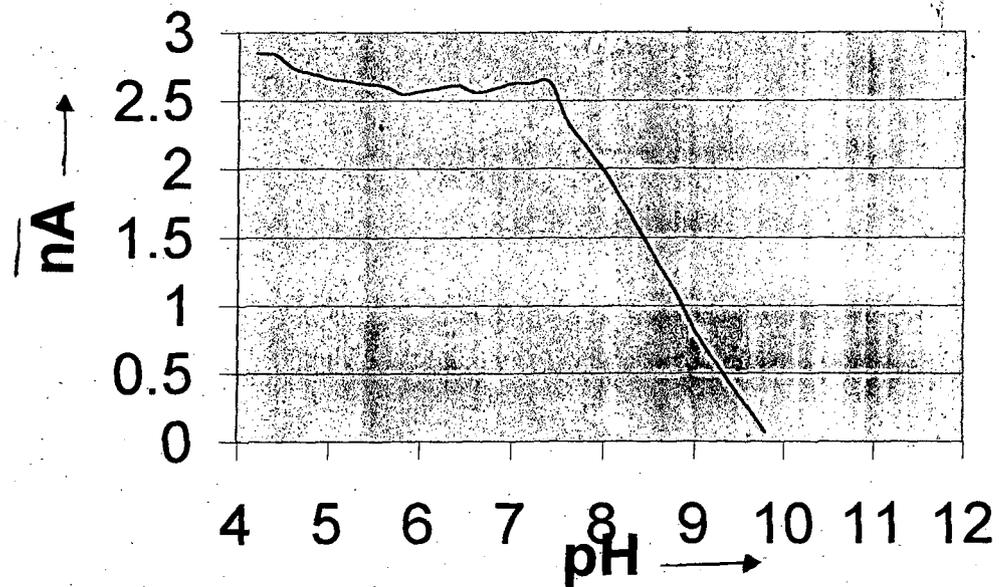


Fig 3.33 **Graph of  $\text{Log}(\bar{n}A/(3-\bar{n}A))$  v/s pH for  $\text{HClO}_4 + \text{N T A}$**

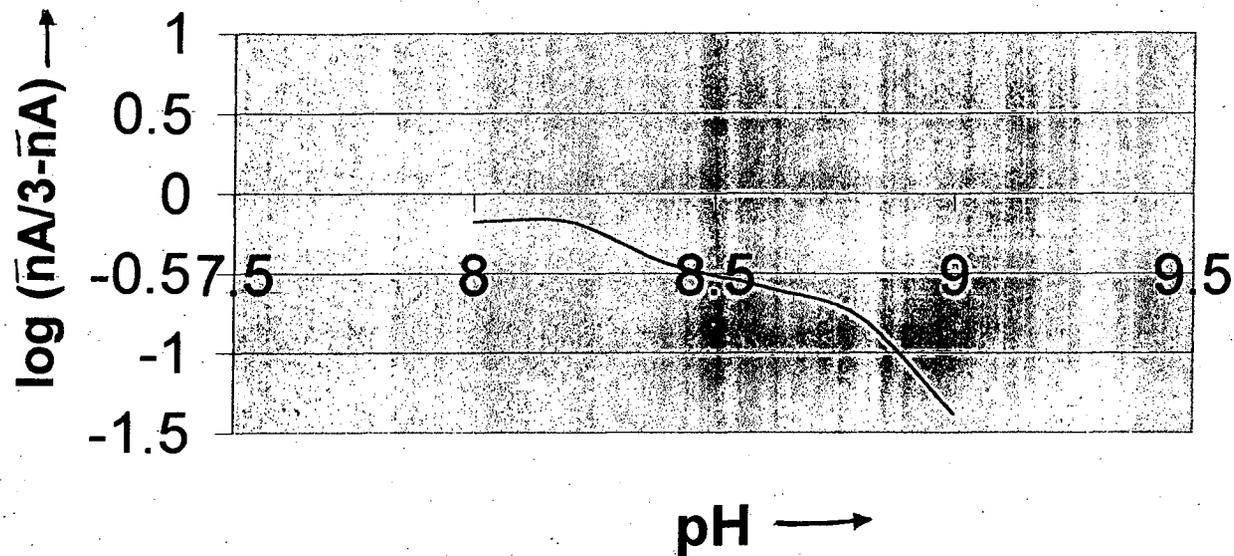


Fig 3.34 Graph of pH v/s  $\log \bar{nA}/(1-\bar{nA})$  for  $\text{HClO}_4 + \text{N}_2\text{H}_3\text{COOH}$

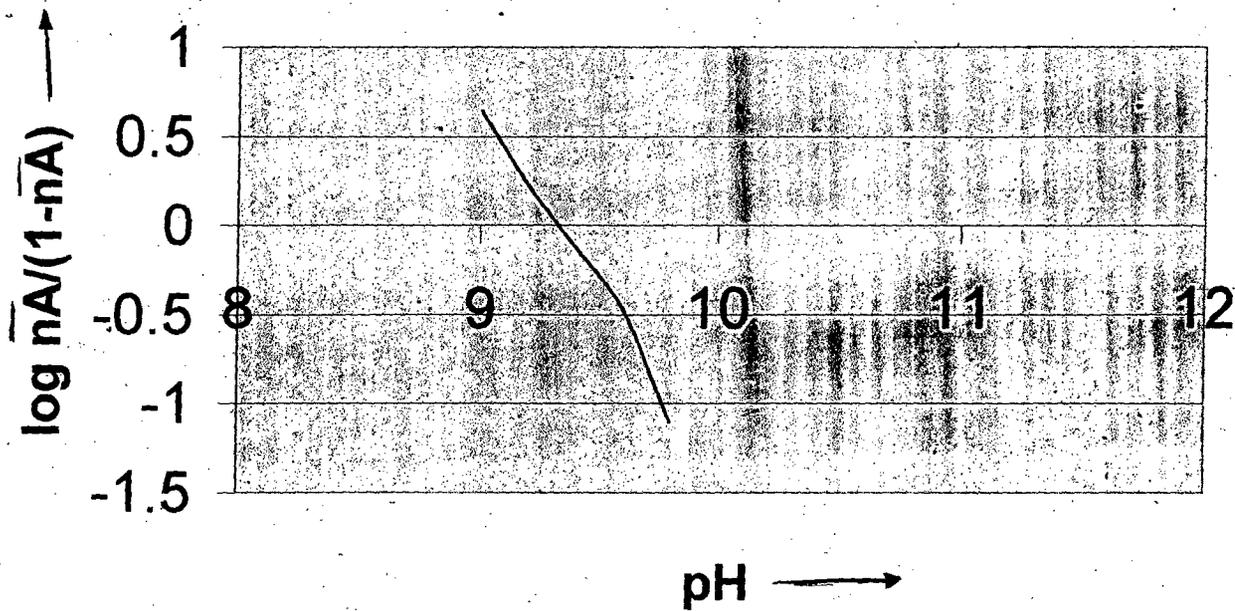


Table 3.21

HClO<sub>4</sub> + NTA system

pH	$\bar{n}_A$	$3-\bar{n}_A$	$\log \bar{n}_A / 3-\bar{n}_A$
7	1.007	1.993	-0.296
7.2	1.047	1.953	-0.271
7.4	1.087	1.913	-0.246
7.6	1.126	1.874	-0.221
7.8	1.166	1.834	-0.197
8.0	1.206	1.794	-0.173
8.2	1.199	1.801	-0.177
8.4	0.808	2.192	-0.433
8.6	0.620	2.380	-0.584
8.8	0.433	2.567	-0.773
9.0	0.120	2.880	-1.381

TABLE 3.22

HClO<sub>4</sub> + N<sub>2</sub>H<sub>3</sub>COOH system

pH	$\bar{n}_A$	$1-\bar{n}_A$	$\log \bar{n}_A / 1-\bar{n}_A$
8.8	1.083	0.083	1.114
9.0	0.082	0.184	0.648
9.2	0.623	0.377	0.218
9.4	0.429	0.571	-0.123
9.6	0.252	0.749	-0.474
9.8	0.073	0.927	-1.103

### 3.4 CALCULATION OF DEGREE OF FORMATION ' $\bar{n}$ '

The stepwise formation of complexes was first suggested by Bjerrum [1], who introduced the concept of the degree of formation or the ligand number  $\bar{n}$ , in order to determine the stability constants of the system. The degree of formation (or formation function) was defined as the average number of ligands bound per metal ion present. Mathematically, it is defined as,

$\bar{n}$  = (concentration of the ligand bound to the metal ion / Total concentration of the metal ion in any of its form).

Or,

$\bar{n}$  = [Ligand bound to metal] / [total Metal].

The total metal concentration is given by,

$T_M = [M] + [ML] + [ML_2] + \dots + [ML_N]$ .

And the total concentration of the ligand  $T_L$  is given by,

$T_L = [L] + [ML] + ML_1 + 2 [ML_2] + \dots + N[ML_N]$ .

By the definition of the formation function,  $\bar{n}$  can be expressed as,

$\bar{n} = T_L - \{[L] / T_M\}$

Where  $T_L$  is the total concentration present in all its forms and  $T_M$  is the total concentration of the metal ion, present in whatever form.

The following equation is used for the calculation of  $\bar{n}$  values,

$$N = (V^{III} - V^{II} / V_0 + V^I) [N + E^0 + T_L (y - \bar{n}A) / nA \cdot T_M^0]$$

Where  $V^{III}$ , is the volume of NaOH corresponding to definite pH in Figs. 3.3, 3.5, 3.6, 3.7, 3.8, 3.9, 3.10, 3.33, 3.12, 3.13, 3.14, 3.15, 3.16, 3.17 and 3.18. The values of  $V^{III}$  for different pH and the calculated values of  $\bar{n}$  for different metal ion involving NTA systems are shown in Tables 3.23 to 3.27 and the values for different metal ions involving  $N_2H_3COOH$ , the  $L_2$  ligand, system are shown in Tables 3.28 to 3.32. Tables 3.33 to 3.38 show  $V^{III}$  values at different pH and calculated values of  $\bar{n}$  for ternary system involving metal ion ( $Ni^{+2}$ ,  $Mn^{+2}$ ,  $Mg^{+2}$ ) and the two ligands, NTA and  $N_2H_3COOH$ . Since the plot of  $\bar{n}$  vs pL helps to find  $\log K_1$  and  $\log K_2$  at  $\bar{n}$  values of 0.5 and 1.5 respectively, only the values  $\bar{n}$  lying in the positive range upto a value equal to 4 is considered for graphic purpose.

### 3.5 CALCULATION OF pL

The pL can be calculated by using the general equation

$$pL = \log_{10} \left\{ \frac{\sum \beta H_i (1 / \text{antilog } [H^+])^i}{T_L^0 - \bar{n} T_M^0} \cdot \frac{V^0 + V^{II}}{V^0} \right\}$$

For a biprotic acid, for example, the above equation reduces to,

$$pL = \log_{10} \frac{[H]^2 / k_{a1} \cdot k_{a2} + [H] k_{a1} + 1}{T_L^0 - \bar{n} T_M^0} (V^0 + V^{III} / V^0)$$

Table 3.23  
NTA + NiCl<sub>2</sub>

pH	V <sup>III</sup>	$\bar{n}$
2.6	0.116	7.518
2.8	0.179	-133.630
3.0	0.216	-12.891
3.2	0.237	-4.706
3.4	0.253	-3.255
3.6	0.258	-1.563
3.8	0.263	-0.483
4.0	0.268	0.458
4.2	0.276	1.639
4.4	0.277	1.663
4.6	0.279	1.688
4.8	0.280	1.458
5.0	0.280	1.211
5.2	0.281	0.946
5.4	0.281	0.762
5.6	0.282	0.571
5.8	0.282	0.348
6.0	0.283	0.144
6.2	0.283	-0.042
6.4	0.284	-0.213
6.6	0.284	-0.273
6.8	0.285	-0.311
7.0	0.285	-0.339
7.2	0.285	-0.392
7.4	0.286	-0.442
7.6	0.286	-0.488
7.8	0.289	-0.154
8.0	0.291	-0.053
8.2	0.295	0.3248
8.4	0.297	-2.153
8.6	0.300	-3.978
8.8	0.307	-5.822
9.0	0.318	-2.755
9.2	0.326	18.417
9.4	0.337	8.671
9.6	0.342	7.549
9.8	0.358	5.661
10.0	0.363	6.506
10.2	0.374	5.970
10.4	0.390	6.570
10.6	0.411	5.171
10.8	0.432	7.106
11.0	0.474	7.363
11.2	0.526	7.734
11.4	0.632	8.212
11.6	0.879	12.421

Table 3.24  
NTA+ CoCl<sub>2</sub>

pH	V <sup>III</sup>	$\bar{n}$
2.6	0.117	-14.878
2.8	0.175	-145.584
3.0	0.208	-16.057
3.2	0.233	-5.677
3.4	0.250	-4.217
3.6	0.262	-0.218
3.8	0.271	1.577
4.0	0.277	2.609
4.2	0.283	3.307
4.4	0.287	3.976
4.6	0.290	4.199
4.8	0.291	4.182
5.0	0.292	4.164
5.2	0.292	3.902
5.4	0.292	3.663
5.6	0.292	3.416
5.8	0.292	2.953
6.0	0.292	2.532
6.2	0.292	2.145
6.4	0.292	1.791
6.6	0.293	1.534
6.8	0.293	1.163
7.0	0.293	0.891
7.2	0.293	0.743
7.4	0.293	0.607
7.6	0.293	0.479
7.8	0.293	0.361
8.0	0.293	0.250
8.2	0.300	1.029
8.4	0.304	-0.700
8.6	0.308	-1.823
8.8	0.312	-3.920
9.0	0.317	-2.919
9.2	0.325	19.297
9.4	0.333	9.611
9.6	0.342	18.961
9.8	0.354	6.163
10.0	0.362	6.588
10.2	0.375	5.849
10.4	0.387	6.799
10.6	0.400	5.836
10.8	0.417	7.972
11.0	0.450	8.422
11.2	0.483	9.247
11.4	0.542	10.680
11.6	0.625	23.288

Table no 3.25  
NTA+ZnCl<sub>2</sub>

pH	V <sup>III</sup>	$\bar{n}$
2.6	0.109	16.321
2.8	0.173	-153.154
3.0	0.218	-12.165
3.2	0.234	-5.492
3.4	0.242	-6.008
3.6	0.249	-4.161
3.8	0.257	-2.270
4.0	0.263	-1.087
4.2	0.266	-0.470
4.4	0.27	-0.195
4.6	0.278	-1.160
4.8	0.279	1.342
5.0	0.281	1.528
5.2	0.282	1.301
5.4	0.283	1.150
5.6	0.283	0.993
5.8	0.284	0.776
6.0	0.284	0.578
6.2	0.285	0.397
6.4	0.286	0.260
6.6	0.287	0.223
6.8	0.287	0.002
7.0	0.288	0.131
7.2	0.289	0.110
7.4	0.293	0.533
7.6	0.294	0.659
7.8	0.296	0.777
8.0	0.3	1.136
8.2	0.304	1.530
8.4	0.308	-0.038
8.6	0.311	-1.069
8.8	0.315	-2.994
9.0	0.326	-1.636
9.2	0.339	9.932
9.4	0.351	4.881
9.6	0.36	3.669
9.8	0.375	3.361
10.0	0.398	2.279
10.2	0.414	2.255
10.4	0.437	1.119
10.6	0.45	2.675
10.8	0.119	3.856
11.0	0.533	4.735
11.2	0.6	5.142
11.4	0.694	6.506
11.6	0.908	11.199

Table no 3.26  
NTA + MnCl<sub>2</sub>

pH	V <sup>III</sup>	$\bar{n}$
2.6	0.115	15.140
2.8	0.168	-166.780
3.0	0.206	-16.878
3.2	0.232	-5.956
3.4	0.24	-7.872
3.6	0.248	-4.546
3.8	0.250	-5.361
4.0	0.254	-3.201
4.2	0.259	-2.029
4.4	0.264	-1.390
4.6	0.269	-0.707
4.8	0.271	-0.630
5.0	0.274	-0.408
5.2	0.278	0.388
5.4	0.280	0.566
5.6	0.282	0.752
5.8	0.284	0.883
6.0	0.286	1.003
6.2	0.288	1.112
6.4	0.289	0.994
6.6	0.290	0.963
6.8	0.291	0.836
7.0	0.292	0.742
7.2	0.293	0.730
7.4	0.296	1.049
7.6	0.299	1.346
7.8	0.302	1.622
8.0	0.305	1.774
8.2	0.307	1.991
8.4	0.310	0.379
8.6	0.312	-0.875
8.8	0.322	-0.547
9.0	0.326	-1.616
9.2	0.331	15.150
9.4	0.338	8.254
9.6	0.346	6.791
9.8	0.357	5.766
10.0	0.370	5.703
10.2	0.374	5.904
10.4	0.389	6.648
10.6	0.408	5.331
10.8	0.432	7.081
11.0	0.466	7.725
11.2	0.518	8.013
11.4	0.586	9.475
11.6	0.749	17.990

Table 3.27  
NTA + MgCl<sub>2</sub>

pH	V <sup>III</sup>	$\bar{n}$
2.6	0.117	14.878
2.8	0.174	-145.584
3.0	0.208	-16.057
3.2	0.230	-6.834
3.4	0.235	-9.699
3.6	0.246	-5.085
3.8	0.254	-2.896
4.0	0.262	-1.087
4.2	0.267	-0.378
4.4	0.268	-0.305
4.6	0.271	-0.246
4.8	0.273	-0.183
5.0	0.275	-0.051
5.2	0.277	0.042
5.4	0.279	0.257
5.6	0.280	0.197
5.8	0.281	0.125
6.0	0.282	0.060
6.2	0.283	0.000
6.4	0.284	-0.081
6.6	0.285	-0.062
6.8	0.286	-0.039
7.0	0.287	-0.023
7.2	0.288	-0.011
7.4	0.289	-0.000
7.6	0.290	0.010
7.8	0.291	0.020
8.0	0.292	0.028
8.2	0.296	0.471
8.4	0.304	-0.700
8.6	0.300	-3.978
8.8	0.312	-3.920
9.0	0.325	-1.803
9.2	0.329	16.510
9.4	0.342	7.380
9.6	0.354	4.934
9.8	0.367	4.482
10.0	0.375	5.031
10.2	0.383	5.081
10.4	0.396	5.833
10.6	0.421	4.519
10.8	0.454	5.793
11.0	0.483	6.932
11.2	0.567	8.013
11.4	0.647	7.936
11.6	0.783	16.512

Table 3.28  
L<sub>2</sub> + NiCl<sub>2</sub>

pH	V <sup>III</sup>	$\bar{n}$
2.6	0.063	2.989
2.8	0.074	0.708
3.0	0.089	0.601
3.2	0.100	0.725
3.4	0.105	0.311
3.6	0.116	0.655
3.8	0.126	1.014
4.0	0.132	1.224
4.2	0.137	1.385
4.4	0.142	1.604
4.6	0.147	1.704
4.8	0.150	1.744
5.0	0.153	1.795
5.2	0.155	1.875
5.4	0.158	1.956
5.6	0.163	2.199
5.8	0.168	2.294
6.0	0.170	2.289
6.2	0.172	2.284
6.4	0.174	2.279
6.6	0.179	2.375
6.8	0.184	2.387
7.0	0.189	2.399
7.2	0.195	2.578
7.4	0.200	2.757
7.6	0.205	2.537
7.8	0.211	2.463
8.0	0.216	2.375
8.2	0.221	2.331
8.4	0.225	2.090
8.6	0.228	1.766
8.8	0.232	1.308
9.0	0.242	1.126
9.2	0.247	0.492
9.4	0.253	-0.714
9.6	0.263	-0.305
9.8	0.279	6.283
10.0	0.284	458.337
10.2	0.289	9.610
10.4	0.305	21.942
10.6	0.337	1.195
10.8	0.363	13.189
11.0	0.416	8.302
11.2	0.484	9.667
11.4	0.579	-66.482
11.6	0.705	-4.452

Table 3.29  
L<sub>2</sub> + CoCl<sub>2</sub>

pH	V <sup>III</sup>	$\bar{n}$
2.6	0.050	1.521
2.8	0.086	1.602
3.0	0.109	1.567
3.2	0.123	1.734
3.4	0.132	1.879
3.6	0.141	2.119
3.8	0.145	2.400
4.0	0.155	2.565
4.2	0.159	2.631
4.4	0.161	2.690
4.6	0.164	2.654
4.8	0.173	3.094
5.0	0.175	3.138
5.2	0.177	3.205
5.4	0.180	3.273
5.6	0.182	3.342
5.8	0.183	3.190
6.0	0.184	3.125
6.2	0.185	3.061
6.4	0.185	2.998
6.6	0.186	2.839
6.8	0.187	2.576
7.0	0.188	2.320
7.2	0.189	2.235
7.4	0.190	2.151
7.6	0.191	1.555
7.8	0.205	2.020
8.0	0.209	1.835
8.2	0.218	2.069
8.4	0.223	1.898
8.6	0.232	2.225
8.8	0.236	2.015
9.0	0.245	1.783
9.2	0.250	1.168
9.4	0.259	1.615
9.6	0.264	0.000
9.8	0.273	19.896
10.0	0.282	622.029
10.2	0.295	6.680
10.4	0.309	17.133
10.6	0.336	1.335
10.8	0.364	12.851
11.0	0.409	9.737
11.2	0.468	14.227
11.4	0.573	-75.039
11.6	0.755	-2.339

Table 3.30  
L<sub>2</sub> + ZnCl<sub>2</sub>

pH	V <sup>III</sup>	$\bar{n}$
2.6	0.048	1.256
2.8	0.076	0.885
3.0	0.100	1.119
3.2	0.119	1.738
3.4	0.129	1.682
3.6	0.133	1.678
3.8	0.138	1.707
4.0	0.143	1.883
4.2	0.148	1.988
4.4	0.152	2.184
4.6	0.154	2.089
4.8	0.156	2.078
5.0	0.157	2.066
5.2	0.160	2.133
5.4	0.162	2.200
5.6	0.163	2.219
5.8	0.165	2.084
6.0	0.167	2.071
6.2	0.171	2.253
6.4	0.173	2.238
6.6	0.175	2.104
6.8	0.176	1.893
7.0	0.181	1.881
7.2	0.190	2.320
7.4	0.195	2.469
7.6	0.2	2.177
7.8	0.205	2.036
8.0	0.210	1.870
8.2	0.219	2.148
8.4	0.224	2.011
8.6	0.233	2.410
8.8	0.243	2.974
9.0	0.252	3.141
9.2	0.262	4.228
9.4	0.271	6.295
9.6	0.286	14.058
9.8	0.295	-29.370
10.0	0.300	-622.026
10.2	0.314	-2.545
10.4	0.329	-7.342
10.6	0.348	-1.971
10.8	0.371	7.343
11.0	0.424	6.584
11.2	0.490	7.883
11.4	0.610	-24.417
11.6	0.771	-1.615

Table 3.31  
L<sub>2</sub> + MnCl<sub>2</sub>

pH	V <sup>III</sup>	$\bar{n}$
2.6	0.064	3.043
2.8	0.086	1.602
3.0	0.105	1.343
3.2	0.120	1.813
3.4	0.127	1.610
3.6	0.136	1.854
3.8	0.141	1.873
4.0	0.145	2.034
4.2	0.150	2.121
4.4	0.155	2.306
4.6	0.157	2.255
4.8	0.159	2.287
5.0	0.160	2.214
5.2	0.106	2.167
5.4	0.161	2.121
5.6	0.161	2.073
5.8	0.162	1.867
6.0	0.162	1.788
6.2	0.163	1.711
6.4	0.163	1.635
6.6	0.164	1.419
6.8	0.163	1.260
7.0	0.168	1.105
7.2	0.173	1.242
7.4	0.177	1.379
7.6	0.182	0.933
7.8	0.191	1.010
8.0	0.2	1.101
8.2	0.214	1.656
8.4	0.218	1.899
8.6	0.227	1.669
8.8	0.236	2.015
9.0	0.241	0.891
9.2	0.250	1.168
9.4	0.259	1.695
9.6	0.273	5.788
9.8	0.282	0.000
10.0	0.295	-311.013
10.2	0.305	0.227
10.4	0.318	5.711
10.6	0.336	1.343
10.8	0.364	12.851
11.0	0.427	5.842
11.2	0.491	5.842
11.4	0.595	-43.773
11.6	0.773	-1.554

Table 3.32  
L<sub>2</sub> + MgCl<sub>2</sub>

pH	V <sup>III</sup>	$\bar{n}$
2.6	0.059	2.535
2.8	0.091	1.922
3.0	0.109	1.567
3.2	0.127	0.218
3.4	0.136	2.147
3.6	0.145	2.384
3.8	0.150	2.408
4.0	0.155	2.565
4.2	0.159	2.631
4.4	0.164	2.818
4.6	0.168	2.919
4.8	0.169	2.846
5.0	0.169	2.771
5.2	0.169	2.719
5.4	0.170	2.667
5.6	0.170	2.614
5.8	0.170	2.410
6.0	0.171	2.317
6.2	0.171	2.225
6.4	0.171	2.135
6.6	0.172	1.922
6.8	0.172	1.637
7.0	0.172	1.360
7.2	0.173	1.242
7.4	0.177	1.379
7.6	0.186	1.244
7.8	0.191	1.010
8.0	0.195	0.734
8.2	0.207	0.828
8.4	0.209	0.475
8.6	0.218	0.556
8.8	0.223	0.000
9.0	0.232	-0.891
9.2	0.236	-2.337
9.4	0.245	-3.390
9.6	0.255	-5.788
9.8	0.264	39.791
10.0	0.273	1244.058
10.2	0.286	11.134
10.4	0.305	22.843
10.6	0.327	4.006
10.8	0.350	22.489
11.0	0.382	15.579
11.2	0.482	10.347
11.4	0.573	-75.039
11.6	0.732	-3.313

Table 3.33

[5ml.HClO<sub>4</sub>+5ml.NaClO<sub>4</sub>+ 5mLNNTA+  
5mLL<sub>2</sub>+5mLof NiCl<sub>2</sub> +25mLH<sub>2</sub>O ]  
v/s 0.4 M NaOH

pH	V <sup>III</sup>	$\bar{n}$
2.6	0.2	0.
2.8	0.219	-13.102
3.0	0.231	-6.327
3.2	0.238	-4.524
3.4	0.25	-4.217
3.6	0.253	-2.956
3.8	0.256	-2.334
4.0	0.263	-1.082
4.2	0.265	-0.839
4.4	0.267	-0.781
4.6	0.269	-0.719
4.8	0.272	-0.398
5.0	0.275	-0.054
5.2	0.277	-0.095
5.4	0.278	-0.021
5.6	0.280	0.055
5.8	0.281	0.125
6.0	0.283	0.319
6.2	0.285	0.497
6.4	0.285	0.660
6.6	0.294	1.792
6.8	0.297	1.935
7.0	0.300	2.041
7.2	0.302	2.154
7.4	0.304	2.254
7.6	0.306	2.349
7.8	0.308	2.438
8.0	0.310	2.521
8.2	0.313	2.700
8.4	0.325	3.435
8.6	0.331	4.091
8.8	0.338	5.346
9.0	0.35	15.455
9.2	0.353	0.482
9.4	0.356	3.475
9.6	0.363	3.127
9.8	0.375	3.361
10.0	0.394	2.695
10.2	0.419	1.817
10.4	0.45	-0.446
10.6	0.5	-0.486
10.8	0.55	0.224
11.0	0.65	-0.513
11.2	0.813	-0.232
11.4	1.15	-6.018

Table 3.34

[5mLHClO<sub>4</sub>+5mLNaClO<sub>4</sub>+ 5mLNNTA+  
5mLL<sub>2</sub>+5mLof NiCl<sub>2</sub> +25mLH<sub>2</sub>O ]  
v/s 0.4 M NaOH

pH	V <sup>III</sup>	$\bar{n}$
2.6	0.2	-18.267
2.8	0.219	-10.934
3.0	0.231	-7.607
3.2	0.238	-8.061
3.4	0.25	-8.878
3.6	0.253	-8.681
3.8	0.256	-8.683
4.0	0.263	-8.890
4.2	0.265	-8.563
4.4	0.267	-8.548
4.6	0.269	-8.813
4.8	0.272	-8.986
5.0	0.275	-9.165
5.2	0.277	-9.229
5.4	0.278	-9.295
5.6	0.280	-9.361
5.8	0.281	-9.385
6.0	0.283	-9.340
6.2	0.285	-9.296
6.4	0.288	-9.299
6.6	0.294	-9.565
6.8	0.297	-9.327
7.0	0.3	-9.137
7.2	0.302	-9.118
7.4	0.304	-9.099
7.6	0.306	-9.465
7.8	0.308	-8.084
8.0	0.310	-10.028
8.2	0.313	-10.669
8.4	0.325	-12.587
8.6	0.331	-14.398
8.8	0.338	-16.960
9.0	0.35	22.283
9.2	0.353	27.676
9.4	0.356	37.924
9.6	0.363	63.200
10.0	0.394	-7036.703
10.2	0.378	-53.719
10.4	0.35	-159.904
10.6	0.5	-46.733
10.8	0.55	118.869
11.0	0.65	-41.868
11.2	0.813	-83.745

Table 3.35

5mLHClO<sub>4</sub>+5mLNaClO<sub>4</sub>+ 5mLNTA+5mLL<sub>2</sub>+5mLof CoCl<sub>2</sub> +25mLH<sub>2</sub>O w/s 0.4 M NaOH

pH	V <sup>III</sup>	$\bar{n}$ (NTA considered)	$\bar{n}$ (L <sub>2</sub> Considered)
2.6	0.146	9.628	-24.258
2.8	0.185	-114.194	-8.580
3.0	0.215	-13.382	-6.786
3.2	0.234	-5.452	-7.882
3.4	0.249	-4.663	-8.806
3.6	0.254	-2.800	-8.712
3.8	0.259	-1.723	-8.818
4.0	0.263	-0.849	-8.943
4.2	0.268	-0.018	-8.709
4.4	0.273	0.704	-9.016
4.6	0.275	0.709	-9.167
4.8	0.276	0.713	-9.356
5.0	0.278	0.718	-9.348
5.2	0.279	0.552	-9.379
5.4	0.280	0.480	-9.409
5.6	0.281	0.406	-9.440
5.8	0.289	0.308	-9.315
6.0	0.283	0.218	-9.315
6.2	0.284	0.194	-9.217
6.4	0.285	0.172	-9.119
6.6	0.287	0.241	-9.109
6.8	0.288	0.272	-8.768
7.0	0.290	0.488	-8.543
7.2	0.293	0.712	-8.546
7.4	0.298	1.279	-8.697
7.6	0.302	1.807	-9.203
7.8	0.307	2.306	-8.024
8.0	0.312	2.758	-10.172
8.2	0.317	3.312	-11.086
8.4	0.322	2.830	-12.269
8.6	0.324	2.329	-13.558
8.8	0.327	1.391	-15.384
9.0	0.337	-2.513	19.653
9.2	0.341	8.284	24.679
9.4	0.351	4.822	36.048
9.6	0.366	2.400	65.344
10.0	0.390	3.132	-6796.805
10.2	0.4	3.545	-44.534
10.4	0.415	3.653	-115.471
10.6	0.435	3.646	-27.532
10.8	0.468	4.972	-61.173
11.0	0.498	6.263	-9.214
11.2	0.576	5.960	-16.340
11.4	0.683	6.803	67.763

Table 3.36

5mL HClO<sub>4</sub> + 5mL NaClO<sub>4</sub> + 5mL NTA + 5mL L<sub>2</sub> + 5mL of ZnCl<sub>2</sub> + 25mL H<sub>2</sub>O w/s 0.4 M NaOH

pH	V <sup>m</sup>	$\bar{n}$ (NTA considered)	$\bar{n}$ (L <sub>2</sub> Considered)
2.6	0.100	17.943	-7.104
2.8	0.150	-221.261	-6.088
3.0	0.178	-29.029	-4.965
3.2	0.222	-8.752	-7.246
3.4	0.233	-10.307	-7.892
3.6	0.244	-5.491	-8.174
3.8	0.261	-1.032	-8.969
4.0	0.267	0.000	-9.133
4.2	0.272	0.850	-8.992
4.4	0.278	1.756	-9.276
4.6	0.283	2.723	-9.666
4.8	0.289	3.758	-9.996
5.0	0.294	4.868	-10.335
5.2	0.289	3.142	-9.976
5.4	0.300	5.835	-10.629
5.6	0.300	5.600	-10.608
5.8	0.294	3.561	-10.214
6.0	0.294	3.085	-10.032
6.2	0.294	2.649	-9.853
6.4	0.294	2.248	-9.674
6.6	0.294	1.942	-9.601
6.8	0.294	1.490	-9.177
7.0	0.300	2.041	-9.137
7.2	0.301	2.045	-9.076
7.4	0.305	2.049	-9.014
7.6	0.304	2.053	-9.322
7.8	0.306	2.057	-7.884
8.0	0.311	2.613	-10.084
8.2	0.314	2.886	-10.796
8.4	0.317	1.781	-11.716
8.6	0.322	1.768	-13.293
8.8	0.328	1.742	-15.524
9.0	0.333	-6.869	19.105
9.2	0.344	6.290	25.445
9.4	0.356	3.661	37.665
9.6	0.367	2.224	65.864
9.8	0.378	2.988	209.987
10.0	0.389	3.301	-6704.090
10.2	0.400	3.545	-44.534
10.4	0.406	4.706	-104.065
10.6	0.422	4.431	-23.886
10.8	0.467	5.066	-60.023
11.0	0.522	5.167	-14.497
11.2	0.572	6.078	-15.377
11.4	0.667	7.249	47.965

Table 3.37

5mL HClO<sub>4</sub> + 5mL NaClO<sub>4</sub> + 5mL NTA + 5mL L<sub>2</sub> + 5mL of MnCl<sub>2</sub> + 25mL H<sub>2</sub>O v/s 0.4 M NaOH

pH	V <sup>III</sup>	$\bar{n}$ (NTA considered)	$\bar{n}$ (L <sub>2</sub> Considered)
2.6	0.117	1.484	-8.964
2.8	0.175	-145.584	-7.850
3.0	0.208	-16.057	-6.475
3.2	0.225	-7.983	-7.394
3.4	0.243	-7.262	-8.385
3.6	0.25	-3.869	-8.498
3.8	0.262	-0.660	-9.051
4.0	0.271	1.087	-9.377
4.2	0.275	1.465	-9.148
4.4	0.279	2.074	-9.355
4.6	0.283	2.723	-9.666
4.8	0.285	2.808	-9.765
5.0	0.287	3.110	-9.917
5.2	0.290	3.434	-10.070
5.4	0.291	3.381	-10.070
5.6	0.292	3.325	-10.097
5.8	0.294	3.380	-10.171
6.0	0.296	3.430	-10.118
6.2	0.297	3.228	-10.003
6.4	0.298	3.042	-9.887
6.6	0.299	2.919	-9.883
6.8	0.300	2.509	-9.519
7.0	0.304	2.704	-9.391
7.2	0.308	3.109	-9.498
7.4	0.310	3.176	-9.479
7.6	0.312	3.239	-9.893
7.8	0.317	3.585	-8.598
8.0	0.319	3.629	-10.702
8.2	0.321	3.814	-11.429
8.4	0.330	4.262	-13.023
8.6	0.333	4.641	-14.653
8.8	0.342	6.890	-17.576
9.0	0.350	15.455	22.283
9.2	0.358	-3.002	29.016
9.4	0.367	0.686	41.808
9.6	0.375	0.417	71.181
9.8	0.383	2.241	222.144
10.0	0.395	2.435	-7179.252
10.2	0.408	2.777	-48.616
10.4	0.425	2.452	-128.494
10.6	0.450	2.675	-32.045
10.8	0.492	3.614	-77.708
11.0	0.533	4.673	-16.877
11.2	0.592	5.412	-20.909
11.4	0.700	6.334	8.855

Table 3.38

5mLHClO<sub>4</sub>+5mLNaClO<sub>4</sub> + 5mLNTA+5mLL<sub>2</sub>+5mLofMgCl<sub>2</sub> +25mLH<sub>2</sub>O v/s 0.4 M NaOH

pH	V <sup>m</sup>	$\bar{n}$ (NTA considered)	$\bar{n}$ (L <sub>2</sub> Considered)
2.6	0.157	7.670	-13.483
2.8	0.186	-113.183	-8.604
3.0	0.2	-19.595	-6.063
3.2	0.214	-10.948	-6.823
3.4	0.241	-14.661	-7.186
3.6	0.225	-11.171	-7.038
3.8	0.229	-9.767	-7.049
4.0	0.232	-0.009	-7.113
4.2	0.236	-7.222	-6.941
4.4	0.243	-6.217	-7.303
4.6	0.244	-6.590	-7.357
4.8	0.245	-6.988	-7.385
5.0	0.246	-7.415	-7.146
5.2	0.247	-7.874	-7.434
5.4	0.248	-8.097	-7.455
5.6	0.249	-8.329	-7.475
5.8	0.25	-8.012	-7.423
6.0	0.257	-6.200	-7.709
6.2	0.259	-5.903	-7.638
6.4	0.260	-5.630	-7.566
6.6	0.261	-5.205	-7.536
6.8	0.263	-4.305	-7.314
7.0	0.264	-3.651	-6.961
7.2	0.269	-2.908	-7.107
7.4	0.273	-2.225	-7.253
7.6	0.278	-1.590	-7.567
7.8	0.286	-0.671	-6.688
8.0	0.3	1.136	-9.186
8.2	0.307	1.983	-10.181
8.4	0.314	1.307	-11.467
8.6	0.329	3.409	-14.070
8.8	0.343	7.332	-17.752
9.0	0.357	24.965	23.676
9.2	0.364	-6.980	30.544
9.4	0.371	-0.586	43.580
9.6	0.386	-1.105	78.038
9.8	0.4	0.000	258.616
10.0	0.419	0.138	-8441.434
10.2	0.429	0.912	-58.530
10.4	0.452	-1.273	-168.875
10.6	0.514	-1.339	-50.928
10.8	0.564	-0.607	-129.079
11.0	.6143	1.075	-34.217
11.2	0.886	-4.863	-104.573
11.4	1.129	-5.439	-610.365

Where,  $K_{a1}$  and  $K_{a2}$  are the dissociation constants. The pL values may thus be obtained corresponding to the same measured pH values at which the  $\bar{n}$  values are calculated. The formation curves are then drawn for the system by plotting the  $\bar{n}$  values as function of pL. Tables 3.39 to 3.58 gives the values of  $\bar{n}$  and pL at different pH values for systems involving single and two ligands. Fig. 3.35 to 3.37 gives the corresponding plots of  $\bar{n}$  v/s pL, which helps one to find the stability constant of the complexes.

### 3.6 STOICHIOMETRIC STABILITY CONSTANT

There are several methods adopted for the determination of stoichiometric stability constant using the values of  $\bar{n}$  and pL, which have been reviewed by Irving and Rossotti [4], Hearon [5] Bjerrum [1] and the least square method of Irving and Rossotti [6] are most commonly employed methods, particularly for systems where  $\bar{n} = 2$ , for such system.

$$\text{Log } K_1 = \text{pL}_{1/2} + \log \left\{ \frac{2}{1 + (1 + 12K_2/K_1)^{1/2}} \right\}$$

$$\text{Log } K_2 = \text{pL}_{3/2} + \log \left\{ \frac{2}{1 + (1 + 12K_2/K_1)^{1/2}} \right\}$$

The spreading factor  $\alpha$  defined by Bjerrum is made in order to relate to successive stability constants  $K_N$  and  $K_{N-1}$ . According to Bjerrum, the spreading factor is given by equation,

$$K_i / K_{i+1} = (i + 1/i) (N-i+1/N-i) \cdot X^2,$$

Fig 3-35 Plot of  $\bar{n}$  v/s pL for  $MnCl_2 + NTA$  system

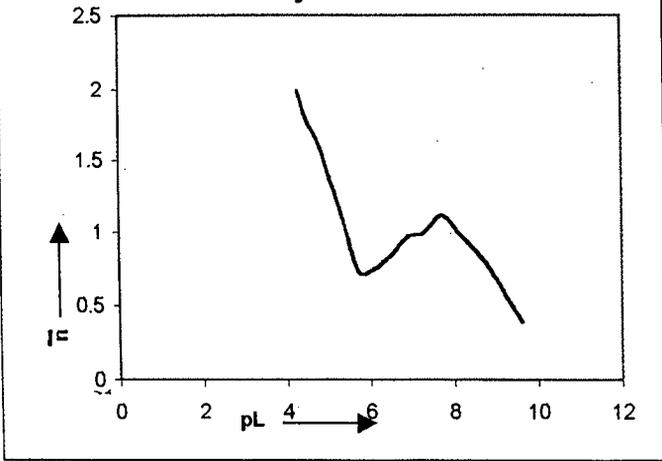


Fig 3-36 Plot of  $\bar{n}$  v/s pL for  $MnCl_2 + N_2H_3COOH$  system

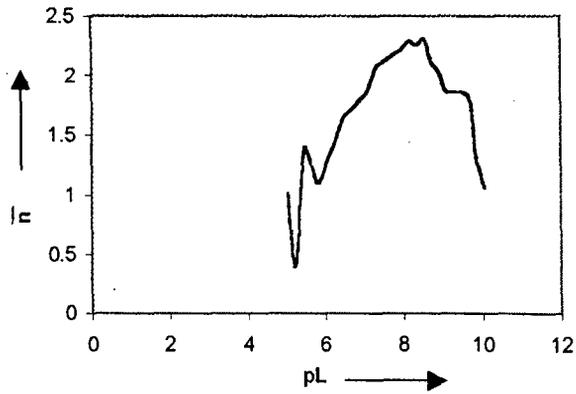


Fig 3-37 Plot of  $\bar{n}$  v/s pL for  $NiCl_2 + NTA (+N_2H_3COOH)$  (ternary) system

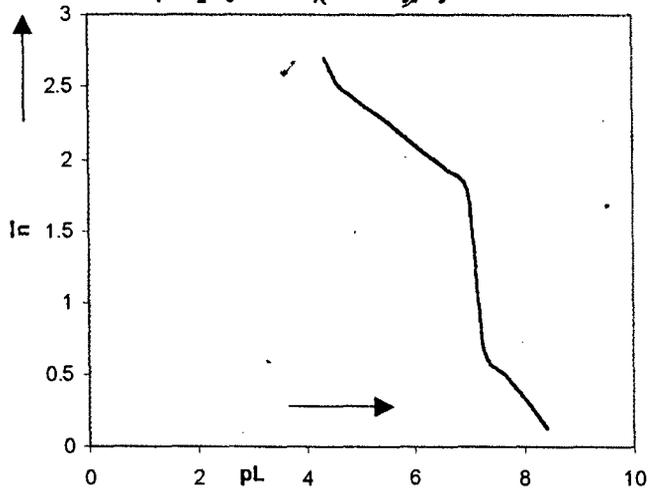


Table 3.39

NiCl<sub>2</sub>+NTA systemT<sup>0</sup>L=0.0003T<sup>0</sup>M=0.00005V<sup>0</sup>=50mLK<sub>a1</sub>=3.926×10<sup>-9</sup>K<sub>a2</sub>=8.39×10<sup>-9</sup>

PH	V <sup>III</sup>	$\bar{n}$	PL	Log 2- $\bar{n}/\bar{n}-1$	$\bar{n}/[L](1-\bar{n})$	2- $\bar{n}[L]/1-\bar{n}$
4	0.2684	0.4578	11.4106	_____	2814.686	3.6885
4.2	0.2758	1.6392	11.7462	-0.2484	-8547.9405	-3.1280
4.4	0.2774	1.6629	11.3486	-0.2938	-8361.3646	-3.0161
4.6	0.2789	1.6882	10.9513	-0.3438	-8176.8008	-2.9053
4.8	0.2795	1.4581	10.5288	0.0728	-10608.8121	-4.3643
5.0	0.2799	1.2115	10.1059	0.0572	-19096.0105	-9.4559
5.2	0.2805	0.9462	9.6827	_____	_____	_____
5.4	0.2810	0.7622	9.2675	_____	10688.3675	8.4120
5.6	0.2815	0.5710	8.8525	_____	4437.3989	4.6620
5.8	0.281	0.3478	8.4359	_____	1778.2003	3.0667
6.0	0.2826	0.1444	8.0218	_____	562.7047	2.3375
9.2	0.2363	18.4171	_____	_____	-3524.7160	-0.1145
9.4	0.3368	8.6712	_____	_____	-3767.859	-0.2604
9.6	0.3421	7.5485	_____	_____	-3842.3557	-0.3051
9.8	0.3579	5.6614	4.7926	_____	-4048.4176	-0.4287
10.0	0.3631	6.5058	_____	_____	-3938.7499	-0.3629
10.2	0.3736	5.9702	5.8346	_____	-4003.9904	-0.4020
10.4	0.3894	6.5698	_____	_____	-3931.7988	-0.3587
10.6	0.4105	5.1707	4.3887	_____	-4132.5463	-0.4792
10.8	0.4315	7.1056	_____	_____	-3879.2782	-0.3272
11.0	0.4736	7.3634	_____	_____	-3857.1598	-0.3139
11.2	0.5263	7.7343	_____	_____	-3828.3103	-0.2966

Table 3.40  
 CoCl<sub>2</sub>+NTA system  
 T<sup>0</sup>L=0.0003  
 Ka<sub>1</sub>=3.926×10<sup>-9</sup>

T<sup>0</sup>M=0.0005  
 Ka<sub>2</sub>=8.39×10<sup>-9</sup>

V<sup>0</sup>=50mL

PH	V <sup>III</sup>	$\bar{n}$	PL	Log 2- $\bar{n}/\bar{n}-1$	$\bar{M}/[L](1-\bar{n})$	2- $\bar{n}[L]/1-\bar{n}$
3.8	0.2708	1.5772	12.540	-0.1351	-9108.5392	-3.4643
4	0.2766	2.6092	11.2554		-5404.7559	-1.2425
4.2	0.2833	3.3073	11.9557	-----	-4778.0108	-0.8664
4.4	0.2875	3.9763	11.6797	-----	-4453.2771	-0.6715
4.6	0.2895	4.1986	11.3304	-----	-4375.4429	-0.6248
4.8	0.2906	4.1821	10.9266	-----	-4380.8464	-0.6281
5.0	0.2916	4.1644	10.4887	-----	-4386.7189	-0.6316
5.2	0.2917	3.9018	10.0646	-----	-4482.0496	-0.6883
5.4	0.2918	3.6631	9.6181	-----	-4584.9859	-0.7506
5.6	0.2919	3.4160	9.1750	-----	-4713.0299	-0.3274
5.8	0.2921	2.9533	8.7044	-----	-5039.847	-1.0234
6.0	0.2922	2.5315	8.2493	-----	-5509.8487	-1.3054
6.2	0.2923	2.1454	7.8057	-----	-6243.5248	-1.7455
6.4	0.2924	1.7905	7.3707	0.5767	-7550.0738	-2.5393
6.6	0.2925	1.5335	6.9504	0.0583	-9581.3808	-3.7479
6.8	0.2926	1.1634	6.5243	0.7093	-23733.1701	-12.2377
7.0	0.2927	0.8911	6.1138	--	27287.0353	18.3697
7.2	0.2928	0.7434	5.7226	---	9658.5727	7.7942
7.4	0.2929	0.6065	5.3444	-----	5238.3514	5.08253
7.6	0.2931	0.4793	4.9857	-----	3068.1825	3.8406
7.8	0.2932	0.3607	4.6549	-----	1880.7028	3.1282
8.0	0.2933	0.2489	4.3623	-----	4.00032	2.6665
8.2	0.2999	1.0286	4.1887	1.5310	-	-
9.4	0.3333	9.610	-	-----	-3720.48	-0.2319
9.8	0.3541	6.1627	-	-----	-3978.9903	-0.3870
10.0	0.3625	6.5878	-	-----	-3929.8710	-0.3575
10.2	0.3749	5.8489	5.1319	-----	-4020.7744	-0.4121
10.4	0.3875	6.7986	-	-----	-3908.1847	-0.3445
10.6	0.3999	5.8363	5.0932	-----	-4022.5654	-0.4132
10.8	0.4166	7.9722	-	-----	-2961.8153	-0.2226
11.0	0.4499	8.4218	-	-----	-3782.4606	-0.2691
11.2	0.4833	9.2465	-	-----	-3737.5452	-0.2422

Table 3.41

ZnCl<sub>2</sub>+NTA systemT<sup>0</sup>L=0.0003K<sub>a1</sub>=3.926×10<sup>-9</sup>T<sup>0</sup>M=0.00005V<sup>0</sup>=50mLK<sub>a2</sub>=8.39×10<sup>-9</sup>

pH	V <sup>III</sup>	$\bar{n}$	PL	Log 2- $\bar{n}/\bar{n}-1$	$\bar{M}/[L](1-\bar{n})$	2- $\bar{n}[L]/1-\bar{n}$
4.8	0.279	1.3424	10.5178	0.28342	-13068.5358	-5.8399
5.0	0.2812	1.5278	10.1356	-0.0483	-9648.8569	-3.7884
5.2	0.2818	1.3069	9.7144	0.3665	-14418.9475	-6.6500
5.4	0.2825	1.4974	9.3332	0.0044	-10034.309	-4.0196
5.6	0.2831	0.9931	8.8877	-----	----	---
5.8	0.2837	0.7761	8.4701	-----	11554.2653	8.9315
6.0	0.2843	0.5783	8.0553	-----	4571.1801	4.7423
6.2	0.285	0.3973	7.6432	-----	2197.3342	3.3182
6.4	0.2857	0.2595	7.2359	-----	1168.1296	2.7007
6.6	0.2865	0.2229	6.8386	-----	-956.1189	2.5735
6.8	0.2872	0.00169	6.4308	-----	5.6663	0.9983
7.2	0.2887	0.1096	5.6731	---	410.3865	2.2462
7.4	0.2825	0.5327	5.3385	-----	3800.759	4.2801
7.6	0.2944	0.6592	5.0001	---	6447.0003	5.8676
7.8	0.2962	0.7769	4.6525	-----	11607.6497	8.9635
8.0	0.3000	1.13626	4.0491	0.802	-27796.3697	-14.6753
8.2	0.3037	1.53	4.0775	-0.0522	-9622.6415	-3.7727
9.2	0.339	9.9316	---	-----	-3706.54	-0.2236
9.4	0.351	4.8808	4.2990	-----	-419.2262	-0.5149
9.6	0.36	3.6689	3.9643	-----	-4582.2873	-0.7489
9.8	0.375	3.3615	3.9004	-----	-4744.8655	-0.8465
10.	0.3975	2.2278	3.9676	-----	-6048.2163	-1.6284
10.2	0.414	2.2545	3.7381	-----	-5990.4344	-1.5937
10.4	0.4365	1.1189	3.6207	0.8698	-31368.8096	-16.8180
10.6	0.45	2.6749	-3.7859	-----	-5323.5019	-1.1936
10.8	0.4875	3.8557	3.9757	---	-4500.5894	-0.6999
11.0	0.5325	4.7351	4.2047	---	-4225.7681	-0.5350
11.2	0.6	5.1419	4.3734	-----	-4138.1169	-0.4825
11.4	0.6937	6.5059	-	-----	-3938.9114	-0.3639

Table 3.42  
MnCl<sub>2</sub>+NTA system  
T<sup>0</sup>L=0.0003  
K<sub>a1</sub>=3.926×10<sup>-9</sup>

T<sup>0</sup>M=0.00005  
K<sub>a2</sub>=8.39×10<sup>-9</sup>

V<sup>0</sup>=50mL

pH	V <sup>10</sup>	$\bar{n}$	pL	Log 2- $\bar{n}/\bar{n}-1$	$\bar{M}/[L](1-\bar{n})$	2- $\bar{n}[L]/1-\bar{n}$
5.2	0.2784	0.3879	9.6372	---	2112.9736	3.2674
5.4	0.2803	0.5661	9.2515	-----	4349.6366	4.6094
5.6	0.2822	0.7515	8.8675	-----	10080.4829	8.04738
5.8	0.2841	0.8829	8.4791	-----	25132.3655	17.0771
6.0	0.2860	1.0027	8.0907	2.5674	---	-----
6.2	0.288	1.1124	7.7026	0.8972	-32978.7738	-17.7843
6.4	0.2889	0.9936	7.2954	-----	-----	---
6.6	0.2899	0.9631	6.8982	-----	-----	-----
6.8	0.2908	0.8356	6.4958	-----	16942.4168	12.1639
7.0	0.2918	0.7418	6.1013	---	9579.5563	7.7468
7.2	0.2928	0.7298	5.7215	-----	9003.2075	7.4011
7.4	0.296	1.0491	5.3816	1.2868	---	---
7.6	0.2992	1.3459	5.0599	0.2767	-12970.0298	-5.7808
7.8	0.3024	1.6224	4.7650	-0.2170	-8688.946	-3.2126
8.0	0.3048	1.7743	4.4962	-0.5353	-7638.2969	-2.5823
8.2	0.3072	1.9914	4.2823	-2.0612	-6695.6159	-2.0167
8.4	0.3096	0.3786	3.9509	-----	2030.8116	3.7859
9.4	0.3384	8.2541	--	-----	-3792.8435	-0.2753
9.6	0.3456	6.7908	--	-----	-3908.9590	-0.3450
9.8	0.3571	5.7656	4.9516	-----	-4032.7905	-0.4193
10.	0.3696	5.7033	4.8430	-----	-4042.0555	-0.4248
10.2	0.3744	5.9042	5.3299	-----	-4013.0228	-0.4074
10.4	0.3888	6.6479	--	-----	-3923.5232	-0.3537
10.6	0.408	5.3305	4.4816	---	-4103.0674	-0.4615
10.8	0.432	7.0811	---	-----	-3881.4797	-0.3285
11.0	0.4656	7.7246	---	-----	-3829.0257	-0.2970
11.2	0.5184	8.0128	---	-----	-3808.6546	-0.2848
11.4	0.5856	9.4745	---	-----	-3726.6702	-0.2356

Table 3.43

MgCl<sub>2</sub>+NTA system T<sup>0</sup>L=0.0003T<sup>0</sup>M=0.00005V<sup>0</sup>=50mLK<sub>a1</sub>=3.926×10<sup>-9</sup>K<sub>a2</sub>=8.39×10<sup>-9</sup>

pH	V <sup>0</sup>	$\bar{n}$	pL	Log 2- $\bar{n}/\bar{n}$ -1	$\bar{n}/[L](1-\bar{n})$	2- $\bar{n}$ [L]/1- $\bar{n}$
5.2	0.2770	0.0420	9.6112	---	146.1377	2.08765
5.4	0.2791	0.2573	9.2275	----	1154.7955	2.6927
5.6	0.2802	0.1968	8.8235	-----	816.7331	2.4899
5.8	0.2812	0.1251	8.4191	-----	476.9307	2.2861
6.0	0.2823	0.0598	7.8896	-----	212.087	2.12723
6.2	0.2833	0.000012	7.6134	----	0.04	2.000
7.6	0.2898	0.01014	4.9503	---	34.1462	2.0205
7.8	0.2907	0.01958	4.6294	----	66.5701	2.0399
8.0	0.2916	0.02841	4.3459	---	97.4691	2.0585
8.2	0.2958	0.4714	4.1426	----	2972.6321	3.7833
9.4	0.3416	7.3795	----	----	-3855.8386	-0.3131
9.6	0.3541	4.9336	4.3039	-----	-4180.7335	-0.5081
9.8	0.3666	4.482	4.1404	-----	-4290.6375	-0.5734
10.0	0.375	5.0307	4.3288	-----	-4160.3236	-0.4958
10.2	0.3833	5.0809	4.3480	-----	-4150.1466	-0.4897
10.4	0.39583	5.8327	5.0835	-----	-4023.0788	-0.4135
10.6	0.4208	4.5190	4.1369	---	-4280.5721	-0.5679
10.8	0.4541	5.7929	4.9905	----	-4072.3947	-0.4169
11.0	0.4833	6.9332	---	----	-3895.2384	-0.3368
11.2	0.5663	8.0128	---	----	-3808.6533	-0.2848
11.4	0.6416	7.9355	---	-----	-3813.9532	-0.2880

Table 3.44

NiCl<sub>2</sub>+N<sub>2</sub>H<sub>3</sub>COOH system T<sup>0</sup>L=0.0003T<sup>0</sup>M=0.00005V<sup>0</sup>=50mLK<sub>a1</sub>=6.31×10<sup>-10</sup>

pH	V <sup>III</sup>	$\bar{n}$	pL	Log 2 $\bar{n}/\bar{n}-1$	$\bar{n}/[L](1-\bar{n})$	2 $\bar{n}[L]/1-\bar{n}$
2.8	0.0737	0.7082	9.9781	-----	8090.01559	6.8532
3	0.0894	0.6007	9.7694	-----	5014.6088	5.0083
3.2	0.0999	0.7251	9.5797	-----	8792.2881	702745
3.4	0.1052	0.3107	9.3468	-----	1502.7009	2.9015
3.6	0.1158	0.6552	9.1741	-----	6335.2283	5.8005
3.8	0.1263	1.0138	9.0043	1.854	-244879.2271	-144.9054
4.0	0.1315	1.2242	8.8231	0.5391	-182011.11	-8.9189
4.2	0.1368	1.3845	8.638	0.2043	-12000.52	-5.2005
4.4	0.1410	1.6044	8.4592	-0.1840	-8848.4447	-3.3080
4.6	0.1474	1.7038	8.2692	-0.3758	-8069.5273	-2.8409
4.8	0.1499	1.7489	8.0738	-0.4745	-7784.3058	-2.6698
5.0	0.1526	1.7954	7.8786	-0.5896	-7524.0969	-2.5138
5.2	0.1552	1.8749	7.6870	-0.8447	-7143.2925	-2.2853
5.4	0.1579	1.9556	7.4955	-1.3328	-6821.5432	-2.0923
5.6	0.1631	2.1986	7.3226	-----	-6114.3556	-1.6681
5.8	0.1684	2.2936	7.1337	-----	-5910.1216	-1.5455
6.0	0.1702	2.2886	6.9332	-----	-5922.8778	-1.5515
6.2	0.1719	2.2838	6.7338	--	-5929.7917	-1.5573
6.4	0.1736	2.279	6.5967	---	-5939.536	-1.5632
6.6	0.1789	2.3754	6.3444	-----	-5756.8707	-1.4536
6.8	0.1842	2.3872	6.1465	-----	-5736.2553	-1.4412
7.0	0.1894	2.3986	5.9489	-----	-5716.669	-1.4295
7.2	0.1947	2.5782	5.7732	-----	-5445.4441	-1.2667
7.4	0.1999	2.7574	5.5986	-----	-5230.0747	-1.1375
7.6	0.2052	2.5369	5.3741	-----	-5502.0747	-1.3008
7.8	0.2105	2.4627	5.1711	-----	-5612.2239	-1.3668
8.0	0.2157	2.3752	4.9701	-----	-5757.2232	-1.4538
8.2	0.2210	2.3307	4.7797	-----	-5838.2806	-1.5024
8.4	0.2245	2.0899	4.5746	-----	-6391.7179	-1.8344
8.6	0.2281	1.7661	4.3736	-0.5152	-7684.3754	-2.6099
8.8	0.2315	1.3078	4.1772	0.3519	--14162.8763	-6.4964
9.0	0.2421	1.1258	4.6566	0.8419	-29830.4186	-15.8955
9.2	0.2473	0.4919	3.8632	-----	3227.055	3.9359
9.8	0.2789	6.2828	---	-----	-3964.3118	-0.3782
10.2	0.2894	9.6099	-----	-----	-3720.4845	-0.2319
10.6	0.3368	1.1946	3.6391	0.6168	-20462.4871	-10.2756
11.0	0.4157	8.3018	---	-----	-3789.8417	-0.2725
11.2	0.4842	9.6661	-----	-----	-3717.9738	-0.2304

Table 3.45

 $\text{CoCl}_2 + \text{N}_2\text{H}_3\text{COOH}$  system  $T^0L = 0.0003$   $T^0M = 0.00005$   $V^0 = 50\text{mL}$   $K_{a1} = 6.31 \times 10^{-10}$ 

pH	$V^{10}$	$\bar{n}$	PL	$\text{Log } 2 - \bar{n} / \bar{n} - 1$	$\bar{n} / [L] (1 - \bar{n})$	$2 - \bar{n} [L] / 1 - \bar{n}$
2.6	0.0499	1.5212	10.2503	-0.03685	-9783.72	-3.8364
2.8	0.0864	1.6019	10.0585	-0.17953	-8871.3518	-3.3220
3	0.1090	1.5666	9.8552	-0.1163	-9216.3783	-3.2899
3.2	0.1227	1.9336	9.6928	-1.1479	-6903.7418	-2.1416
3.4	0.1318	1.8785	9.4871	-0.8591	-7127.6797	-2.2759
3.6	0.1409	2.1190	9.3133		-6312.1835	-1.7867
3.8	0.1454	2.14	9.1157		-6257.3099	-1.7538
4.0	0.1545	2.5648	8.9664		-5463.531	-1.2776
4.2	0.159	2.6306	8.7748		-5377.5706	-1.2260
4.4	0.1613	2.6898	8.5825		-5305.9533	-1.1830
4.6	0.1636	2.6535	8.3779		-5349.2591	-1.2090
4.8	0.1727	3.0943	8.2393		-4924.9550	-0.9545
5.0	0.1749	3.1383	8.0459		-4892.2040	0.9348
5.2	0.1772	3.2053	7.8563		-4844.8435	-0.9064
5.4	0.1795	3.2732	7.6670		-4799.6950	-0.8793
5.6	0.1818	3.342	7.4781		-4756.6182	-0.8535
5.8	0.1827	3.19	7.2541		-4855.4033	-0.9128
6.0	0.1836	3.1249	7.2442		-4902.0346	-0.9407
6.2	0.1845	3.0608	6.8348		-4950.8281	-0.97
6.4	0.1854	2.9978	6.6258		-5001.8353	-1.0006
6.6	0.1863	2.8386	6.4038		-5146.3069	-1.0873
6.8	0.1872	2.5758	6.1698		-5448.6609	-1.2687
7.0	0.18818	2.3201	5.9395		-5858.3945	-1.5145
7.2	0.1890	2.2354	5.7452		-6031.5147	-1.6183
7.4	0.1899	2.1508	5.5241		-6229.8690	-1.3258
7.6	0.1909	1.5548	5.2655	-0.09558	-9341.5044	-3.6041
7.8	0.2045	2.0198	5.1198		-6601.9481	-1.9605
8.0	0.2090	1.8345	4.9079	-0.7026	-7327.7411	-2.3959
8.2	0.2182	2.0694	4.7498		-6450.3459	-1.8696
8.4	0.2227	1.8984	4.5538	-0.9465	-7043.6331	-2.2255
8.6	0.2318	2.2247	4.4234		-6055.0883	-1.6325
8.8	0.2363	2.01484	4.2482		-6617.9233	-1.9994
9.0	0.24545	1.7826	4.0905	-0.5562	-7592.6399	-2.5549
9.2	0.2499	1.1683	3.9201	0.6938	-23129.2355	-11.8814
9.4	0.259	1.6949	3.8817	-0.3574	-8130.1865	-2.8773
10.2	0.2954	6.68			-3920.1877	-0.3517
10.4	0.3090	17.1325			-3539.9555	-0.1236
10.6	0.3363	1.3352	3.652	0.29738	-13277.6452	-5.9654
10.8	0.3636	12.8506			-3614.6130	-0.1684
11.0	0.4090	9.7367			3714.8656	-0.2285
11.2	0.4681	14.2268		-----	-3585.3469	-0.1508

Table 3.46

ZnCl<sub>2</sub>+N<sub>2</sub>H<sub>3</sub>COOH system T<sup>0</sup>L =0.0003T<sup>0</sup>M=0.00005V<sup>0</sup>=50ml.K<sub>a1</sub>=6.31×10<sup>-10</sup>

pH	V <sup>10</sup>	$\bar{n}$	pL	Log 2- $\bar{n}/\bar{n}-1$	$\bar{n}/[L](1-\bar{n})$	2- $\bar{n}[L]/1-\bar{n}$
2.6	0.0476	1.2556	10.8026	0.4642	-16374.5435	-7.8232
2.8	0.0762	0.8849	9.9928	-----	-25626.991	-17.3738
3	0.0999	1.119	9.8133	0.8694	-31344.5378	-16.8039
3.2	0.119	1.7379	9.6724	-0.4495	-7850.6573	-2.7096
3.4	0.1285	1.6868	9.4673	-0.3410	-8186.7598	-2.9113
3.6	0.1333	1.6776	9.2664	-0.3225	-8252.6564	-2.9508
3.8	0.138	1.7069	9.0694	-0.3823	-8048.7575	-2.8225
4.0	0.1428	1.8825	8.8876	-0.8756	-7110.4815	-2.2656
4.2	0.1476	1.9881	8.6989	-1.9192	-6706.8110	-2.0235
4.4	0.1523	2.1836	8.5206	----	-6147.9103	-1.6892
4.6	0.1539	2.0891	8.31	-----	-6393.9644	-1.8358
4.8	0.1555	2.0778	8.1088	-----	-6426.0531	-1.8550
5.0	0.1571	2.0662	7.9075	-----	-6459.7011	-1.8752
5.2	0.1595	2.1325	7.715	-----	-6276.6740	-1.7654
5.4	0.1619	2.1997	7.5226	-----	-6111.8057	-1.6605
5.6	0.1635	2.219	7.3249	-----	-6067.8151	-1.6401
5.8	0.1650	2.084	7.1098	-----	-6408.3640	-1.8444
6.0	0.1666	2.0707	6.9084	-----	-6446.5614	-1.8673
6.2	0.1714	2.2529	6.7292	-----	-5993.8276	-1.5957
6.4	0.1730	2.2382	6.5277	-----	-6025.4132	-1.6147
6.6	0.1746	2.1041	6.3130	-----	-6352.3835	-1.8108
6.8	0.1762	1.8942	6.0907	-0.9223	-7065.2336	-2.2385
7.0	0.1804	1.8808	5.8905	-0.8686	-7117.7717	-2.2700
7.2	0.1904	2.3195	5.741	----	-5859.5427	-1.5152
7.4	0.1952	2.4686	7.5615	-----	-5603.0686	-3613
7.6	0.2	2.1768	5.3311	-----	-6165.8735	-1.6989
7.8	0.2047	2.0358	5.1216	-----	-6551.4578	-1.9303
8.0	0.2047	1.8694	4.9133	-0.8232	-7167.3951	-2.2998
8.2	0.219	2.1482	4.7586	-----	-6236.428	-1.7412
8.4	0.2238	2.0114	4.566	-----	-6629.0949	-1.9768
8.6	0.2333	2.4102	4.4453	-----	-5697.0642	-1.4177
8.8	0.2428	2.9743	4.3678	-----	-5021.6954	-1.0125
9.0	0.2523	3.1409	4.2592	-----	-4890.3109	-0.9337
9.2	0.2619	4.2283	4.3558	-----	-4365.8685	-0.6191
9.4	0.2714	6.2953	--	-----	-3962.8223	-0.3773
10.8	0.3714	7.3432	-----	-----	-3858.8304	-0.3149
11.0	0.4238	6.5868	-----	-----	-3930.2983	-0.3578
11.2	0.4904	7.8833	-----	-----	-3817.5972	-0.2902

Table 3.47

MnCl<sub>2</sub>-N<sub>2</sub>H<sub>3</sub>COOH system T<sup>0</sup>L=0.0003 T<sup>0</sup>M=0.00005 V<sup>0</sup>=50mL K<sub>a1</sub>=6.31×10<sup>-10</sup>

pH	V <sup>m</sup>	$\bar{n}$	pL	Log 2- $\bar{n}/\bar{n}-1$	$\bar{n}/[L](1-\bar{n})$	2- $\bar{n}[L]/1-\bar{n}$
2.8	0.08636	1.0619	10.0584	-0.1795	8871.3518	-3.322
3	0.1045	1.3428	9.8348	0.2826	-13057.1762	-5.8331
3.2	0.12045	1.8127	9.6801	-0.63739	-7434.8878	-2.4602
3.4	0.1272	1.6101	9.4596	-0.1944	-8796.9185	-3.2773
3.6	0.13636	1.8542	9.2846	-0.7678	-7235.620	-3.3407
3.8	0.1409	1.8725	9.0865	-0.8352	-7153.7726	-2.2916
4.0	0.1454	2.0342	8.9333	---	-6556.4365	9333
4.2	0.1499	2.1240	8.7136	-----	-6305.6492	-1.7828
4.4	0.1545	2.3056	8.5347	-----	-5886.4379	-1.5313
4.6	0.1568	2.2554	8.329	-----	-5988.5295	-1.5925
4.8	0.1590	2.2871	8.1327	-----	-5923.1346	-1.5533
5.0	0.1595	2.2135	7.9241	-----	-6081.2087	-1.6475
5.2	0.1601	2.1674	7.7190	-----	-6188.6814	-1.7126
5.4	0.1606	2.1206	7.5137	-----	-5861.2493	-1.7842
5.6	0.1611	2.0732	7.3085	-----	-6439.3092	-1.863
5.8	0.1616	1.8671	7.0863	-0.8149	-7137.6146	-2.3056
6.0	0.1621	1.7883	6.8782	-0.5709	-7561.8419	-1.9993
6.2	0.1626	1.7108	6.6705	-0.3950	-8022.885	-2.8130
6.4	0.1631	1.6346	6.4631	-0.2397	-8585.9859	-3.1508
6.6	0.1636	1.4193	6.2426	0.1414	-11283.0908	-4.7688
6.8	0.1659	1.2599	6.0284	0.4544	-16158.7790	-7.6934
7.0	0.1681	1.1048	5.8154	0.9315	---	--
7.2	0.1727	1.2419	5.6293	0.4960	-17113.1321	-8.2663
7.4	0.1772	1.3787	5.4446	0.2150	-12135.3754	-5.2663
7.6	0.1818	0.3929	5.2086	---	---	---
7.8	0.1909	1.0099	5.0215	2.000	---	---
8.0	0.2	1.1007	4.8392	0.9500	---	---
8.2	0.2136	1.6555	4.7063	-0.27938	-8418.51	-3.0503
8.4	0.21818	1.8984	4.5538	-0.9465	-7043.6331	-2.2255
8.6	0.2272	1.6685	4.3636	-0.3046	-8319.621	-2.991
8.8	0.2363	2.0148	4.2481	---	-6618.0528	-1.9702
9.0	0.2409	0.8913	4.0072	---	-----	---
9.2	0.2499	1.1683	3.9201	0.6938	-23139.2355	-11.8814
9.4	0.22590	1.6949	3.8817	-0.3574	-8130.1865	-2.8773
9.6	0.2727	5.7883	5.1232	---	-4029.4746	-0.4176
10.2	0.3045	2.2266	3.7683	-----	-6050.8723	-1.6300
10.4	0.31818	5.5108	4.4121	-----	-4040.9172	-0.4242
10.6	0.3363	1.3432	0.36528	0.28188	-13045.8431	-5.8263
10.8	0.3636	12.8506	-----	-----	-----	-----
11.0	0.4272	5.8420	5.1128	-----	-4021.7541	-0.4126
11.2	0.4909	5.8920	5.1109	---	-4021.7541	-4127

Table 3.48

MgCl<sub>2</sub>+N<sub>2</sub>H<sub>3</sub>COOH system T<sup>0</sup>L=0.0003 T<sup>0</sup>M=0.00005 V<sup>0</sup>=50mL K<sub>a1</sub>=6.31×10<sup>-10</sup>

PH	V <sup>tit</sup>	n	pL	Log 2- $\bar{n}/\bar{n}-1$	$\bar{n}/[L](1-\bar{n})$	$2-\bar{n}[L]/1-\bar{n}$
2.6	0.0590	2.5354	10.3617	---	-5504.3202	-1.9995
2.8	0.0909	1.9223	10.0914	-1.07445	-6947.4863	-2.1678
3	0.1091	1.5666	9.8552	-0.11638	-9216.3784	-3.5290
3.2	0.1272	2.1753	10.7194	---	-6169.4886	-1.7011
3.4	0.1363	2.1468	9.5163	---	-6239.9721	-1.7434
3.6	0.1454	2.3839	9.344	---	-5741.9852	-1.4446
3.8	0.1499	2.4075	9.1469	---	-5701.5985	-1.4204
4.0	0.1545	2.5648	8.9664	----	-5463.531	-1.2776
4.2	0.1590	2.6306	8.7748	----	-5377.5706	-1.2260
4.4	0.1636	2.8179	8.5997	---	-5166.9508	-1.0997
4.6	0.1681	2.9188	8.4137	----	-5070.5302	-1.0418
4.8	0.1685	2.8459	8.2036	----	-5139.1372	-1.0830
5.0	0.1688	2.771	7.9934	----	-5215.5091	-1.1288
5.2	0.1692	2.7192	7.7865	----	-5272.2196	-1.1628
5.4	0.16958	2.6668	7.5796	----	-5333.1733	-1.1994
5.6	0.1699	2.6136	7.3728	----	-5399.1075	-1.2389
5.8	0.1702	2.41	7.1475	---	-5697.3995	-1.4179
6.0	0.1706	2.3168	6.9365	----	-5864.7225	-1.5183
6.2	0.1709	2.2252	7.0017	---	-6053.9775	-1.6318
6.4	0.1713	2.1352	6.5025	----	-6269.6734	-1.7612
6.6	0.1716	2.19215	6.2931	-1.0696	-6950.6239	-2.1697
6.8	0.172	1.6368	6.0644	-0.2438	-8567.8392	-3.1399
7.0	0.1723	1.3597	5.8386	0.2504	-12600.3150	-5.559
7.2	0.1723	1.2418	5.6294	0.4963	17118.8309	-8.2697
7.4	0.1727	1.3787	5.4446	0.2150	-12135.3754	-5.2801
7.6	0.1772	1.2438	5.2361	0.4916	-17005.7424	8.2019
7.8	0.1863	1.0099	5.0215	2.000	---	-----
8.0	0.1909	0.7338	4.8077	---	9188.58	7.5123
8.2	0.1954	0.8277	4.2724	--	16012.7684	11.6062
8.4	0.2045	0.4746	4.4243	----	3011.0392	3.8063
8.6	0.2090	0.5561	4.2643	---	4175.8654	4.5051
9.8	0.2181	39.7912	---	---	-3419.2634	-0.0512
10.2	0.2636	11.1335	---	---	-3662.2752	-0.1970
10.6	0.2863	4.0056	4.021	---	-4442.3742	-0.665
10.8	0.3272	22.4886	---	---	-3488.4543	0.0927
11.0	0.3499	15.5787	---	---	-3561.9774	-0.1368
11.2	0.4818	10.3468	---	---	-3689.9616	-0.2136

Table 3.49

NiCl<sub>2</sub>+NTA+N<sub>2</sub>H<sub>3</sub>COOH ternary system  $T^0L=0.0003$   $T^0M=0.00005$   $V^0=50\text{mL}$   $K_{a1}=3.926\times 10^{-9}$   
 $K_{a2}=8.39\times 10^{-9}$

PH	$V^{\text{III}}$	$\bar{n}$	pL	Log $2-\bar{n}/\bar{n}-1$	$\bar{n}/[L](1-\bar{n})$	$2-\bar{n}[L]/1-\bar{n}$
5.6	0.2796	0.05468	8.813	---	192.8095	2.1156
5.8	0.2812	0.1252	8.4191	----	477.0614	2.28622
6.0	0.2833	0.3191	8.035	----	1562.1481	2.9371
6.2	0.2854	0.4966	7.6509	---	3288.3062	3.9726
6.4	0.2875	0.6597	7.2673	----	6461.9453	5.8765
6.6	0.2937	1.7921	6.9763	-0.5808	-7541.5562	-2.5242
6.8	0.2968	1.9354	6.5998	-1.1607	-6896.8712	-2.1375
7.0	0.300	2.0407	6.2246	-----	06536.5150	-1.9212
7.2	0.3030	2.1514	5.8580	----	-6228.3596	-1.7364
7.4	0.3041	2.2539	5.5371	---	-5991.7058	-1.5945
7.6	0.3062	2.3493	5.1654	---	-5803.750	-1.4173
7.8	0.3083	2.4393	4.8545	----	-5651.2064	-1.3902
8.0	0.3104	2.521	4.5806	---	-5524.8739	-1.3144
8.2	0.3125	2.7001	4.3668	---	-5294.8739	-1.1759
8.4	0.325	3.3438	4.2918	---	-4702.3711	-0.8209
8.6	0.3312	4.0907	4.2858	----	-4411.8852	-0.6467
8.8	0.3375	5.346	4.6586	----	-4100.9512	-0.4598
9.0	0.35	15.4549	---	----	-3563.9356	-0.1380
9.2	0.3531	0.4824	3.6315	---	-3106.646	3.8637
9.4	0.3562	3.4752	3.8008	---	-4680.0258	-0.8076
9.6	0.3625	3.1269	3.8735	----	-4900.5595	-0.9399
9.8	0.375	3.3615	3.9004	----	-4744.8655	-0.8465
10.0	0.3937	2.6950	3.7963	----	-5299.9016	-1.1794
10.2	0.4187	1.8167	3.6901	-0.6489	-7414.7994	-2.4482

Table 3.50

CoCl<sub>2</sub>+NTA+N<sub>2</sub>H<sub>3</sub>COOH ternary system T<sup>0</sup>L=0.0003 T<sup>0</sup>M=0.00005 V<sup>0</sup>=50mL K<sub>a1</sub>=3.926×10<sup>-9</sup>  
K<sub>a2</sub>=8.39×10<sup>-9</sup>

pH	V <sup>III</sup>	$\bar{n}$	pL	Log 2- $\bar{n}/(1-\bar{n})$	$\bar{n}/[L](1-\bar{n})$	2- $\bar{n}[L]/1-\bar{n}$
4.4	0.2731	0.7044	11.2623	---	7943.1664	6.7651
4.6	0.2747	0.7085	10.8686	----	8101.7724	6.8603
4.8	0.2764	0.7129	10.4627	----	8277.0231	6.9654
5.0	0.2780	0.7175	10.0632	----	8466.0766	7.0788
5.2	0.2790	0.5518	9.6501	----	4103.8226	4.4619
5.4	0.2799	0.4804	9.2447	----	3081.8578	3.8488
5.6	0.2809	0.4063	8.8395	----	2281.1745	2.8887
5.8	0.2841	0.3077	8.4328	---	1481.5359	2.8887
6.0	0.2853	0.2179	8.0273	----	928.6962	2.5571
6.2	0.2865	0.1938	7.6277	---	801.29	2.4807
6.4	0.2878	0.1717	7.2293	----	690.4876	2.4142
6.6	0.2902	0.2414	6.8399	----	1069.0876	2.6363
6.8	0.2926	0.2715	6.4718	----	1242.2786	2.7452
7.0	0.3024	0.4878	6.0783	---	3174.5412	3.9044
7.2	0.3073	0.7118	5.7199	----	8223.4559	6.9388
7.4	0.2975	1.2794	5.4023	0.4114	-15263.6602	-7.1568
7.6	0.3024	1.8069	5.1052	-0.6210	-7464.3698	-2.4779
7.8	0.3073	2.3062	4.8387	----	-5885.2651	-1.5306
8.0	0.3170	2.7575	4.6113	---	-5229.9668	-1.1375
8.2	0.3219	3.3116	4.4559	--	-4775.336	-0.8647
8.4	0.3243	2.8297	4.1998	----	-5155.1256	-1.0926
8.6	0.3243	2.3285	4.1995	---	-5842.4288	-1.5049
8.8	0.3268	1.3908	3.8105	0.1928	-11862.8454	-5.1166
9.2	0.3414	8.2837	---	----	-3790.9762	-0.2742
9.4	0.3512	4.8220	4.2737	---	-4205.4770	-1.996
9.6	0.3658	2.3998	3.7755	---	-5714.6258	-1.4283
9.8	0.3804	2.2636	3.7933	---	-5386.3841	-1.2313
10.0	0.3902	3.1317	3.8578	----	-4897.0305	-0.9377
10.2	0.4	3.5448	3.9213	----	-4643.1939	0.7854
10.4	0.4146	3.6534	3.9385	----	-4589.5831	-0.7533
10.6	0.4346	3.6463	3.9320	----	-4592.9536	-0.7553
10.8	0.4683	4.972	4.2948	----	-4172.5411	-0.5031
11.0	0.4975	6.2628	--	----	-3966.7097	-0.3796
11.2	0.5756	5.9595	5.6992	----	-4005.444	-0.4029
11.4	0.6829	6.8029	---	-----	-3907.7587	-0.3443

Table 3.51

ZnCl<sub>2</sub>+NTA+N<sub>2</sub>H<sub>3</sub>COOH ternary system T<sup>0</sup>L=0.0003 T<sup>0</sup>M=0.00005 V<sup>0</sup>=50mL K<sub>a1</sub>=3.926×10<sup>-9</sup>  
K<sub>a2</sub>=8.39×10<sup>-9</sup>

pH	V <sup>III</sup>	$\bar{n}$	pL	Log 2- $\bar{n}/\bar{n}^2-1$	$\bar{n}/[L](1-\bar{n})$	2- $\bar{n}[L]/1-\bar{n}$
4.0	0.2666	0.00001	12.0075	----	100000	2.00002
4.2	0.2722	0.8504	11.674	----	18948.3066	13.3672
4.4	0.2777	1.7564	11.358	---	-7740.1727	-2.6434
4.6	0.2833	2.7234	11.0705	----	-5267.4945	-1.160
4.8	0.2888	3.7580	10.8354	----	-4541.9386	-0.7247
5.0	0.2999	4.8675	10.7351	----	-4195.9386	-0.5167
5.2	0.2999	3.1423	9.9304	----	-9169.5118	-1.9995
5.4	0.2944	5.8345	10.768	----	-4022.822	-0.4133
5.6	0.2944	5.5999	9.9852	----	-4057.9867	-0.4344
5.8	0.2944	3.5609	8.8009	---	-4634.959	-0.7805
6.0	0.2944	3.0846	8.3248	----	-4932.3611	-0.9589
6.2	0.2944	2.6486	7.8664	---	-5236.4571	-1.2126
6.4	0.2944	2.2477	7.4206	----	-6004.9157	-1.6024
6.6	0.2944	1.9424	6.9921	-1.2138	-6870.4018	-2.1216
6.8	0.2944	1.4895	6.5546	-0.01824	-10143.003	-4.0848
7.0	0.3	2.0407	6.2246	---	-6536.3056	-1.9212
7.2	0.3013	2.045	5.8462	----	-6523.126	-1.9132
7.4	0.3027	2.049	5.4796	----	-6510.9628	-1.9060
7.6	0.3041	2.0528	5.1315	----	-6499.4934	-1.8991
7.8	0.3055	2.057	4.8104	----	-6486.9126	-1.8915
8.0	0.3111	2.6133	4.5923	---	-5399.4917	-1.2392
8.2	0.3138	2.8858	4.392	--	-5100.9297	-1.06
8.4	0.3166	1.7810	4.0756	-0.5522	-7601.3657	-2.5601
8.6	0.3222	1.7679	3.940	-0.5196	-7674.1763	-2.6038
8.8	0.3277	1.7424	3.845	-0.4596	-7740.6609	-2.6932
9.2	0.3444	6.2895	--	----	-3963.5126	-0.3777
9.4	0.3555	3.6611	3.9786	---	-4585.9481	-0.7511
9.6	0.3666	2.2235	3.7548	---	-6057.7577	-1.6341
9.8	0.3777	2.9879	3.8416	---	--5010.1447	-1.0056
10.0	0.3888	3.3005	3.8841	----	-4782.2937	-0.8689
10.2	0.3999	3.5448	3.9213	----	-4643.1939	-0.7854
10.4	0.4055	4.7057	4.1969	----	-4232.8485	-0.5393
10.6	0.4222	4.4311	4.1118	----	--4304.839	-0.5825
10.8	0.4666	5.0664	4.3366	----	-4153.839	-0.4914
11.0	0.5222	5.1667	4.3858	----	-4133.3269	-0.4796
11.2	0.5722	6.077	---	----	-3989.889	-0.3935
11.4	0.6666	7.2492	---	-----	-3866.7349	-0.3196

Table 3.52

MnCl<sub>2</sub>+NTA+N<sub>2</sub>H<sub>3</sub>COOH ternary system T<sup>0</sup>L =0.0003 T<sup>0</sup>M=0.00005 V<sup>0</sup>=50mL Ka<sub>1</sub>=3.296×10<sup>-9</sup>  
Ka<sub>2</sub>=8.39×10<sup>-9</sup>

pH	V <sup>III</sup>	$\bar{n}$	pL	Log 2- $\bar{n}/\bar{n}-1$	$\bar{n}/[L](1-\bar{n})$	2- $\bar{n}[L]/1-\bar{n}$
4.0	0.2708	1.0871	12.0943	1.0204	----	----
4.2	0.2749	1.4646	11.7292	0.0616	-10507.9638	-4.3038
4.4	0.2791	2.0735	11.3918	---	-6438.4412	-1.8624
4.6	0.2833	2.7234	11.0705	----	-5267.4944	-1.16
4.8	0.2849	2.8080	10.682	----	-5176.9911	-1.1057
5.0	0.2874	3.1098	10.3552	----	-4913.2619	-0.9475
5.2	0.2899	3.4341	9.9772	----	-4702.7648	-0.8212
5.4	0.2908	3.3805	9.5685	----	-4733.5994	-0.8397
5.6	0.2916	3.3249	9.1599	----	-4767.0867	-0.8598
5.8	0.2937	3.38	8.7690	---	-4733.8935	-0.8399
6.0	0.2958	3.4303	8.3796	----	-4704.9061	-0.8225
6.2	0.2968	3.228	7.9489	---	-4829.4434	-0.8972
6.4	0.2979	3.042	7.524	----	-4965.7198	-0.9789
6.6	0.2989	2.9193	7.1117	-----	-5070.0776	-1.0415
6.8	0.2999	2.5086	6.6659	-----	-5542.8874	-1.3252
7.0	-.3041	2.7040	6.3042	---	-5289.5148	-1.1732
7.2	0.3083	3.1085	5.9823	----	-4914.236	-0.9481
7.4	0.3104	3.176	5.6255	----	-4865.196	-0.9186
7.6	0.3125	3.2388	5.2867	----	-4822.2262	-0.8929
7.8	0.3166	3.5845	5.0233	----	-4623.0734	-0.7734
8.0	0.3187	3.6289	4.7472	---	-4601.2907	-0.7603
8.2	0.3208	3.8144	4.4138	--	-4517.7184	-0.7102
8.4	0.3291	4.2617	4.4608	-----	-4355.2952	-0.6127
8.6	0.3333	4.6409	4.4334	-----	-4248.8578	-0.5489
8.8	0.3416	6.8904	---	-----	-3899.2258	-0.3392
9.0	0.3499	15.4648	---	----	-3563.9372	-0.1380
9.4	0.3666	0.6864	3.6224	---	7295.9183	6.3769
9.6	0.3749	0.4169	3.5851	---	2383.2390	3.4297
9.8	0.3883	2.2409	3.7467	---	-6019.5557	-1.6119
10.0	0.3858	2.435	3.7634	----	-5656.2137	-1.3932
10.2	0.4083	2.7767	3.8032	----	-5209.4707	-1.1252
10.4	0.4249	2.4519	3.7591	----	-5629.1755	-1.3769
10.6	0.4499	2.6748	3.7858	----	-5323.6207	-1.1937
10.8	0.4916	3.6136	3.9292	----	-4608.7134	-0.7648
11.0	0.5333	4.6728	4.1838	----	-4240.9061	-0.5441
11.2	0.5916	5.4118	4.5373	----	-4088.8828	-0.4529
11.4	0.6999	6.3342	-----	-----	-3958.2317	-0.3746

Table 3.53

MgCl<sub>2</sub>+NTA+N<sub>2</sub>H<sub>3</sub>COOH ternary system T<sup>0</sup>L=0.0003 T<sup>0</sup>M=0.00005V<sup>0</sup> = 50 mL

$$K_{a1}=3.296 \times 10^{-9}$$

$$K_{a2}=8.39 \times 10^{-9}$$

pH	V <sup>III</sup>	$\bar{n}$	pL	Log 2- $\bar{n}/\bar{n}-1$	$\bar{n}/[L](1-\bar{n})$	2- $\bar{n}[L]/1-\bar{n}$
7.0	0.0642					
7.2	0.2690					
7.4	0.2738					
7.6	0.2785					
7.8	0.2857					
8.0	0.3	1.1362	4.4351	0.8022	-27807.1463	-14.6817
8.2	0.3071	1.9833		-1.7699	-6723.2787	-2.0333
8.4	0.3142	1.5575		0.3529	-14180.4968	-6.5070
8.6	0.3285	3.4093	4.1532		-416.861	-0.8296
8.8	0.3428	7.3316			-3859.7932	-0.3155
9.0	0.357	24.9648			-3472.4262	-0.831
10	0.4142	0.1376	3.5476		531.8491	2.3190
10.2	0.4285	0.9116	3.6051			
11.0	0.6142	1.0746	3.615	1.0936		

Table 3.54

NiCl<sub>2</sub>+NTA+N<sub>2</sub>H<sub>3</sub>COOH ternary system T<sup>0</sup>L=0.0003 T<sup>0</sup>M=0.00005V<sup>0</sup>=50mL

$$K_{a1}=6.31 \times 10^{-10}$$

pH	V <sup>III</sup>	n	pL	Log 2- $\bar{n}/\bar{n}-1$	$\bar{n}/[L](1-\bar{n})$	2- $\bar{n}[L]/1-\bar{n}$
7.4	0.3041	-9.0989				
7.6	0.3062	-9.4646				
8.0	0.3104	-10.0283				
8.2	0.3125	-10.6694				
8.4	0.325	-12.5871				
8.6	0.3312	-14.3982				
8.8	0.3375	-16.9604				
9.0	0.35	22.2834				
9.2	0.3531	27.6755				
9.4	0.3562	37.9236				
9.6	0.3625	63.2002				
9.8	0.375	203.908				
10.8	0.55	118.8685				
11.4	1.15	636.4578				

Table 3.55

CoCl<sub>2</sub>+NTA+N<sub>2</sub>H<sub>3</sub>COOH ternary system T<sup>0</sup>L=0.0003 T<sup>0</sup>M=0.00005V<sup>0</sup>=50mL

$$K_{a1}=6.31 \times 10^{-10}$$

pH	V <sup>III</sup>	$\bar{n}$	pL	Log 2- $\bar{n}/\bar{n}-1$	$\bar{n}/[L](1-\bar{n})$	2- $\bar{n}[L]/1-\bar{n}$
7.4	0.2975	-8.6972				
7.6	0.3024	-9.2034				
8.0	0.3122	-10.172				
8.2	0.317	-11.086				
8.4	0.3219	-12.2685				
8.6	0.3243	-13.5584				
8.8	0.3268	-15.3835				
9.0	0.3366	19.6529				
9.2	0.3414	24.6792				
9.4	0.3512	36.0478				
9.6	0.3658	65.344				
9.8	0.3804	215.9173				
11.4	0.6829	67.7627				

Table 3.56

ZnCl<sub>2</sub>+NTA+N<sub>2</sub>H<sub>3</sub>COOH ternary system T<sup>0</sup>L=0.0003 T<sup>0</sup>M=0.00005V<sup>0</sup>=50mL

$$K_{a1}=6.31 \times 10^{-10}$$

pH	V <sup>III</sup>	$\bar{n}$	pL	Log 2- $\bar{n}/\bar{n}-1$	$\bar{n}/[L](1-\bar{n})$	2- $\bar{n}[L]/1-\bar{n}$
7.8	0.3055	-7.884				
8.0	0.3111	-10.0844				
8.2	0.3388	-10.796				
8.4	0.3166	-11.7163				
8.6	0.3222	--13.293				
8.8	0.3277	--15.5237				
9.0	0.3333	19.0152				
9.2	0.3444	25.4454				
9.4	0.3555	37.6647				
9.6	0.3666	65.8638				
9.8	0.3777	209.987				
11.4	0.6666	47.9648				

Table 3.57

MnCl<sub>2</sub>+NTA+N<sub>2</sub>H<sub>3</sub>COOH ternary system T<sup>0</sup>L=0.0003 T<sup>0</sup>M=0.00005 V<sup>0</sup>=50mL  
 K<sub>a1</sub>=6.31×10<sup>-10</sup>

pH	V <sup>III</sup>	$\bar{n}$	pL	Log 2- $\bar{n}/\bar{n}-1$	$\bar{n}/[L](1-\bar{n})$	2- $\bar{n}[L]/1-\bar{n}$
7.8	0.3166	-8.5977				
8.0	0.3187	-10.7019				
8.2	0.3208	-11.429				
8.4	0.3291	-13.0225				
8.6	0.3333	-14.6532				
8.8	0.3416	-17.5761				
9.0	0.3499	22.2834				
9.2	0.3583	29.0156				
9.4	0.3666	41.807				
9.6	0.3749	71.191				
11.4	0.6999	8.855				

Table 3.58

MgCl<sub>2</sub>+NTA+N<sub>2</sub>H<sub>3</sub>COOH ternary system T<sup>0</sup>L=0.0003 T<sup>0</sup>M=0.00005 V<sup>0</sup>=50mL  
 K<sub>a1</sub>=6.31×10<sup>-10</sup>

pH	V <sup>III</sup>	$\bar{n}$	pL	Log 2- $\bar{n}/\bar{n}-1$	$\bar{n}/[L](1-\bar{n})$	2- $\bar{n}[L]/1-\bar{n}$
7.0	0.2642	-6.9614				
7.2	0.269	-7.1072				
7.4	0.2738	-7.2527				
7.6	0.2785	-7.5671				
8.0	0.3	-9.1862				
8.2	0.3071	-10.1808				
8.4	0.3142	-11.4669				
8.6	0.3285	-14.0701				
8.8	0.3428	-17.752				
9.0	0.3571	23.6757				
9.2	0.3642	30.5442				
9.4	0.3714	43.5802				
9.6	0.3857	78.0375				
9.8	0.4	258.6156				

where 'x' is equal to unity in this case, but when  $N > 2$  it was assumed to be constant for the whole system with any value between 0 and 1. The shape of the plot  $\bar{n}$  v/s  $pL$ , depends on the value of 'x'. If  $x \geq 100$ , the curve has a wave like character, indicating that the two steps are distinct. At  $x \leq 2$ , it is difficult to distinguish between the two successive steps, while at  $x = 0$ , the consumption of the ligand occurs in the single step. The value of 'x' can be obtained from the midpoint slope of the curve obtained by plotting  $\bar{n}$  as a function of  $d pL$  from the relation,

$$\text{slope} = - 2.303 \{1/ 1+ x\},$$

where 'x' has high or moderately high values,  $K_2 / K_1$  become very small and hence we get:

$$\text{Log } K_1 = pL_{1/2} * \dots\dots\dots 3.3$$

$$\text{And, log } K_2 = pL_{3/2} \dots\dots\dots 3.4$$

The log K values obtained in this manner are known as "half integral". This are obtained in the present investigation.

The equation 3.3 and 3.4 show that at  $\bar{n} = 1/2$  only M and ML are present in solution in significant quantities and  $ML_2$  makes negligible contribution. For log  $K_1$  to be accurate within  $\pm 0.03$  which is the usual accuracy with the pH meter can read, the  $\log K_1/ K_2$  need only to be 1.78 or 'x' be 3.90 hence half integral values can be used in such cases.

The  $\log k_1$  and  $\log K_2$  values obtained from Figures 3.35 to 3.37 for various complexes of metals where  $\bar{n}$  is plotted v/s pL. Further, more refined values of  $\log k_1$  are obtained by plotting  $\log 2-\bar{n} / \bar{n}-1$  v/s pL for the same complexes of metals wherever possible. These are shown in Figures 3.38 to 3.45

### 3.7 THE LEAST SQUARE METHOD OF IRVING AND ROSSOTTI

For  $\bar{n} = 2$ , 'n' is expressed in terms of [L], the concentration of unbound ligand and step wise formation constants  $K_1, K_2, \dots, K_N$  as,  

$$\bar{n} / (\bar{n}-1) [L] = (2-\bar{n}) [L] K_1 K_2 / (\bar{n}-1) - K_1 \dots \dots \dots 3.5$$
, and, a plot of  $\bar{n} / (\bar{n}-1) [L]$  v/s  $(2-\bar{n}) [L] / (\bar{n}-1)$  is expected to give a straight line with an intercept of  $K_1$  and a slope of  $K_1, K_2$ . However, since  $[L]$  may vary by several power of ten and it is not very convenient to determine the value of  $K_1$  and  $K_2$  from such plots. On the other hand, a number of values of  $\bar{n} / (\bar{n}-1) [L]$  and  $(2-\bar{n}) [L] / (\bar{n}-1)$  may be tabulated for several points on the curve to get the values of  $K_1$  and  $K_2$  using equation 3.5. Irving and Rossotti [6] have shown that the values of ' $\bar{n}$ ' obtained from the experimental values of pL, together with  $K_1$  and  $K_2$  values calculated by the least square method agree with the experimental ' $\bar{n}$ ' values better than those obtained from the  $K_1$  and  $K_2$  values calculated by any other methods.

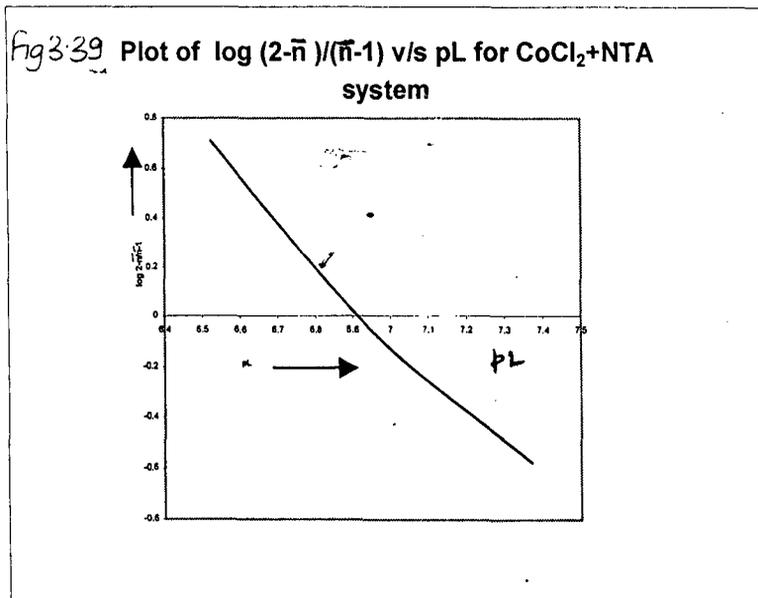
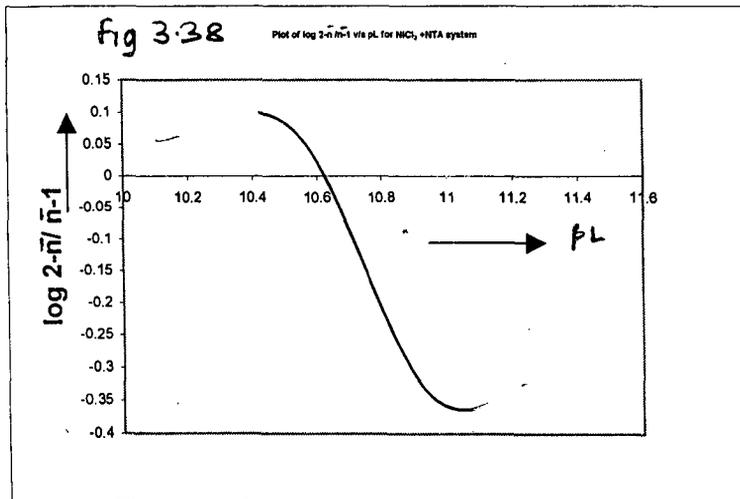


Fig 3.40 Plot of  $\log(2-\bar{n}) / (\bar{n}-1)$  v/s pL for  $\text{ZnCl}_2$  +NTA system

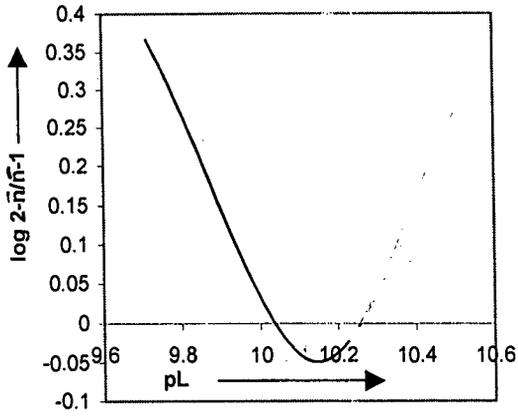


Fig 3.41 Plot of  $\log(2-\bar{n}) / (\bar{n}-1)$  v/s pL for  $\text{MnCl}_2$  +NTA system.

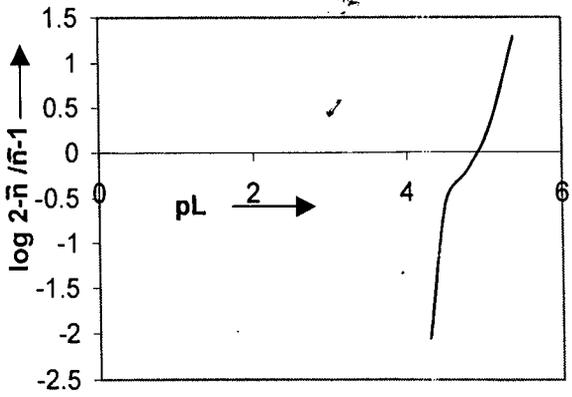


Fig 3.42 plot of  $\log \frac{(2-\bar{n})}{(\bar{n}-1)}$  v/s pL for  $\text{NiCl}_2 + \text{N}_2\text{H}_3\text{COOH}$  system

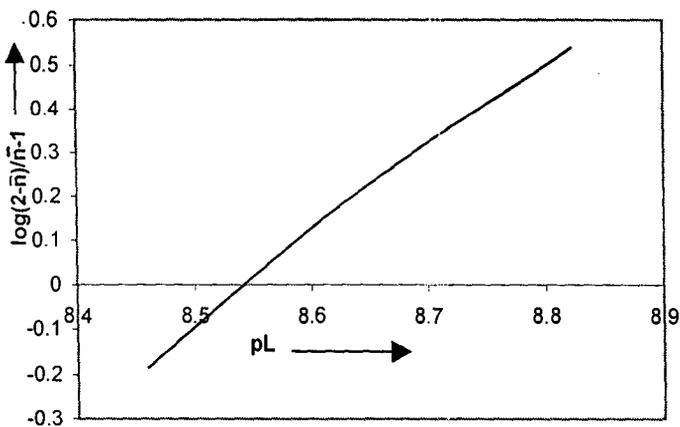


Fig 3.43 Plot of  $\log \frac{(2-\bar{n})}{(\bar{n}-1)}$  v/s pL for  $\text{CoCl}_2 + \text{N}_2\text{H}_3\text{COOH}$  system

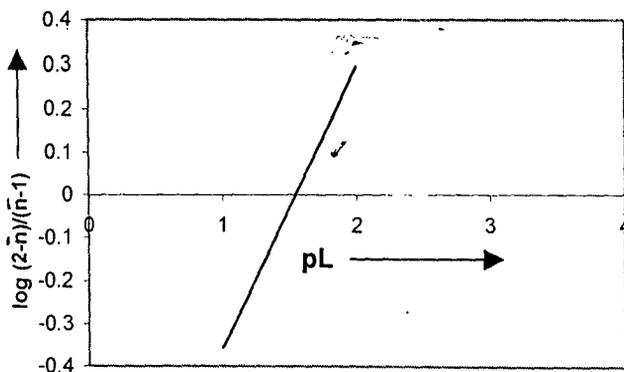


Fig 3-44 Plot of  $\log \frac{(2-\bar{n})}{(\bar{n}-1)}$  v/s pL for  $\text{CoCl}_2 + \text{NTA} + \text{N}_2\text{H}_3\text{COOH}$  ternary system

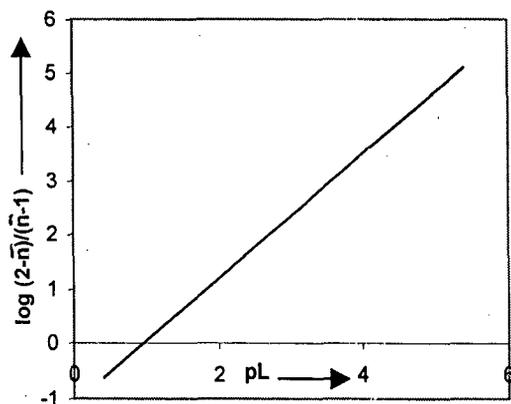
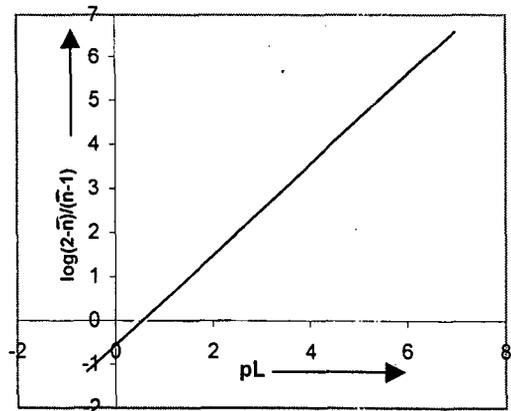


Fig 3-45 Plot of  $\log \frac{(2-n)}{(n-1)}$  v/s pL for  $\text{NiCl}_2 + \text{NTA} + \text{N}_2\text{H}_3\text{COOH}$  ternary system



In the case of this method, the points lying within the range of  $0.90 < \bar{n} < 1.10$  are best rejected in view of the susceptibility of  $(\bar{n}-1)$  to even small errors in  $\bar{n}$ , when  $\bar{n}$  is close to an integer. This method has the advantage of using all the experimental points and can be applied even when the formation curve is incomplete.

Tables 3.39 to 3.58 illustrate these values and Figures from 3.46 to 3.56 gives the plots  $\bar{n} / [L](1-\bar{n})$  v/s  $(2-\bar{n})[L]/(1-\bar{n})$ , which are used to find the values of  $K_1$  and  $K_2$ .

Fig 3-46 Plot of  $(2-\bar{n})L/(1-\bar{n})$  v/s  $\bar{n}/L(1-\bar{n})$  v/s for  $\text{NiCl}_2 + \text{NTA}$  system

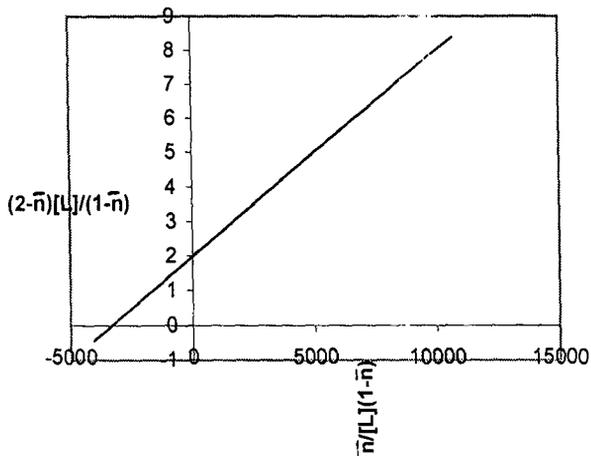


Fig 3-47 plot of  $(2-\bar{n})L/(1-\bar{n})$  v/s  $\bar{n}/L(1-\bar{n})$  for  $\text{CoCl}_2 + \text{NTA}$  system

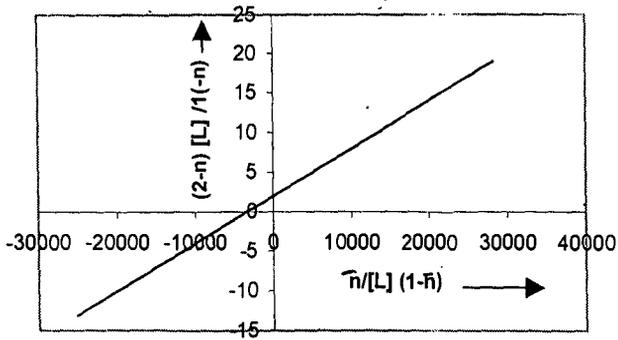


Fig 3-48 Plot of  $(2-\bar{n})[L] / (1-\bar{n})$  v/s  $\bar{n} / [L] (1-\bar{n})$  for  $ZnCl_2 + NTA$  system

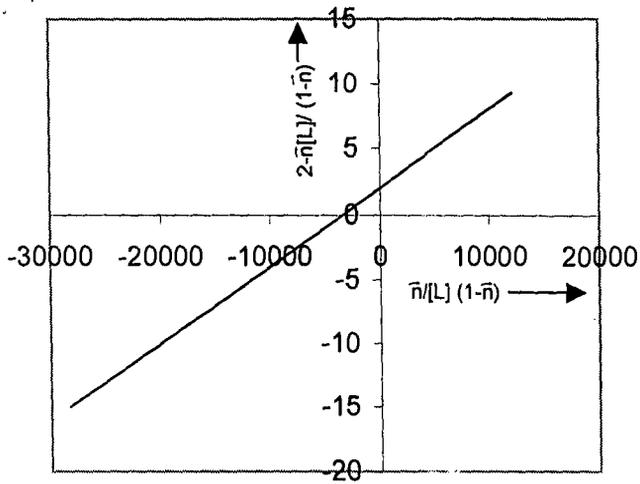


Fig 3-49 Plot of  $(2-\bar{n})[L] / (1-\bar{n})$  v/s  $\bar{n} / [L] (1-\bar{n})$  for  $MnCl_2 + NTA$  system

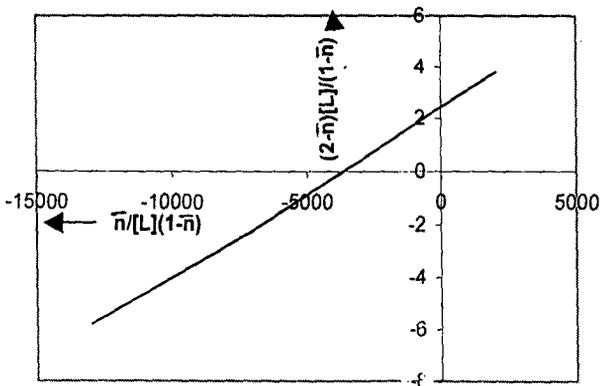


Fig 3.50 Plot of  $(2-\bar{n})[L]/(1-\bar{n})$  v/s  $\bar{n}[L]/(1-\bar{n})$  for  $\text{NiCl}_2 + \text{N}_2\text{H}_3\text{COOH}$  system

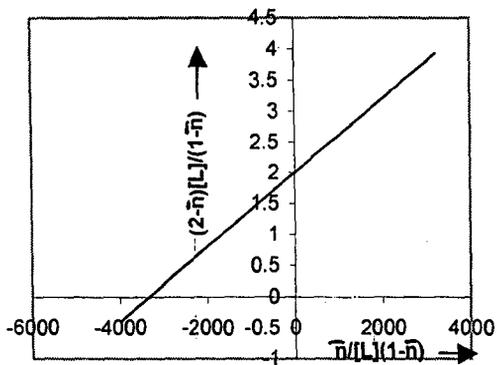
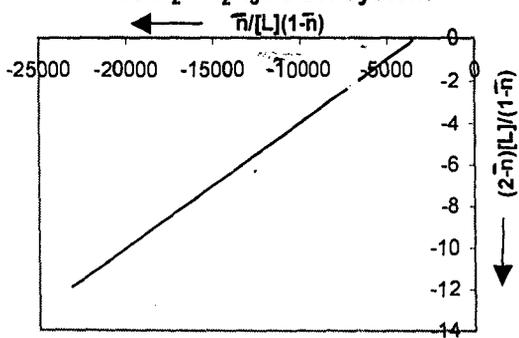


Fig 3.51 Plot of  $(2-n)[L]/(1-n)$  v/s  $n/[L](1-n)$  for  $\text{CoCl}_2 + \text{N}_2\text{H}_3\text{COOH}$  system



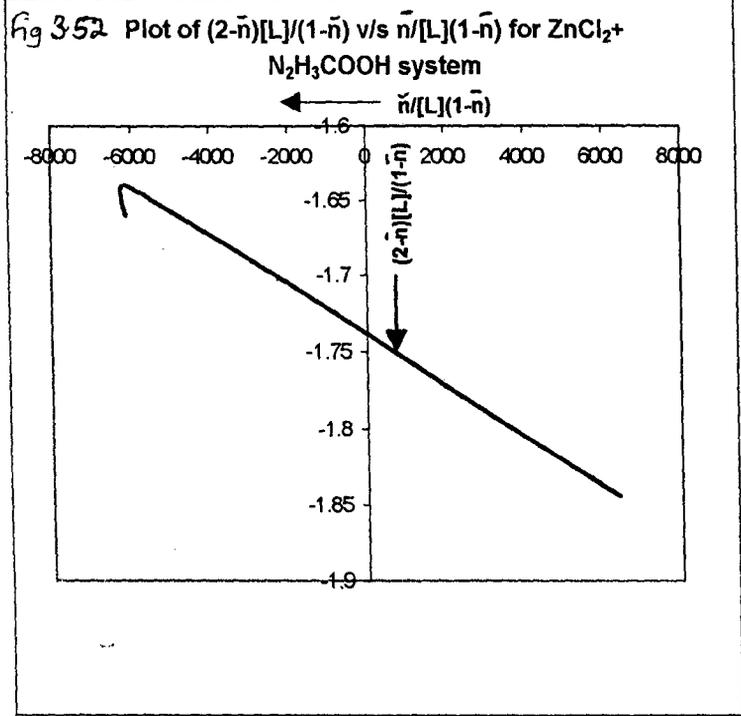


Fig 3.53 Plot of  $(2-\bar{n})[L]/(1-\bar{n})$  v/s  $\bar{n}[L]/(1-\bar{n})$  for  $\text{CoCl}_2 + \text{NTA} + \text{N}_2\text{H}_3\text{COOH}$  ternary system

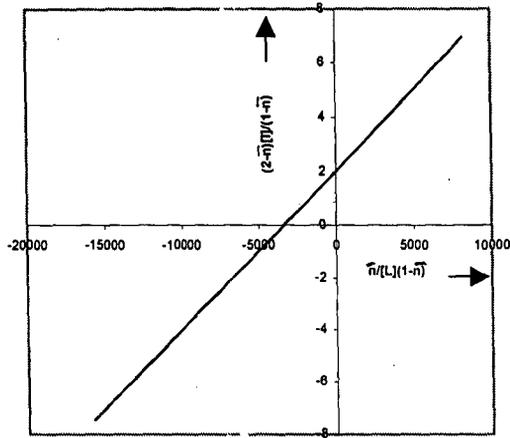


Fig 3.54 Plot of  $(2-\bar{n})[L]/(1-\bar{n})$  v/s  $\bar{n}[L]/(1-\bar{n})$  for  $\text{NiCl}_2 + \text{NTA} + \text{N}_2\text{H}_3\text{COOH}$  ternary system

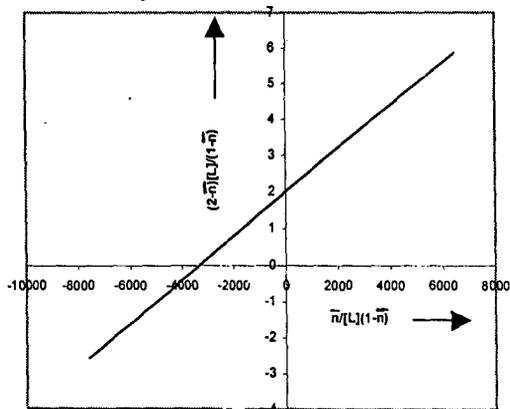


Fig 3.55 Plot of  $(2-\bar{n})[L]/(1-\bar{n})$  v/s  $\bar{n}/[L](1-\bar{n})$  for  $ZnCl_2 + NTA + N_2H_3COOH$  ternary system

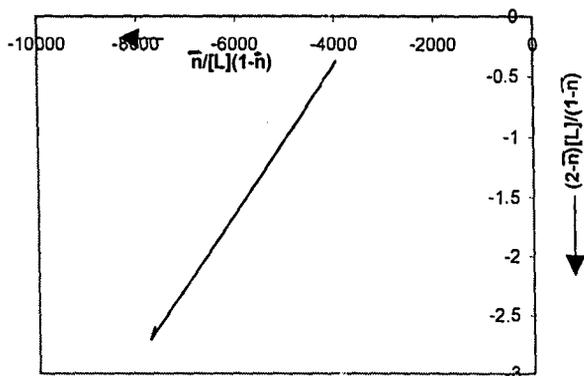
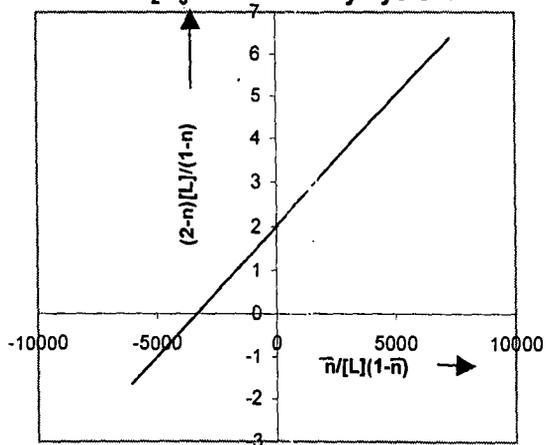


Fig 3.56 Plot of  $(2-\bar{n})[L]/(1-\bar{n})$  v/s  $\bar{n}/[L](1-\bar{n})$  for  $MnCl_2 + NTA + N_2H_3COOH$  ternary system



## REFERENCES

1. Jannik Bjerrum , "Metal Ammine formation in aqueous solution", Published by P. Haase and Son [1957].
2. A. Braibanti, F. Dallavalle, M. A. Pellilghelli and E. Lepori , Journal Inorganic Chemistry , Vol. 7, No. 7[1968]1430.
3. K. C. Patil, R. Soundararajan and E. P. Goldbery, Synthetic React. Inorg. Met-Org-Chem,13(1) [1983]29-43.
4. H. Irving and H. S. Rossotti, J. Chem. Soc. ,2904[1954].
5. J. Z. Hearon and J. B. Gilbert, J. Amer. Chem. Soc. 77,2594 (1955).
6. H. Irving and H. S. Rossotti, J. Chem. Soc. ,3397 (1953).
7. B.N. Sivasanker and S. Govind Rajan , Indian Journal Chemistry , Vol. 33A, [1994]329.
8. S. Ramamoorthy and M. Santappa. Dept. of Physical Chemistry, Univ. of Madras, Madras-25, India Stability Constants in aqueous solution of complexes of Uranyl ion with mixed dibasic acids- II , 1 st July 1970.
9. S. Ramamoorthy, C. Guarnaschelli and D. Fecchio, Inland waters Branch, Dept. of Fisheries and Forestry, Ottawa Ontario, Canada. Equilibrium studies of Cu(II)-Nitrilotriacetic Acid with a solid state cupric ion selective electrode, March, 1971.
10. S. N. Dubey, A. Singh, D.M. Puri. Dept of chemisry, Kurukshetra Univ., Kurukshetra-132 119, India. A study in the complex formation of Iminodiacetic acid and nitrilotriacetic acid with aluminium , chromium and Beryllium ions. 3<sup>rd</sup> July 1980.
11. Pradyotkumar Dutta (Chem lab. D. H. S. K. College Dibrugarh 786001, India ) Madhup Chandra and Arun K. Dey ( Chem lab . Univ. of Allahabad, Allahabad, India). Ternary Complexes of copper (II), Ni (II) and Zn (II) with nitrilotriacetic acid as a primary ligand and some phenolic acids as secondary ligands. Transition metal . Chem . 5, (1980) 1-3

**CHAPTER IV**  
**RESULTS AND DISCUSSION**

# CHAPTER IV

## RESULTS AND DISCUSSION

### INTRODUCTION

Bjerrum method can be conveniently used in the determination of the dissociation constants of the two acid ligands used in the present investigation and further, the same method can be extended in the determination of stability constants of metal complexes. The stability constant values of metal complexes with NTA or  $N_2H_3COOH$  independently or in the ternary system in combination, so obtained can be interpreted in relation to each other. The possible applications of these stability constants can be visualised.

### 4.1 RESULTS AND DISCUSSION

The stability of metal complexes of any ligand depends on the magnitude of the acid dissociation constant of the ligand. In the determination of the stability constants of the metal complexes, it is necessary to have the knowledge of the acid dissociation constants of the ligands [1,2] first. Table 4.1 summarises the step wise dissociation constants of the two acids namely nitrilotriacetic acid (NTA) and hydrazido carboxylic acid ( $N_2H_3COOH$ ), which were used in the present study. The values of the dissociation constants used in the calculation of the stability constants of the metal complexes depends on the solvent employed, which in the present case is water. The determination of dissociation constants of  $N_2H_3COOH$  has not been reported in the literature. The  $K_a$  value for  $N_2H_3COOH$  was found to be  $6.31 \times 10^{-10}$

Table 4.1 : Acid dissociation constants of NTA and  $N_2H_3COOH$  at 273 K to 277 K in aqueous medium.

Reagents	$PKa_1$ (half integral method and average value)	$PKa_2$
1.Nitrilotriacetic acid(NTA)	8.75 8.406	8.0769
Hydrazidocarboxylic acid ( $N_2H_3COOH$ )	9.3529 9.2	-----

The evidence in support of the formation of complexes in this study of the various metal complexes may be summarised on the basis of the following.

1. There is a considerable displacement of the metal ion titration curve relative to the reagent titration curve , as a result of the liberation of protons due to complexing with acidic reagent.
2. There is no precipitation of the metal ion even at pH values much higher then the pH of the hydrolysis of simple metal ion.

These facts are all brought out by the data given in chapter III for the various systems studied as well as by the titration curves. Some typical titration curves are shown in Fig3.21 to 3.29 in the previous chapter.

The  $pK_{a1}$  values are associated with dissociation of the carboxylic proton in the aqueous medium. Due to higher dielectric constant of water, it is easier for the carboxylic proton to ionize in water. The  $pK_{a2}$  values are associated with the dissociation of the second carboxylic proton, as in the nitrilotriacetic acid. This acid has three carboxylic acid groups, out of which two of them are involved in complex formation with bivalent metal and the dissociation of the third carboxylate proton will depend on the pH of the solution.

The reduction of  $pK_{a2}$  value shows the electron withdrawing effect due to the presence of nitrogen. Hydrazidocarboxylic acid being a monobasic acid has only one  $pK_a$  value. From the observed values in Table 4.1, it is evident that hydrazidocarboxylic acid is a weaker acid than nitrilotriacetic acid probably due to the presence of N-N linkage

The complex formation between some metal ions and NTA has been reported [3-6] by many workers. The same has been extended in the present investigation involving  $Ni^{++}$  /  $Co^{++}$  /  $Zn^{++}$  /  $Mn^{++}$  /  $Mg^{++}$ . In this attempt, the complex formation is also studied by replacing NTA by hydrazidocarboxylic acid and also by using both in a ternary system .

Table 4.2 Calculated stability constants of metal complexes from ternary system of NTA and  $N_2H_3COOH$  in aqueous solution at 273K to 277K by least square method.

$MCl_2 +$	NTA	$N_2H_3COOH$	NTA+ $N_2H_3COOH$ (ternary system)
$NiCl_2 +$	Log $K_1 = 3.519$ Log $K_2 = 3.302$ Log $\beta_2 = 6.824$	Log $K_1 = 3.5228$	Log $K_1 = 3.5228$ Log $K_2 = 2218$ Log $\beta_2 = 5.7408$
$CoCl_2 +$	Log $K_1 = 3.556$ Log $K_2 = 3.2218$ Log $\beta_2 = 6.778$	Log $K_1 = 3.5413$	Log $K_1 = 3.5326$ Log $K_2 = 3.2316$ Log $\beta_2 = 6.7642$
$ZnCl_2 +$	Log $K_1 = 3.56$ Log $K_2 = 3.1848$ Log $\beta_2 = 6.7448$	Log $K_1 = 3.9312$	Log $K_1 = 3.6553$ Log $K_2 = 3.1963$ Log $\beta_2 = 6.8296$
$MnCl_2 +$	Log $K_1 = 3.573$ Log $K_2 = 3.1249$ Log $\beta_2 = 6.6171$	Log $K_1 = 3.5144$	Log $K_1 = 3.53$ Log $K_2 = 3.229$ Log $\beta_2 = 6.759$
$MgCl_2 +$	Log $K_1 = 3.5166$ Log $K_2 = 3.1963$ Log $\beta_2 = 6.7129$	Log $K_1 = 3.5341$	Log $K_1 = 3.379$ Log $K_2 = 3.092$ Log $\beta_2 = 6.471$

The values of  $\log K_1$  and  $\log K_2$  in the above tables are derived from the formation curves on the basis of least square method [7], which is considered more accurate. The values obtained by the half integral values are almost identical. In most of the cases the values are sufficiently close to those obtained from the formation curves.

The results in Table 4.2 show that the stability constants of metal ion - NTA complex is different from that of metal ion -NTA ( $+N_2H_3COOH$  system), evident by the stability of metal nitrilotriacetate salt is altered when ternary system is used. The stability

constant of metal ion  $N_2H_3COOH$  complex could easily be determined where as the stability constant of metal ion  $N_2H_3COOH$  (+NTA ) could not be evaluated due to negative or very high values of  $n$  which is irrelevant. It appears therefore, in a ternary system, NTA plays a dominant role in complex formation as compared to  $N_2H_3COOH$ . However as the values of the stability constants for metal ion NTA system are different from those of metal ion - NTA ( $+N_2H_3COOH$  ). It could probably due to weak participation of  $N_2H_3COOH$  in complex formation in ternary system. This means that, most complexes in ternary system are of the type



where  $M = Ni/Co/ Zn/ Mn /Mg$ .

Thus we can conclude that more stability is imparted to complexes in ternary system ( as both the ligand viz. Nitrioltriactic acid and hydrazidocarboxylic acid are involved in complex formation ) as compared to a single ligand viz. Nitrioltriactic acid or hydrazidocarboxylic acid. Further as metal ion complexes with NTA or  $N_2H_3COOH$  or both has appreciable stability, these salts therefore, can be conveniently used in such applications where fairly stable complexation of the salt is required[8-9].

## REFERENCES

1. J. Bjerrum, "Metal Amine Formation in Aqueous Solution", Copenhagen, Publisher P. Haase & sons (1957).
2. S.C. Galagali, "Stability of some bivalent Metal complexes of Amino acid schiff bases. Ph. D Thesis, Karnataka University (1981).
3. S. Ramamoorthy, C. G. Uainasehelli and D. Fecchio, Ind. J. Chem ( March 1971).
4. P. Kumar Datta, M. Chandra, A. K. Dey , Transition Mat. Chem. , 5.1-3 (1980).
5. S. Ramamoorthy and M. Santtapa, Ind. J. Chem., - II (July 1972).
6. S. N. Dubey , A. Singh, D. M. Puri, J. Nucl. Chem . Vol. 43, pp 407-407 (1981).
7. M. Calvin , K. W. Wilson, "Stability Of Chelate Compound", Contribution from the Chemical Laboratories of the University of California.
8. G. G. Gawirilov, " Chemical ( electroless ) Nickel Plating" Portcullis press, Red Hill (1979).
9. W. Ridell, " Electroless Nickel Plating" , A. S. M. International, Ohio (1991),

**CHAPTER V**  
**ELECTROLESS DEPOSITION**  
**OF Ni-Fe ALLOY**

## CHAPTER –V

### ELECTROLESS DEPOSITION OF Ni-Fe ALLOY

#### INTRODUCTION

Electroless deposition, as one of the surface treatment techniques [1], is emerging as a major branch of the plating methods in surface modification. The demand [2] for various electroless deposits has made electroless plating industry flourish into a promising field in metal finishing. Initially, the thrust in the research and the growing demand were for single metal deposition. But subsequently, the method was also found to be useful for alloy deposition. In this technique, it is possible to obtain thin film deposition of alloy, even where high precision and fine quality are of importance. In addition, the coated metals protect the base metal which is susceptible to atmospheric oxidation. Efforts have been made to deposit various types [3,4] of metals or alloys on substrate material having the useful characteristics to meet the requirement of the users, especially in electronic industry.

The stability studies on metal nitrilotriacetate complexes have shown that, these complexes have appreciable stabilities as is seen from their stability constants (Chapter III ). The stability constant values for ternary system consisting of a metal ion and two ligands, namely

nitrilotriacetic acid (NTA) and hydrazidocarboxylic acid ( $L_2$ ) are also promising in this regard.

One of the important components in an electroless plating bath is the complexing agent. As mentioned in Chapter I, it is the partial complexation of the metal ion, so controlled by the stability of the salt in aqueous solution, that regulates the reduction of metal ion during plating. Free metal ions from the aqueous solution of complex salts can be conveniently reduced by using strong reducing agents such as hydrazine and/or sodium hypophosphite. The rate of deposition of metal or metals and the composition of alloy deposited are governed, among other factors, by the stability of the metal ion complexes in the ternary system. In the presence of two different metal ions forming complexes, one can expect the reduction of these metal ions by strong reducing agents and the deposition of alloy. One of the important merits of the electroless plating technique is that metal or the alloy can be deposited on conducting as well as non-conducting material.

Although vast patented literature is available in the field of electroless nickel plating, very few reports are available on nickel-iron alloy plating by this technique. The present investigation is an attempt to work out a suitable bath composition for the deposition of Ni-Fe alloy by electroless plating technique.

Iron in ferrous state is highly susceptible to atmospheric oxidation. As a result, the formulation of plating bath for electroless deposition of Fe containing alloy is a challenging task. For the electroless deposition of Ni-Fe alloy, one needs a suitable bath solution wherein proper control of temperature and pH is very essential for retaining Fe(II) in solution. All the important constituents in the electroless bath including the metal ions, the complexing agent and the reducing agent require continuous monitoring with respect to their concentration. In the present investigation,  $\text{Fe}^{+2}$  and  $\text{Ni}^{+2}$  are used as metal ions along with nitrilotriacetic acid (NTA) [5] and hydrazidocarboxylic acid in combination as complexants. The reducing agents used were hydrazine and sodium hypophosphite, singly or in combination. Not much work [7] has been reported with NTA as complexing agent in an electroless bath for such a system and there are no reports on the use of hydrazidocarboxylic acid as complexing agent.

As such, in a study of this nature, it is necessary to establish the role and significance of NTA and hydrazidocarboxylic acid in Ni-Fe alloy deposition on conducting and non conducting substrate material. The knowledge of stability constants of complexes, as reported in previous chapter, were used to explain the process of electroless deposition of the alloy.

## 5.1 SETTING UP ELECTROLESS BATH FOR DEPOSITION

Generally, deposition of a metal or an alloy, whether in electrolytic or in electroless plating, is influenced by various important factors [3] such as:

1. pre-plate treatment of the surface,
2. bath composition,
3. bath temperature,
4. pH of the medium (bath),
5. mobility of the ions in the bath solution,
6. relationship between exposed surface area and volume of bath solution,
7. concentration of component metal ions,
8. complexing agents.

In addition to the above factors, in electroless plating the concentration of reducing agent influences both the nature and the rate of deposition. For obtaining desired good quality coating, it is essential to standardise the bath for an optimum operating parameters keeping in view the factors mentioned above.

### 5.1.1 BATH COMPOSITION

The various compositions of the electroless bath tried during this study are given in Table 5.1. In these baths, the reducing agent used for the deposition of Ni-Fe alloy was either hydrazine hydrate in combination with sodium hypophosphite or sodium hypophosphite singly. The complexing agent used for these baths was either nitrilotriacetic acid or a mixture of nitrilotriacetic acid and hydrazidocarboxylic acid in ternary system. Since all the experiments were carried out in the alkaline medium, liquor ammonia was used to adjust the pH of the bath solution. The methods of preparation for these bath solutions have already been discussed in Chapter II. The pH of the solution was continuously monitored, and the rate of deposition as well as the thickness of the plated layer was calculated by using the weight gain method described in Chapter II. Ascorbic acid was the stabilizer used in these experiments.

As can be seen in the Table 5.1, the  $\text{Fe}^{+2}$  and  $\text{Ni}^{+2}$  ion concentration was kept constant in all the baths whereas the concentration of NTA, hydrazine hydrate and sodium hypophosphite was varied in different baths.

**Table 5.1:** Composition of various bath solutions used in electroless plating.

Component	Bath A g L <sup>-1</sup>	Bath B g L <sup>-1</sup>	Bath C g L <sup>-1</sup>	Bath D g L <sup>-1</sup>
FeSO <sub>4</sub> .7H <sub>2</sub> O	27.801	27.801	27.801	27.801
NiSO <sub>4</sub> xH <sub>2</sub> O	28.077	28.077	28.077	28.077
NTA	38.2	19.1	19.1	38.2
N <sub>2</sub> H <sub>4</sub> . H <sub>2</sub> O	20.007	10.003	5.001	5.001
Na H <sub>2</sub> PO <sub>2</sub> .H <sub>2</sub> O	21.198	21.198	10.598	21.198
Ascorbic acid	4.032	4.032	4.032	4.032

## 5.1.2 EXPERIMENTAL

Conducting (Cu) and non conducting (polythene) substrate materials in the form of plates were initially pre-treated as explained in Chapter II and then were separately immersed in the bath solution maintained at a temperature 343K and pH = 7.5. Liquor NH<sub>3</sub> was used to adjust the pH of the bath solution. Deposition was continuously monitored and the pH maintained at the required value by adding NH<sub>3</sub> periodically. These experiments were repeated at temperature 348 K, 353K, and 358K. Two similar sets of experiments were carried out with the bath pH maintained at 8 and 8.5.

Necessary precaution was taken to replenish N<sub>2</sub>H<sub>4</sub>.H<sub>2</sub>O, which is lost from bath partly due to chemical reaction and partly by vaporization at these temperatures. Rate of deposition and thickness of plating were calculated by using the formula given below.

$$\text{Rate of deposition} = [W / A \cdot \rho \cdot t] 10^4 \mu\text{m} / \text{h}$$

Where W= weight of the deposit in 'g'

A= area of the surface deposit in cm<sup>2</sup>

$\rho$  = density of metal (s) deposited in g / cm<sup>3</sup>

t = time of deposit in hours.

$$\text{Thickness of plating} = (\text{Rate of deposition} \times \text{time in hours}) \mu\text{m}$$

## 5.2 RESULTS AND DISCUSSION

Experiments were carried out as explained in the previous sections in this chapter. During the plating, continuous monitoring of the process is necessary, especially with respect to the nature of finished product, the stability of the bath etc.

### 5.2.1 STANDADIZATION OF BATH<sup>R</sup>

#### 5.2.1.1 BATH A

Experiments were carried out by using Bath A at temperatures 343, 348K, 353K, 358K and pH maintained at 7.5 by addition of  $\text{NH}_3$ . Similar experiments were carried out with pH of bath maintained at 8.0, and 8.5. In all these experiments, no deposition was observed, on the conducting as well as the non-conducting plates. Moreover, it was also observed that, there was a decrease in weight in the case of the copper plates. In addition, the bath was found to be unstable with turbidity appearing within a short duration. Thus Bath A was found to be unsuitable for plating.

### **5.2.1.2 BATH B**

Experiments were carried out by using Bath B at temperatures 353K , 358K and at pH 7.5, 8.0, and 8.5 separately. In this study, the deposition was found to occur at all the above mentioned temperatures and pH. The most desirable result in the form of thin film of silvery-gray deposit was obtained at temperature 353K and pH of the bath solution maintained at 8.0. Experiments were repeated with Bath B at temperature 353K and pH = 8.0. The results are presented in Tables 5.2 to 5.5. A rusty brown deposit was observed on the substrate during the experiments carried out with the bath pH of 8.5, although the bath solution was stable.

### **5.2.1.3 BATH C**

Experiments were carried out at temperatures 353K and 358 K and pH of 7.5, 8.0, and 8.5. It was seen that the bath operating at temperature 358K and pH 7.5 or 8.0 does not give appreciable results.

The following tables show the result at 353K, 358K and pH 8.5, 8.0, 7.5.

The results are presented in table 5.6 to 5.9.

**Table 5.2:** Rate, thickness and the quality of deposition by electroless plating from Bath B at temperature 353 K and pH =7.5

Density of Ni-Fe alloy = 8.86g/ cm<sup>3</sup>

Substrate Code	Area of coated film cm <sup>2</sup>	Weight gain g	Deposition time in hrs	Rate of Deposition $\mu\text{m} / \text{h}$	Thickness of deposition $\mu\text{m}$	Nature of coating
C-4	6.9	0.0088	1.0	1.439	1.439	Rusty Deposit
C-5	6.6	0.0104	1.5	1.185	1.7775	Do
C-6	6.6	0.0107	2.0	0.9149	1.8298	Do
C-7	7.2	0.0083	2.5	0.520	1.3	Rusty burnt deposit

**Table 5.3:** Rate, thickness and the quality of deposition by electroless plating  
from Bath B at temperature 353 K and pH= 8

Density of Ni-Fe alloy = 8.86 g/ cm<sup>3</sup>

Substrate Code	Area of coated film cm <sup>2</sup>	Weight gain g	Deposition time in hrs	Rate of Deposition $\mu\text{m/h}$ .	Thickness of Deposition $\mu\text{m}$ .	Nature of coating
C-1	7.1	0.0084	1.5	0.8902	1.3353	Silvery deposit
C-2	10.5	0.0298	3	1.0677	3.2032	Do
NC-1 (Th)	9.6	0.0137	1.5	5	1.6107	Do
NC-2 (Tk)	17	0.0126	2.0	1.0738	0.83654	Do
NC-3 (Tk)	14.92	0.0175	2.5	0.5295	1.3238	Do
C-3	10.5	0.0162	1.0	1.741	1.741	Do
NC-4 (Th)	9.6	0.0293	1.5	2.2965	3.4447	Do
NC-5 (Th)	9.6	0.0419	2.5	1.9704	4.926	Do

Key: C= conducting material, Th= Thin, Tk= Thick, NC = Non-conducting material

**Table 5.4:** Rate, thickness and the quality of deposition by electroless plating from Bath B at temperature 353 K and pH =8.5

Density of Ni-Fe alloy = 8.86g/cm<sup>3</sup>

Substrate Code	Area of coated film cm <sup>2</sup>	Weight gain g	Deposition time in hrs	Rate of Deposition μm/h.	Thickness of deposition μm.	Nature of coating
C-8	5.4	0.0007	1.0	0.1463	0.1463	Rusty brown Deposit
C-9	5.7	0.0018	1.5	0.2376	0.3564	Do
C-10	6.3	0.0065	2.0	0.5822	1.1644	Do
C-11	6.9	0.0032	2.5	0.2093	0.5232	Rusty burnt deposit

**Table 5.5:** Rate, thickness and the quality of deposition by electroless plating from Bath B at temperature 358 K and pH= 8

Density of Ni-Fe alloy = 8.86g/ cm<sup>3</sup>

Substrate Code	Area of coated film cm <sup>2</sup>	Weight gain g	Deposition time in hrs	Rate of Deposition μm/h.	Thickness of deposition μm	Nature of coating
C-12	8.1	0.0011	1.0	0.1537	0.1537	Rusty brown Deposit
C-13	7.5	0.0004	1.5	0.04013	0.06019	Do
C-14	6.3	0.0002	2.0	0.01791	0.03582	Do
C-15	8.1	0.0005	2.5	0.02786	0.06965	Rusty burnt deposit

**Table 5.6:** Rate, thickness and the quality of deposition by electroless plating from Bath C at temperature 353 K and pH= 7

Density of Ni-Fe alloy = 8.86g/ cm<sup>3</sup>

Substrate Code	Area of coated film cm <sup>2</sup>	Weight gain g	Deposition time in hrs	Rate of Deposition μm/hr	Thickness of Deposition μm	Nature of coating
C-29	10.2	0.008	2.0	0.4426	0.8852	Dark brown
C-30	10.2	0.0193	2.5	0.8542	2.1355	Do
C-31	9.0	0.0034	3.0	0.1421	0.4263	Do
C-32	7.8	0.0054	3.5	0.2232	0.7812	Do

**Table 5.7:** Rate, thickness and the quality of deposition by electroless plating from Bath C at temperature 353 K and pH= 7.5

Density of Ni-Fe alloy = 8.86g/ cm<sup>3</sup>

Substrate Code	Area of coated film cm <sup>2</sup>	Weight gain g	Deposition time in hrs	Rate of Deposition μm/hr	Thickness of Deposition μm	Nature of coating
C-21	8.7	0.0053	2.0	0.3437	0.6875	Rusty Deposit
C-22	9.0	0.0016	2.5	0.08026	0.2006	Do
C-23	5.1	0.0020	3.0	0.1475	0.4425	Do
C-24	13.2	0.0047	3.5	0.1148	0.4018	Do

**Table 5.8:** Rate, thickness and the quality of deposition by electroless plating  
from Bath C at temperature 353 K and pH= 8

Density of Ni-Fe alloy = 8.86g/ cm<sup>3</sup>

Substrate Code	Area of coated film cm <sup>2</sup>	Weight gain g	Deposition time in hrs	Rate of Deposition $\mu\text{m/hr}$ .	Thickness of Deposition $\mu\text{m}$ .	Nature of coating
C-16	9.0	0.0059	1.5	0.4932	0.7398	Silvery grey Deposit
C-17	9.6	0.0149	2.0	0.8758	1.7516	- do -
C-18	9.3	0.0067	2.5	0.3252	0.813	Light grey film
C-19	7.5	0.0073	3.0	0.3662	1.0986	Deposit on beaker
C-20	8.4	0.0195	3.5	0.7486	2.6201	-do-

**Table 5.9:** Rate, thickness and the quality of deposition by electroless plating  
from Bath C at temperature 358K and pH= 8

Density of Ni-Fe alloy = 8.86g/ cm<sup>3</sup>

Substrate Code	Area of coated film cm <sup>2</sup>	Weight gain g	Deposition time in hrs	Rate of Deposition $\mu\text{m} / \text{hr}$	Thickness of Deposition $\mu\text{m}$	Nature of coating
C-25	8.4	0.0116	2.0	0.7793	1.5586	Rusty brown
C-26	8.7	0.0102	2.5	0.5293	1.32325	-do-
C-27	9.6	0.0085	3.0	0.3331	0.9993	-do-
C-29	10.5	0.0087	3.5	0.2671	0.9348	Do

#### **5.2.1.4 BATH D**

Experiments carried out with Bath D solution indicated that this bath was not suitable (Table 5.10) for plating, irrespective of pH or temperature control.

#### **5.2.1.5 MODIFIED BATH B**

The plating carried out with Bath B gave the desired deposit at the temperature 353K and pH 8. It was thought worthwhile to try some modifications in this bath. This was done by using ( i ) two ligands viz. NTA and hydrazidocarboxylic acid and sodium hypophosphite as reducing agent, (ii) by using two ligands and two reducing agents namely sodium hypophosphite and hydrazine (hydrate) and (iii) by using one ligand (NTA) and two reducing agents namely sodium hypophosphite and hydrazine (hydrate). In addition, to above modification saccharin was added as brightner. The composition of the modified Bath B is given in Table 5.11 and the results are presented in Tables 5.12 to 5.14.

#### **5.2.2 TESTING THE QUALITY OF DEPOSIT**

The quality of deposit was tested with respect to the adhesion and porosity. The adhesion was tested [1] by (a) the peel off test, (b) the bending test and (c) the quenching test. These tests are described in Chapter II.

**Table 5.10:** Rate, thickness and the quality of deposition by electroless plating from Bath D at temperatures 353 K and pH=8

Density of Ni-Fe alloy = 8.86g/ cm<sup>3</sup>

Substrate Code	Area of coated film cm <sup>2</sup>	Weight gain g	Deposition time in hrs	Rate of Deposition μm/h	Thickness of Deposition μm.	Nature of coating
C-33	11.4	0.0018	1.0	0.1782	0.1782	Dark brown
C-34	9.6	0.0013	1.5	0.10189	0.1528	-do-

**Table 5.11:** Modified Bath B formulation used in electroless plating .

Component	Bath B g L <sup>-1</sup>	Bath B <sub>1</sub> g L <sup>-1</sup>	Bath B <sub>2</sub> g L <sup>-1</sup>	Bath B <sub>3</sub> g L <sup>-1</sup>
FeSO <sub>4</sub> .7H <sub>2</sub> O	27.801	27.801	27.801	27.801
NiSO <sub>4</sub> .XH <sub>2</sub> O	28.077	28.077	28.077	28.007
NTA	19.1	19.1	19.1	19.1
N <sub>2</sub> H <sub>3</sub> COOH	-	15.2	15.2	-
N <sub>2</sub> H <sub>4</sub> .H <sub>2</sub> O	10.003	-	10.003	10.003
NaH <sub>2</sub> PO <sub>2</sub> .H <sub>2</sub> O	21.198	21.198	21.198	21.198
EDTA	4.032	4.032	4.032	4.032
Ascorbic acid	-	-	-	0.3892
Saccharin	-	-	-	-

**Table 5.12:** Rate, thickness and the quality of deposition by electroless plating from bath B<sub>1</sub> at temperatures 353 K and pH= 8

Density of Ni-Fe alloy = 8.86g/ cm<sup>3</sup>

Substrate Code	Area of coated film cm <sup>2</sup>	Weight gain g	Deposition time in hrs	Rate of deposition μm / h	Thickness of deposition μm	Nature of coating
C-35	-	0.0004	1.0	-	-	Deposit on plate in parts .
C-36	-	0.0033	2.0	-	-	Brownish black
C-37	10.5	0.0175	2.5	0.6840	1.881	Silvery
NC-6 (Th)	4.8	0.060	2.5	0.9406	1.4109	-do-
NC-7 (Th)	6.6	0.011	1.5	0.7524	1.881	-do-
NC-8 (Tk)	13.36	0.0432	2.5	1.3271	3.6495	-do-

**Table 5.13:** Rate, thickness and the quality of deposition by electroless plating from Bath B<sub>2</sub> at temperature 353 K and pH= 8

Density of Ni-Fe alloy = 8.86g/ cm<sup>3</sup>

Substrate Code	Area of coated film cm <sup>2</sup>	Weight gain g	Deposition time in hrs	Rate of deposition μm/h	Thickness of deposition μm	Nature of coating
C-38	-	-	1.0	-	-	No deposit
C-39	8.4	0.0007	2.5	0.03762	0.09405	Silvery deposit
NC-9 (Th)	6.0	0.0065	1.5	0.81514	1.2271	-do-
NC-10 (Th)	5.1	0.0077	2.0	0.8520	1.704	do
NC-11 (Tk)	10.46	0.0397	3.0	1.4279	4.2837	do

**Table 5.14:** Rate, thickness and the quality of deposition by electroless plating from Bath B<sub>3</sub> at temperature 353 K and pH= 8

Density of Ni-Fe alloy = 8.86g/ cm<sup>3</sup>

Substrate Code	Area of coated film cm <sup>2</sup>	Weight gain g	Deposition time in hrs	Rate of deposition μm / hr	Thickness of deposition μm	Nature of coating
C-40	-	0.0083	1.0	-	-	Silvery deposit in parts
C-41	6.9	0.0108	3.0	0.5887	1.7666	Silvery shining deposit
NC-12 (Th)	7.5	0.0063	1.5	0.6320	0.948	-do-
NC-13 (Th)	6.6	0.0074	2.5	0.50619	1.021238	-do-

There was no peeling off of the deposit, thereby showing good adhesion. The porosity was tested by (i) ferroxyl test [3] and (ii) the hot water test described elsewhere [6]. The tests, described in Chapter II, were carried out by using copper / plastic substrate with the deposit. The tests were negative confirming the non-porous nature of the deposit. The plated materials were further subjected to high resolution photography which revealed fairly uniform deposit on the substrate (Fig 5.1 to 5.8). Where the substrate material had crevices, partial oxidation of the metals was observed.

### **5.2.3 EFFECT OF pH ON THE STABILITY OF THE BATH**

Presence of the OH ions is essential [3] in the reduction of metal ions in hydrazine based electroless plating bath. Hence, the pH of bath solution plays an important role in stability as well as the nature of coating. Studies carried out at various pH values, regulated by the addition of ammonia, are indicated in Tables 5.2 to 5.10.

At lower value of pH equal to 7, hypophosphite ions appear to be the more effective reducing species than hydrazine. As a result of this, the metal ions in the bath solutions are precipitated out as metal phosphites, due to the side reaction occurring during the reduction process. At pH equal to 8.5 and above, due to the presence of excessive OH ions in solutions, the metal ions are precipitated as hydroxides rendering the bath unstable.

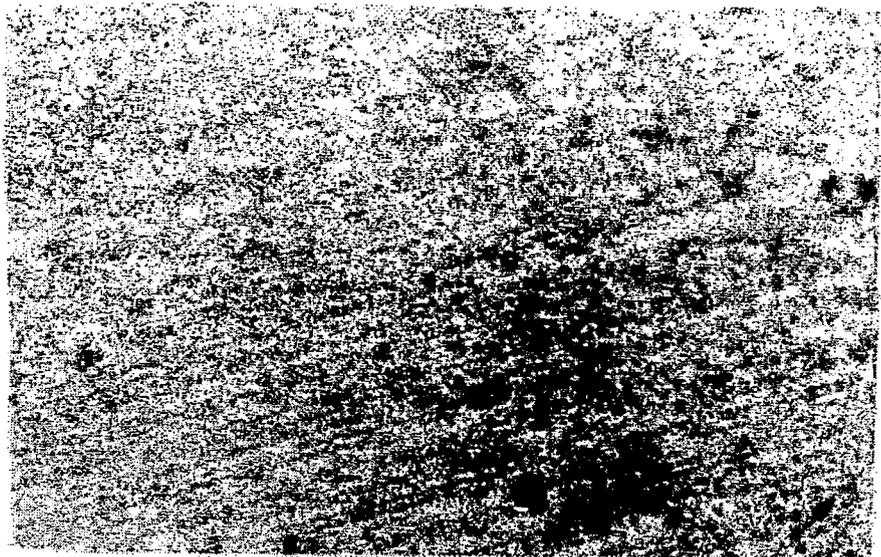


Fig 5.1 Surface morphology of coated plate number NC-7 (X 250 magnification) of Ni – Fe alloy on plastic plate.

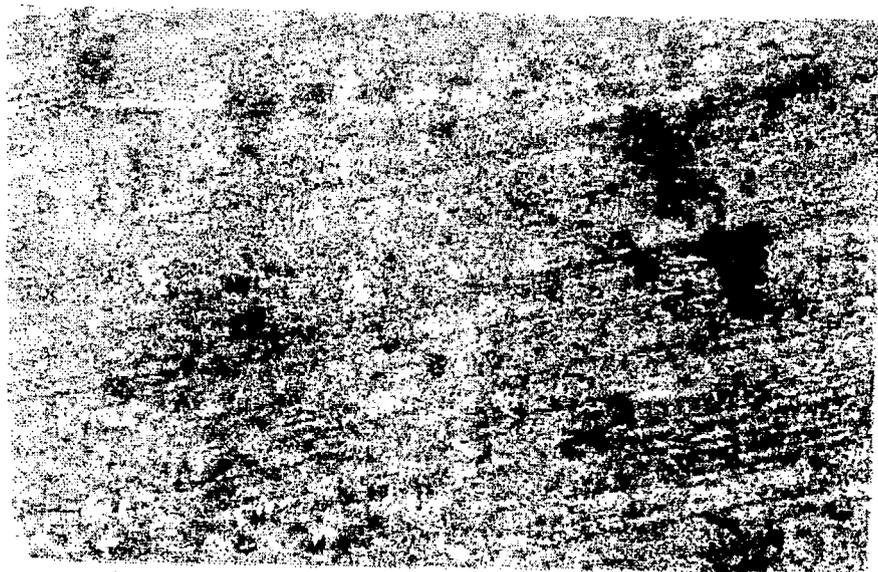


Fig 5.2 Surface morphology of coated plate number C-2 (X 250 magnification) of Ni – Fe alloy on copper plate.

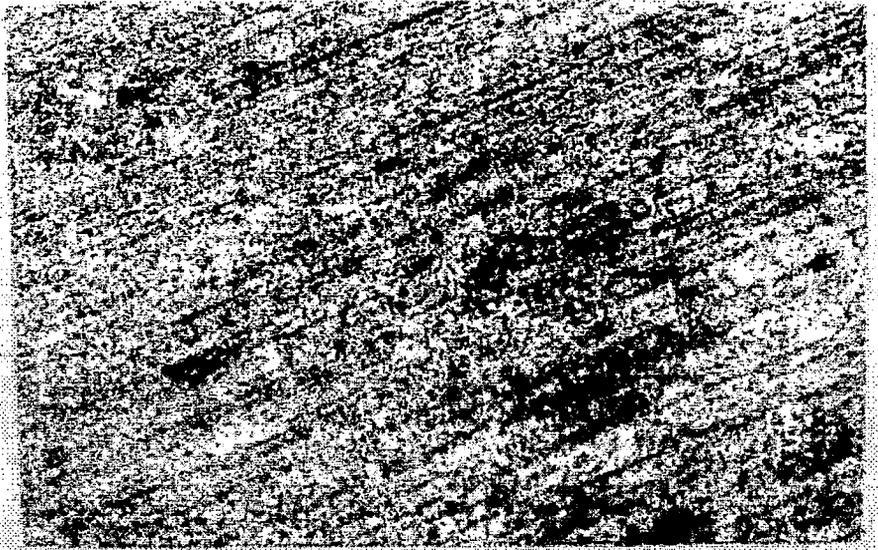


Fig 5.3 Surface morphology of coated plate number NC-8 (X 250 magnification) of Ni – Fe alloy plastic plate.

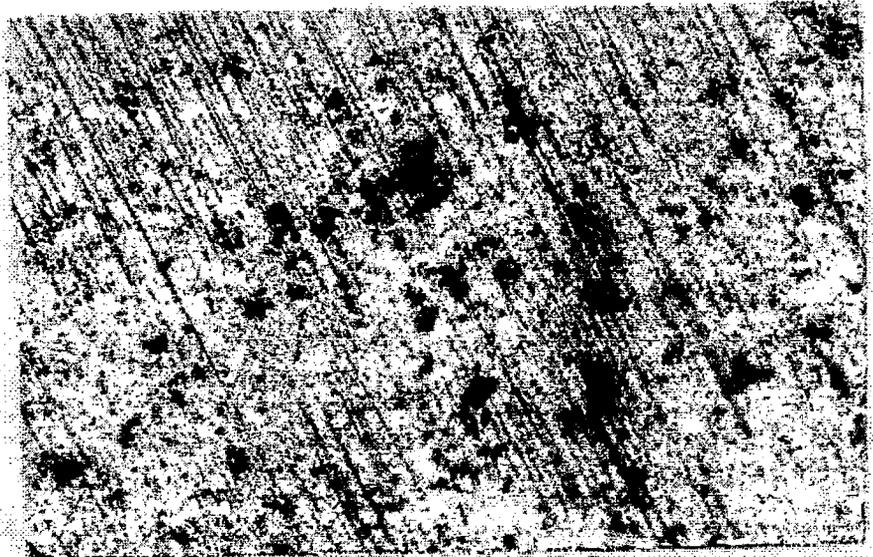
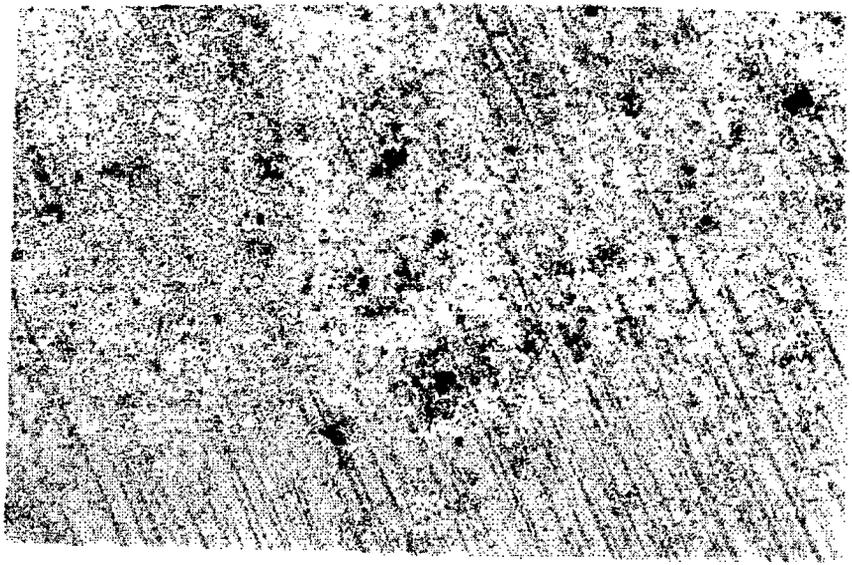
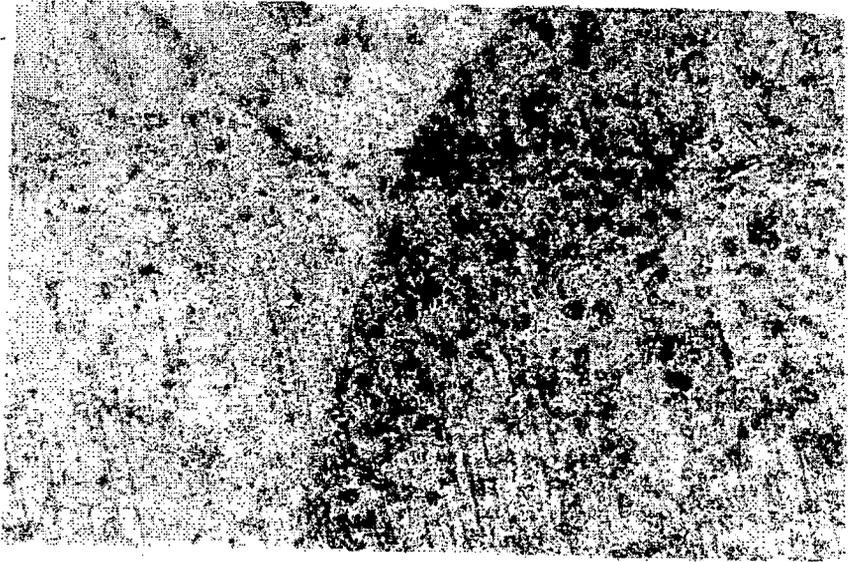


Fig 5.4 Surface morphology of coated plate number C-37 (X 250 magnification) of Ni – Fe alloy on copper plate.



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Fig 5.5 Surface morphology of coated plate number C-37 (X 250 magnification) of Ni – Fe alloy on copper plate.



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Fig 5.6 Surface morphology of coated plate number C-13 (X 250 magnification) of Ni – Fe alloy on copper (partly exposed for corrosion)

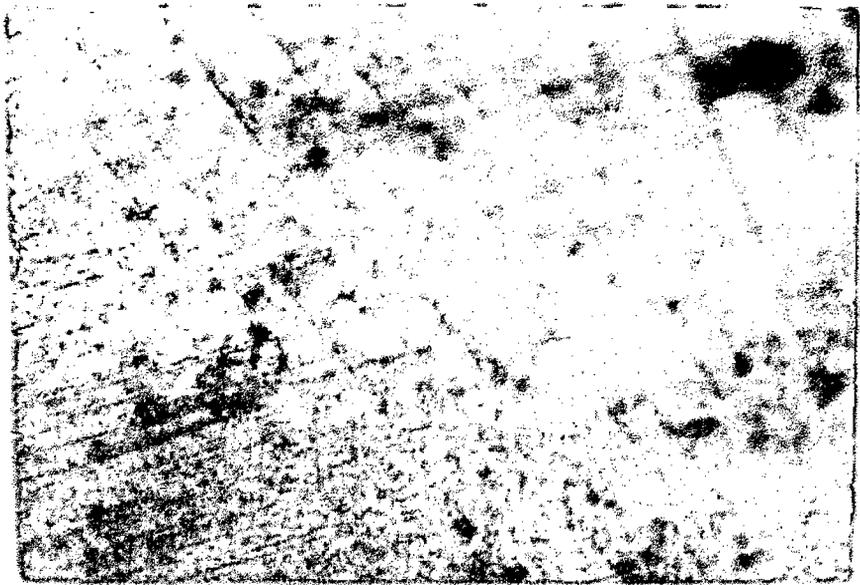


Fig 5.7 Surface morphology of coated plate number NC-32 (X 250 magnification) of Ni - Fe alloy on plastic plate.

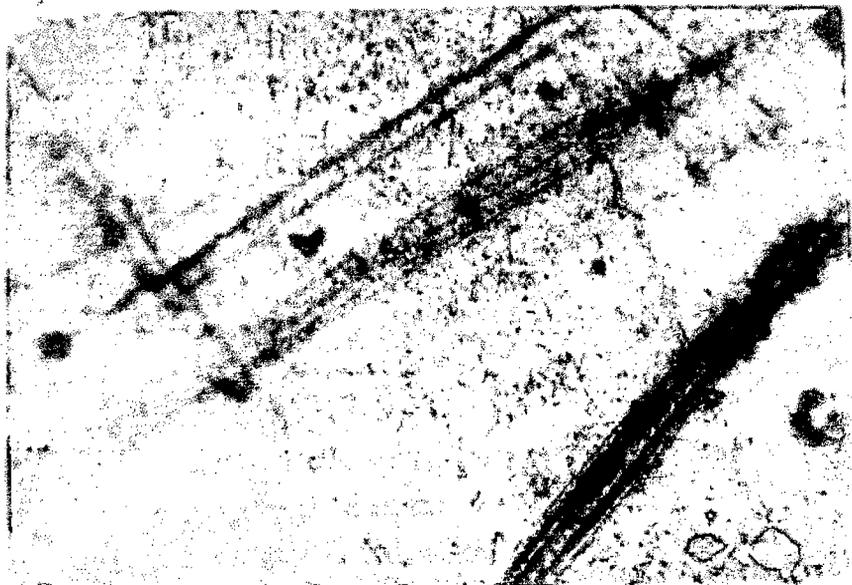


Fig 5.8 Surface morphology of coated plate number NC-32 (X 250 magnification) of Ni - Fe alloy on plastic plate.

A good deposit was obtained by using bath B at  $\text{pH} = 8$  as shown in Table 5.2. Interestingly, this bath was seen to be also stable. All the subsequent experiments were therefore carried out at standardized  $\text{pH}$  of 8 using fixed concentration of metal ions in the bath solution to get a deposit of Ni-Fe alloy. Interestingly no hydroxyl precipitation in solution was observed at  $\text{pH} = 8$ .

The speed of separation of metal depends to a marked degree on the  $\text{pH}$  value of solution [8,9]. The  $\text{pH}$  of the bath solution drops as electroless deposition proceeds. Because of this, all electroless baths must incorporate of buffer and during operation,  $\text{OH}^-$  ions are required to be supplied by continuous dosing with dilute alkaline [ $\text{NH}_4\text{OH}$  or  $\text{NaOH}$ ]. It is reported that, lower the bath  $\text{pH}$ , greater will be the phosphorous content of the deposit.

#### **5.2.4 EFFECT OF TEMPERATURE ON THE STABILITY OF THE BATH**

The reducing reaction needs energy, which is provided in the form of heat. Increase in temperature increase the rate of deposition but bath becomes unstable due to dissociation of reducing medium at higher temperatures.

Besides this higher temperature affects the phosphorous content of the deposit when sodium hypophosphite is used as a reducing agent

In an attempt to investigate the optimum temperature for Ni-Fe alloy deposition of desired quality by electroless plating from the novel bath, experiments were carried out at temperature ranging from 343 K to 358K. Since the temperatures of 343 , 348 and 358 K gave rusty deposit these temperatures were rejected. The results of investigation between temperature of 353 K and 358 K are presented in Tables 5.2 to 5.10.

Results show, that a good silvery grey deposit is obtained at temperature of 353 K and the best silvery deposit of Ni- Fe alloy was obtained at this temperature using bath B as represented in Table 5.2. Indexing done on the basis of the X-ray powder diffraction patterns (Fig. 5.9) of the plates are tabulated in Table 5.15. The alloy deposited in the electroless plating appear to have cubic structure.

### **5.2.5 EFFECT OF COMPLEXING AGENTS**

The complexing agents helps to form stable complexes with metal ions thereby help not only by reducing the concentration of free metal ions in solution but also control the release of free metal ions . In the present investigation the complexing agent used were NTA and  $N_2H_3COOH$ . These were either used singly or both together forming ternary system with metal ion. Tables 5.2 to 5.10 gave the result obtained using only NTA

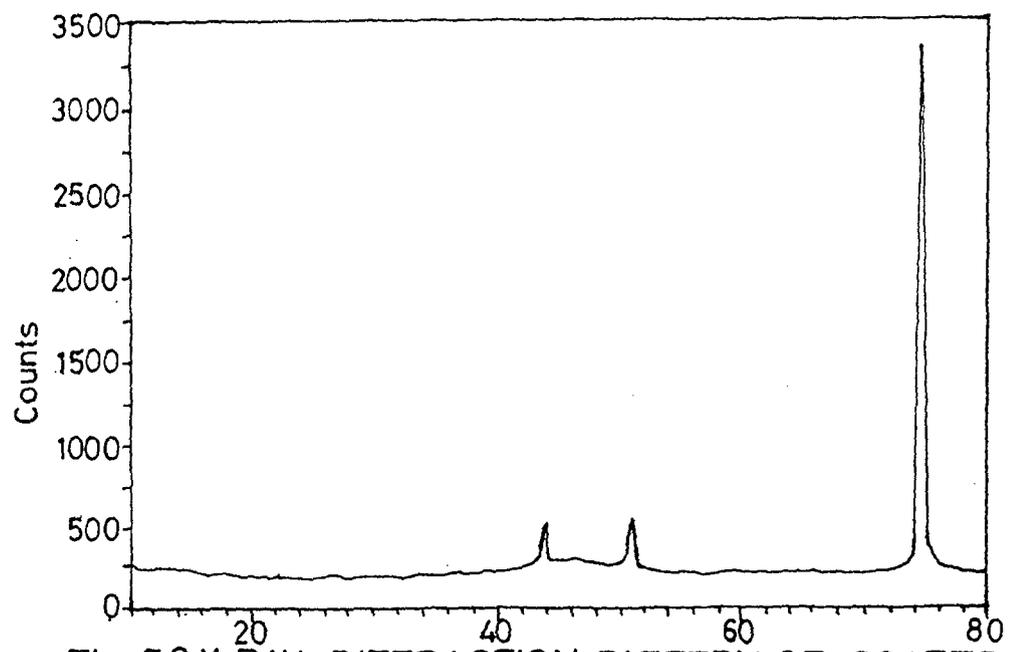
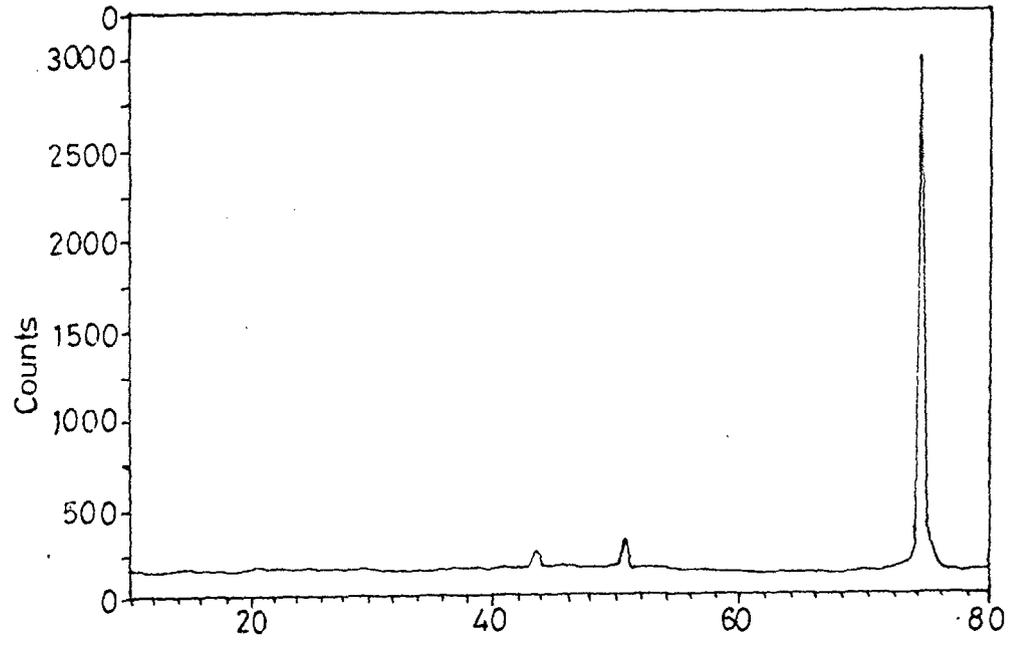
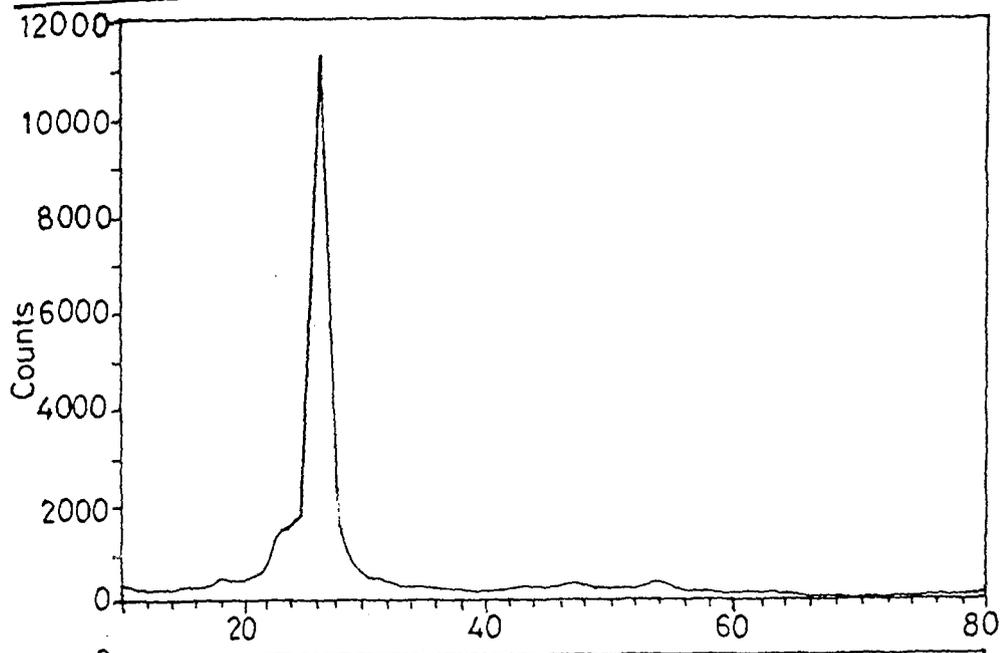


Fig. 5.9 X-RAY DIFFRACTION PATTERN OF COATED PLATES

**Table 5.15 :** Indexing on the basis of X - ray powder diffraction patterns.

Sample code (B) : Plate NC-1 (Th)		$\lambda = 1.54051 \text{ \AA}$			
d values	Relative intensity	h	k	l	Other parameters
4.9172	0.8	0	0	4	a = 7.8930A C = 19.6688 C/a = 2.4919 V= 1061.20 Structure: Hexagonal
3.8694	3.0	1	1	1	
3.4171	98.6	2	0	0	
3.3846	100	1	1	3	
1.9386	0.8	2	2	2*	
1.6979	0.9	4	0	1?	
1.2999	0.2	2	0	14	

Sample code (C) : Plate C - 16		$\lambda = 1.54051 \text{ \AA}$			
d values	Relative intensity	h	k	l	Other parameters
2.0776	4.3	-	-	-	a = 2.2099A V= 10.79 Structure: Cubic
1.7994	6.5	-	-	-	
1.2779	67.7	1	1	1	
1.2759	100	2	0	0	
1.2737	82.9	2	2	0	

Sample code (D) : Plate C-2		$\lambda = 1.54051 \text{ \AA}$			Other parameters
d values	Relative intensity	h	k	l	
8.4584	0.7	0	0	2	a = 9.1482A C = 16.9168 C/a = 1.8492 V= 1226.09 Structure: Hexagonal
3.7309	0.8	1	0	4	
2.4555	0.4	2	1	4?	
2.0767	7.4	3	0	5*	
1.7937	9.4	4	0	4	
1.2728	100	4	2	7	
1.2695	50.2	4	3	3	

as a complexing agent and Tables 5.12 , 5.13 results when two complexing agents are used [NTA and  $N_2H_3COOH$ ] .Table 5.13 gives results when two complexing agents and two reducing agents are used. Table 5.12 gives results with one reducing agent whereas Table 5.13 gives the results under same conditions with two reducing agents. From the results we can infer that the rate of deposition and thickness of deposit on non conducting substrate is moderately enhanced when two reducing agents are used as compared to single reducing agents. Secondly due to presence of two complexing agents the rate of deposition slows down irrespective of fact that whether one or two reducing agent are used. Comparison of tables 5.2 and 5.13 shows that rate of deposition is faster in table 5.2 where one complexing agent is used , and it is slow in table 5.13 where two complexing agent are used though in both cases two reducing agents are used.

### **5.3 EFFECT OF ADDITIVES ON THE NATURE OF THE COATINGS**

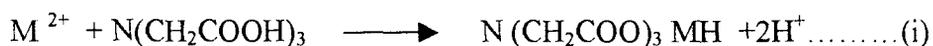
Additives are generally added to improve the appearance and brightness of the deposit. The brightness of a deposit can be judged by the clarity with which the image of an object is reflected at its surface. Brightness is measured with a reflectometer. Even metallic contaminants like Zn can significantly increase reflectance value .

In the present investigation Saccharin was used as an additive to improve the nature of the coating. It is observed that the deposit takes a silvery grey shining tinge as compared to silvery color when no Saccharin was used. The results are tabulated in table 5.14.

#### 5.4 METAL ION REDUCTION BY N<sub>2</sub>H<sub>4</sub> AND NaH<sub>2</sub>PO<sub>2</sub> IN PRESENCE OF NTA.

The reduction of metal ions (Ni<sup>+2</sup>/ Fe<sup>+2</sup>) by hydrazine in the presence of nitrilotriacetate as the complexing agent can be explained as follows.

Metal ions react with nitrilotriacetic acid to give metal nitrilotriacetate. An aqueous solution of this salt, when treated with hydrazine hydrate yields metal hydrazinium nitrilotriacetate [10].



Metal hydrazinium nitrilotriacetate

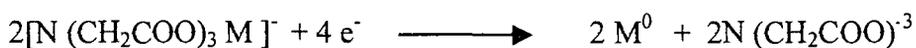
Metal hydrazinium nitrilotriacetate ionizes in aqueous medium to give hydrazinium ion, a source for hydrazine which is a strong reducing agent.



Thus, in an alkaline plating bath, the  $OH^-$  ions are continuously consumed in the electroless plating process, involving neutralization (equation v) and reduction of metal ions (equations vi & vii). As a result, there is a gradual lowering of pH of the bath solution. It is therefore essential to maintain the alkalinity of the bath by periodic addition of ammonia. In addition, hydrazine is also consumed continuously (equation vi) during the reduction process. It is therefore essential to maintain the concentration of hydrazine to a desired value so as to bring about continuous deposition of metal / metals. This is achieved by timely replenishment of hydrazine, in the bath through the addition of hydrazine hydrate. In the present investigation, therefore, about 1.5mL liquor ammonia was added every 15 minute to maintain  $pH = 8.0$ .

Besides this 0.1 mL hydrazine hydrate and 2mL of water was added every half an hour to make up for the loss.

It appears that, the metal ion from  $[N(CH_2COO)_3 M]^-$  which is formed in equation( i ) further undergoes reduction to metal which is deposited on the substrate.



Nitrilotriacetate ions so formed during this process combine with  $H^+$  ions to regenerate nitrilotriacetic acid [11]. This is evident from the infrared spectrum of the solid residue separated from the bath after the completion of the plating process. The IR spectrum shows typical NTA absorptions.

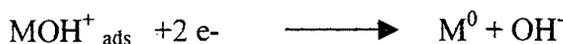
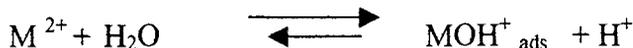
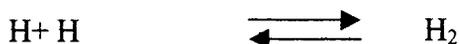
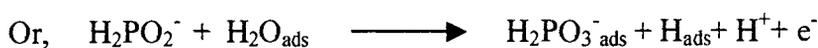
When two metal ions are present in the bath solution, initially they will both form metal complexes and then, undergo reduction to metal/s due to the presence of the reducing agents. In the present investigation, the metal ions used were  $Ni^{+2}$  and  $Fe^{+2}$  whereas, the reducing agents used were  $N_2H_4$  and sodium hypophosphite. The standard reduction potential of  $Fe^{+2}/Fe$  is  $-0.44$  V whereas that of  $Ni^{+2}/Ni$  is  $-0.24$  V. Hence nickel ions will be reduced to a greater extent as compared to ferrous ions. However, since there is not much of a difference in these potentials, the reduction of both the metal ions takes place to an appreciable extent. As a result, Ni-Fe alloy is deposited on the substrate.

## 5.5 METAL ION REDUCTION BY NaH<sub>2</sub>PO<sub>2</sub> IN THE PRESENCE OF NTA

The reactions of metal ions in the alkaline solution occur in the same manner [3], as those in the acid solutions, when sodium hypophosphite is used as a reducing agent. Such reactions are accompanied by the liberation of hydrogen and oxidation of hypophosphite to phosphite. The overall reaction in the hypophosphite reduction of the metal ions may be written as:



[11]. According to Sadakow and Gorbunowa [12], the adsorption of H<sub>2</sub>PO<sub>2</sub><sup>-</sup> and OH<sup>-</sup> ions on the catalytically active metal surface forms a key parts of the overall process. The adsorbed ions and molecules initiate a chain of consecutive reactions.



The alkaline solutions have a lower speed of separation and the coating obtained are less porous and less resistant to corrosion. The bath solution becomes more stable due to the presence of strong complexing agent NTA and due to better solubility of phosphite in alkaline medium. The results obtained by using a single reducing agent (sodium hypophosphite) and two complexing agents (NTA and hydrazidocarboxylic acid) are presented in the table 5.12. It is observed that, the rate of deposition is slowed down (Table 5.2), when two reducing agents and one complexing agent is used whereas the rate is moderately increased (Table 5.13), when two reducing agents and two complexing agents are used. The slow rate of deposition will make the deposit non-porous, resistant to corrosion and the deposit will have better adhesion.

## **5.6 ATOMIC ABSORPTION SPECTROSCOPIC ANALYSIS OF DEPOSIT**

The study by atomic adsorption spectroscopy (AAS)[13,14] was carried out to find the composition of Fe and Ni in the alloy deposited. The details of this technique are described in Chapter II.

The deposit of thick plastic plate [NC-3 (Tk) in table 5.2] was leached out in 0.2 N HNO<sub>3</sub>, which was prepared by using AAS grade HNO<sub>3</sub> and millicure water. The blank used was 0.2N HNO<sub>3</sub>.

In the gravimetric technique iron was precipitated as  $\text{Fe}(\text{OH})_3$ , then ignited and weighed as  $\text{Fe}_2\text{O}_3$ . After the removal of Fe as  $\text{Fe}(\text{OH})_3$  the remaining solution was subjected to volumetric estimation of Ni as described in Chapter II. The weight of Fe and Ni obtained were almost in agreement with that obtained by AAS studies.

From the weight of Fe and Ni in the alloy the density of the Fe-Ni alloy was found out using law of mixing.

## REFERENCES

1. W. Riedel, "Electroless Nickel Plating" ASM International, Ohio and Finishing Publication Ltd, England (1989).
2. R. Parkinson, Nickel Development Institute, Techn. Ser. No .10081 (1998).
3. G. G. Gawrilov, "Chemical (Electroless) Nickel Plating", Portcullis Press Redhill (1979).
4. A. K. Sharma, M. R. Suresh, H.Bhojraj, H. Narayanamurti and R. P. Sahu, "Electroless Nickel Plating on Magnesium Alloy", ISRO Satellite Centre, Bangalore, India.
5. V. L. Snoeyink and D. Jenkins "Water Chemistry", John Wiley & Sons, N. Y. (1980).
6. Oxymetal Industr. Corp. Fr. Patent, 2405312 (1979); C. A. :91(1979)148532Z.
7. A. Kutzelnigg, Die Prufung Metallischer, Uberzuge Eugen G. Leuze, Verlag, Sauigau, 1965.
8. G. Dutzeit, Plating, 46(1959) 1158, 1275, 1377; 49 (1960)63 .
9. K. Muller, Metallobenfl, 14(1960) 3.6584,102
10. J.S. Budkuley and G. K. Naik, "J.Therm. Anal." 50,(1997), 815.
11. S.S. Hinde, "Electroless Nickel Plating on Alluminium, Ph. D thesis (1998), Goa University.
12. G. A. Sadakow and K. M. Gorbunowa, Electrochimija, 16,(1980),230.
13. Nick Antanasopoulos, Flame Methods Manual foe Atomic Absorption, GBC Scientific Equipment PTY Ltd ; Victoria, Australia 3175 ,Analytical Data 9-8.
14. W. Merritt, Dean and Settle, "Instumental Methods of Analysis", Sixth Edn., CBS Publisher and Distributors, Delhi, India 140-145.

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