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SYNTHESIS, CHARACTERIZATION, SPECTRAL AND THERMAL PROPERTIES
OF
METAL NITRILOTRIACETATE HYDRAZINATES

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BY

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STATEMENT

I hereby state that this thesis for the Ph. D. degree on "SYNTHESIS, CHARACTERIZATION, SPECTRAL AND THERMAL PROPERTIES OF METAL NITRILOTRIACETATE HYDRAZINATES" is my original work and that it has not previously formed the basis for the award of any degree, diploma, associateship and fellowship or any other similar title to the best of my knowledge and information.

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CERTIFICATE

As required under the university ordinance, I certify that the thesis entitled SYNTHESIS, CHARACTERIZATION, SPECTRAL AND THERMAL PROPERTIES OF METAL NITRILOTRIACETATE HYDRAZINATES submitted by Shri. Ganpat Keshav Naik for the award of Doctor of philosophy in Chemistry is a record of research done by the candidate during the period of study under my guidance and that it has not previously formed the basis for the award to the candidate of any Degree Diploma, Associateship, fellowship or other similar titles.

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ABSTRACT

Nitrilotriacetic acid (NTA), $N(CH_2COOH)_3$, is a tribasic acid with three carboxylic acid groups. It is known to form simple and complex salts with either single or more metal ions. Since its isolation in 1862, syntheses of different metal salts of this acid have been reported. Metal salts of this acid find various applications. In fact its uses as a detergent builder or as a complexing agent in plating industry is well known. Chelation of NTA with different metal ions has been investigated through stability studies with both single as well as ternary system. However, the ternary system with NTA and hydrazine (N_2H_4) ligand has not been investigated so far as revealed from literature survey. Secondly, in plating industry, since the temperature of the working bath is fairly high, the knowledge of thermal stability of M-NTA complex becomes essential. The objective in the present study is to understand the thermoanalytical properties of metal - NTA and metal - NTA hydrazinates.

Alkaline earth metals Mg, Ca and Sr and transition metals Ni and Zn are used in present study. Metal NTA is synthesized by known method. The hydrazinates of these salts are prepared under different preparative conditions, especially with respect to the pH. The composition of these product salts and complexes are fixed with the help of chemical analysis and infrared spectra. It is then confirmed with the help of thermal analysis. Whereas, simple salts decompose above 200°C, the hydrazinates do so ~ 170°C. Hydrazinates are found to decompose through simple salts to carbonates to oxides. The kinetic parameters of these complexes are calculated from the TG data by known methods. In the case of hydrazinates, the initial decomposition of hydrazine is confirmed from the activation energy value for the decomposition step. The details of the present investigation is presented in five chapters.

CHAPTER I.

Chapter I, presents the literature survey on nitrilotriacetic acid (NTA) and hydrazine with respect to the synthesis, spectral and thermal properties. Similarly various methods of synthesis, spectral and stability studies of metal - nitrilotriacetate salts are also reviewed in this chapter. Tribasic acid NTA has three different dissociation constants with large difference between the first two. Consequently, pH plays important role in the reaction between NTA and aqueous metal ion.

The scope for the present investigation and its objective is briefly given at the end of this chapter.

CHAPTER II.

In chapter II, various analytical procedures and instrumental methods, used in the present study are described. The instrumental techniques employed include thermogravimetric analysis (TGA), differential thermal analysis (DTA), infrared spectroscopy (IR) and magnetic susceptibility measurements by Gouy's balance.

The use of the thermal data to obtain the kinetic parameters which is used in this study is also described in this chapter.

CHAPTER III.

Chapter III, contains the results of the study on metal ion-NTA hydrazine system. The products obtained depend on the preparative conditions and are tabulated here.

The compositions of these organo metallic complexes obtained under different preparative conditions, are assigned on the basis of chemical analysis and spectral studies. The infrared spectra show typical carboxylic ($-COO^-$) and metal nitrogen (M-N), metal oxygen (M-O) absorptions. Shifting of the $-COO^-$ absorption to ~ 1680 cm^{-1} indicates the presence of ionic carboxylic group. The stretching N - N absorption 950 - 1000 cm^{-1} is used as the criteria for assuming the presence of N_2H_4 ligand or ionic $N_2H_5^+$. The magnetic susceptibility values and densities of these complexes are tabulated and briefly discussed at the end of this chapter. Two carboxylic acid groups in NTA are co-ordinated to divalent Ni whereas the third is preferentially neutralized by $N_2H_4.H_2O$ (i.e. N_2H_5OH).

CHAPTER IV.

Chapter IV, deals with the thermal analyses of metal nitrilotriacetates, metal - nitrilotriacetate hydrazinates and mixed metals nitrilotriacetate hydrazinates. Decomposition steps are given on the basis of the weight loss observed in the TG. The interpretation of the thermal data is described in this chapter. These salts decompose through dehydrated salt to carbonate to oxide as intermediates. The decomposition of products includes ammonia (NH_3) carbon dioxide (CO_2) and acetone (CH_3COCH_3). For some of the salts, the residue obtained on heating to ~ 700°C is found to be the mixture of oxide and metal (mostly metal). Ni - NTA hydrazinates are found to be good precursor for fine powder Ni.

$$N(CH_2COO)_3M(N_2H_5) \dashrightarrow N(CH_2COO)_3MH \dashrightarrow (MCO_3) \dashrightarrow M / MO$$

CHAPTER V.

Thermogravimetric data is used to evaluate the kinetic parameters involved in different decomposition reactions. Chapter V highlights the activation energy values obtained from the dynamic TG data of the samples. The three different methods used are as given by 1.) Freeman - Carroll, 2.) Coats - Redfern, 3.) Metzger - Horowitz. The comparison and interpretation of activation energy values of simple salts and hydrazinate complexes are also discussed. Activation energy values for hydrazine decomposition are found to be lower in case of salts in comparison to its hydrazinates which may be due to co-ordinated hydrazine in the latter.

CONTENTS

CHAPTER ONE

LITERATURE SURVEY

CHAPTER TWO

EXPERIMENTAL

CHAPTER THREE

SYNTHESIS, CHARACTERIZATION AND PROPERTIES OF METAL HYDRAZINIUM NITRILOTRIACETATES

CHAPTER FOUR

THERMAL STUDIES OF METAL-NTA SALTS AND THEIR HYDRAZINE DERIVATIVES

CHAPTER FIVE

THERMAL DECOMPOSITION KINETICS OF METAL-NTA SALTS AND THEIR HYDRAZINE DERIVATIVES

CODE FOR COMPOUNDS

Code	Formula
MG-1	$HMg[Y].3H_2O$
MG-3	$(N_2H_5)Mg[Y].H_2O$
MG-4	$(N_2H_5)Mg[Y].2H_2O$
CA-1	$HCa[Y].2H_2O$
CA-3	$(N_2H_5)Ca[Y].2H_2O$
SR-1	$HSr[Y].4H_2O$
SR-3	$(N_2H_5)Sr[Y].H_2O$
BA-1	$HBa[Y].3H_2O$
ZN-1	$HZn[Y].2H_2O$
ZN-3	$(N_2H_5)Zn[Y].H_2O$
NI-1	$HNi[Y].5H_2O$
NI-3	$(N_2H_5)Ni[Y].4H_2O$
NI-4	$(N_2H_5)Ni[Y].N_2H_4.5H_2O$
NI-5	$(N_2H_5)Ni[Y].0.5N_2H_4.7H_2O$
NI-6	$(N_2H_5)Ni[Y].3H_2O$
NI-8	$(N_2H_5)Ni[Y]0.5N_2H_4.2H_2O$
NI-9	$Na(N_2H_5)Ni_2[Y]_2.2N_2H_4.3H_2O$
NI-10	$Na(N_2H_5)Ni_2[Y]_2.N_2H_4.3H_2O$
NI-11	$K(N_2H_5)Ni_2[Y]_2.N_2H_4.3H_2O$
NI-12	$K(N_2H_5)Ni_2[Y]_2.2N_2H_4.3H_2O$

LIST OF TABLES

CHAPTER ONE

CHAPTER TWO

CHAPTER THREE

CHAPTER FOUR

Table 4 Thermoanalytical data of the samples

CHAPTER FIVE

Calculated kinetic parameters of the compounds

LIST OF FIGURES

CHAPTER THREE

CHAPTER FOUR

CHAPTER FIVE

CHAPTER ONE

CHAPTER ONE

LITERATURE SURVEY

1. INTRODUCTION

The interest in nitrilotriacetic acid develops from its wide applications. Most important among them are (i) as asequestrian agent[1] in laundry detergent and (ii) as an additive in the plating industry[2]. In both these applications, the acid acts as the complexing agent.

As a complexing agent in detergent, it masks the hardness components in hard water,namely,calcium and magnesium,thereby increasing the detergent efficiency. Whereas , in plating industry, this acid complexes the metal ion thus controlling the rate of deposition of metal on the substrate. It also supresses the precipitation of the metal ion.

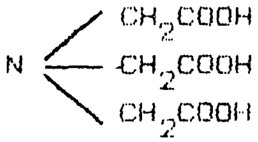
The other component in the plating process, namely electroless (EL) plating, is the reducing agent. Hydrazine is one such reducing agent, among various others, which has been explored for its use in EL plating bath. It is envisaged that hydrazine, along with nitrilotracetic acid as complexing agent for metal ion, could make component of EL plating bath.

1.1.1 NITRILOTRIACETIC ACID

Nitrilotriacetic acid, also refered as NTA, inthe subsequent discussion, is a triprotic acid with the molecular formula $C_6H_9O_6N$ or $H_3[N(CH_2COO)_3]$ It has also various other names such as,

i) N, N – Bis (Carboxymethyl) glycine,
ii) Triglycollamine acid,
iii) α, α',α'' –– Trimethylamine carboxylic acid,
iv) Tri (carboxymethyl) amine.
v) Ammonia Triacetic Acid,
vi) Triglycine,
vii) Trilon A (Commercial).

NTA has three carboxylic acid groups and its structural formula can be given as

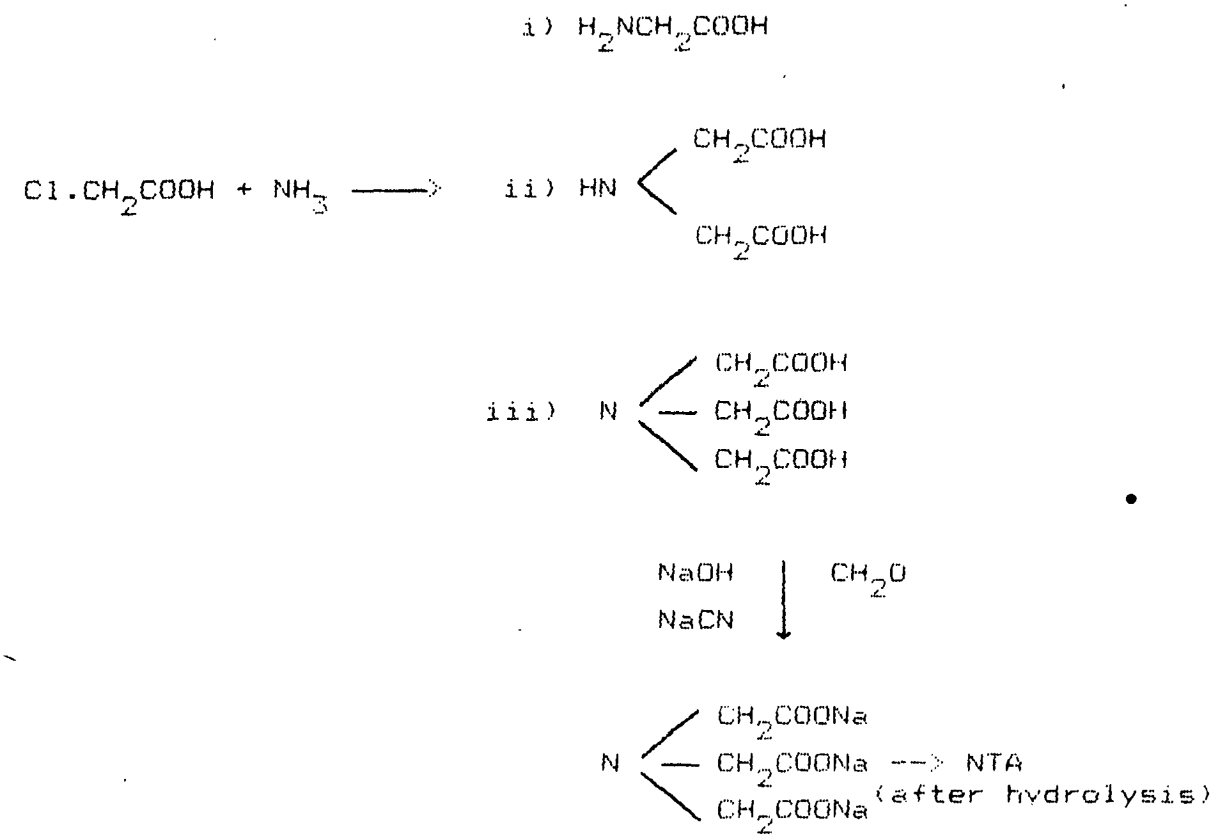


$$N \begin{cases} CH_2COOH \\ CH_2COOH \\ CH_2COOH \end{cases}$$

1.1.1.1 SYNTHESIS OF NTA

NTA has been first isolated and identified by Heintz[3] in 1862. Subsequently, several workers have reported[4-6] the synthesis of this acid. Martell and Bersworth[7] synthesized NTA using chloroacetic acid and concentrated ammonia.

Monoglycine and diglycine are converted to triglycine in presence of NaOH + NaCN and formaldehyde. Na salt is then hydrolised with H_2SO_4 at pH = 1.2 to obtain NTA in solid form. Commercial method of preparation of NTA has been reported and patented by Singer[8].



1.1.1.2 PHYSICAL PROPERTIES OF NTA

Nitrilotriacetic acid (Molecular weight 191.14) is sparingly soluble in water with solubility[7] of 1.28 g in one litre at 22.5°C. The pH of the saturated aqueous solution of this acid has been found to be 2.3 and the melting point of the solid compound to be in the range[4] of 230-235° C. However, Bird[8] reported the m.p. to be 241.5°C. Being a tribasic acid, it has three different dissociation constants for -COOH groups, and the pKa values have been found out[9] to be $pK_1 = 3.03$, $pK_2 = 3.07$ and $pK_3 = 10.7$ at 20°C. However potentiometrically determined pka values differ[10], $pK_1 = 1.89$, $pK_2 = 2.49$ and $pK_3 = 9.73$. (Table 1.1). Souchay[11] has reviewed different physical properties of nitrilotriacetic acid.

TABLE 1.1

Equilibrium Constants for NTA

Reaction	Temp °C	Ionic Strength	pK_a
$H_3A \rightleftharpoons H_2A^- + H^+$	20	0.1	1.89
$H_2A \rightleftharpoons HA^{2-} + H^+$	20	0.1	2.49
$HA^{2-} \rightleftharpoons A^{3-} + H^+$	20	0.1	9.73

1.1.1.3 THERMAL PROPERTIES OF NTA

C. Duval[12] studied the pyrolysis of nitrilotriacetic acid on a thermobalance. It was found that this acid is stable upto a temperature of 286°C, Beyond this temperature, it undergoes decomposition with the formation of volatile products. However, investigations carried out by Wendlandt[13,14] reveal that the acid is decomposed at about 240°C. Table 1.2 elucidates the thermal properties of NTA.

TABLE 1.2

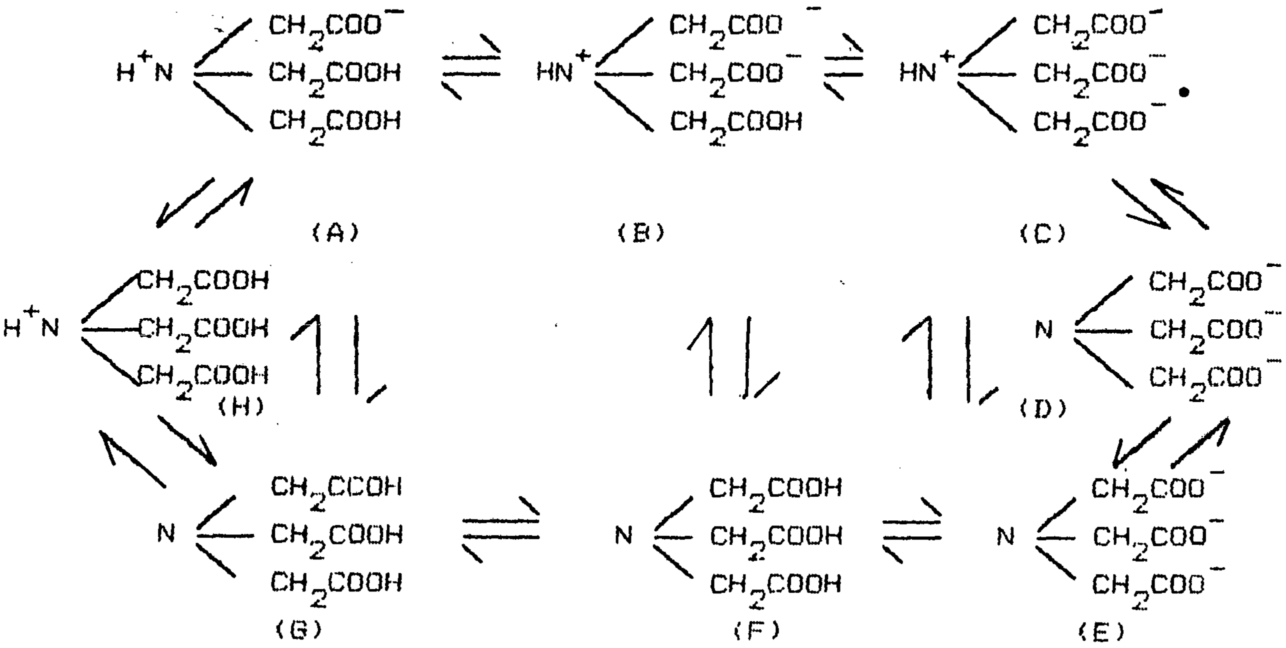
TG, DTA Data for NTA

Compound	TG Temp. Range °C	DTA Peak temp. °C
NTA	240-355	260 (endotherm)

1.1.1.4 SPECTRAL PROPERTIES OF NTA

Literature survey indicatesthat the infrared spectral properties of nitrilotriacetic acid, both in solid[15] as well as in solution[16], have been systematically investigated. In aqueous solution, the equilibrium of the acid can be given on the basis of the formation of $HN^{+}(CH_2COOH)_3$ or H_4Y, where $Y = N(CH_2COO)_3$. The aqeuous solution of the NTA, may have the presence of as many as eight different ionic/non-ionic species, which are shown by the sequence of equilibrium given below :

The equilibria of NTA in solution[15]



The presence of a particular species depends on the pH of the aqueous solution since the acid has three different pK_a values. Consequently, the observed antisymetric carboxyl (or carboxylate) stretching frequencies will be different for solutions having different pH.

Tomita et al[16] have studied antisymetric stretching bands of carboxyl group at various pH (Table 1.3). Chelated carboxyl group is observed at ~ 1610 cm^{-1}.

TABLE - 1.3

IR Absorption Frequencies of NTA Solutions at Various pH

Observed IR band cm^{-1}	Carboxyl/ Carboxylate Group	Species Present (mostly)	pH
~ 1720-30	-COOH	-COOH (Undissociated)	3.2
~ 1625	$-COO^{-}$	$-COO^{-}$ (with $-NH^{+}$)	4.2
~1610	-COO co-ordinated	-COOM	10-11.6

1.1.1.5 APPLICATIONS OF NTA

Nitrilotriacetic acid (NTA), also known as ammonia triacetic acid, as mentioned earlier is used as an additive in detergents.[18,19] It removes hardness from water which is used in laundering, by complexing and masking of calcium and magnesium. It is used as a levelling agent for dyes,[8] for bleaching, softening of boiler water, for prevention and removal of scales and also other applications.[20-27]

It is extensively used in various electrodeposition processes.[28] NTA has been a constituent of electrocleaners in the pre-treatment processes prior to electrodeposition. Better cleaning was observed[29] when it was used along with the alkalies. Similarly, addition of NTA to the mixture of nitric acid, citric acid and surfactant was found to improve[30] the electropolishing of stainless steel. NTA was used as one of the constituents of the bath in the deposition of metals on plastic surfaces.[31] Thus, in electrodeposition processes, NTA is added to advantage for better cleaning, increased deposition speed, more uniform covering power and good adherance of the deposited metal.

1.1.2 METAL NITRILOTRIACETATES

Ammonium nitrilotriacetate, $NH_4.H_2[N(CH_2COO)_3]$ was the first[9] salt of the NTA to be isolated along with the acid. Since then, the NTA salt of practically all the metals[32-36] in the periodic table have been synthesized. Nitrilotriacetic acid, is an amino acid derivative of acetic acid, and like ethylene diammine tetracetic acid, forms complexes, though with lesser stability.

1.1.2.1 SYNTHESES OF METAL-NTA SALTS

Earliest reports[37-40] on the syntheses of metal-NTA salts are based on the reaction between aqueous solution of metal salt (chloride etc.) and NTA suspension (since solubility of NTA is very low). For example,

$$M^{2+} + H_3[N(CH_2COO)_3] \text{ ----> } HM[N(CH_2COO)_3] + 2H^+$$

Complex salt of the acid containing two metals, sodium-vanadium, has also been isolated by similar reaction.

Other methods of preparation involve the double decomposition reaction[41] between the metal salt (chloride or sulphate) and the sodium salt of the NTA in aqueous medium or the reaction[42] between metal carbonate and the NTA in aqueous medium which is warmed to ~60°C

$$M^{2+} + HNa_2[N(CH_2COO)_3] \text{ --> } HM[N(CH_2COO)_3] + 2Na^+$$

$$MCO_3 + H_3[N(CH_2COO)_3] \text{ --> } HM[N(CH_2COO)_3] + H_2O + CO_2$$

With hydrazine hydrate, $N_2H_4.H_2O$, nitrilotriacetic acid has been found to yield dihydrazinium salt;[43] $H(N_2H_5)_2[N(CH_2COO)_3]$. Third carboxyl proton remains undissociated, probably, due to high third pK value.

Though the complex formation in the ternary systems;[9,44,45] with NTA as the primary ligand, has been extensively investigated, not many of such complexes have been isolated in the solid state from the solutions. Metals like nickel, copper, cadmium, indium, lead, iron, zinc and chromium are known[46-54] to form complexes with nitrilotriacetic acid.

1.1.2.2 PHYSICAL PROPERTIES OF METAL-NTA SALTS

The physical properties of metal nitrilotriacetate salts in aqueous solution have beenstudied by several workers.[9,44] The investigations carried out, in these studies, are mostly with respect to the stability of metal-NTA complex salts in simple[46,55-65] and ternary[66] systems. Some of the equilibrium constant values (log) are summarized in Table - 1.4

Nitrilotriacetic acid has been found to form complexes with metal ion, which are more stable[67] compared to mono - or di -amino acetic acid. It can be seen that the zinc complex of the NTA is more stable (Table 1.5) compared to the complex of that metal with glycine or imino diacetic acid.[68]

TABLE 1.4

The Equilibrium Constant for Nitrilotriacetates

[MY]/[M][Y]   Where M = Mg,Ca,Fe,Cu,Zn,Ni,Co

and $Y = H[N(CH\ COO)_3]^{2-}$

Metal ion	Metal Chelate Form	Equilibrium Constant Value (log)	t °C	μ
Mg^{2+}	MY	5.41	20	0.1
Ca^{2+}	MY	6.41	20	0.1
Fe^{2+}	MY	8.82	20	0.1
Cu^{2+}	MY	12.68	20	0.1
Zn^{2+}	MY	10.45	20	0.1
Ni^{2+}	MY	11.26	20	0.1
Co^{2+}	MY	10.61	20	0.1

TABLE 1.5

Stability Constant values (log) of

Zinc complexes of Amino Acetic Acids

Stability Constant	With Glycine (Mono acetic acid)	With imino diacetic acid	With NTA (triacetic acid)
First	4.8	7.8	10.5
Second	4.1	5.7	3.0

The greater difference between the two values in the case of nitrilotriacetate has been ascribed[60] to the fact that zinc ion cannot accept all the possible donor groups in two of the donor anions.

1.1.2.3 SPECTRAL PROPERTIES OF METAL-NTA SALTS

The characteristic infrared absorption frequencies, for the carboxyl groups, as mentioned in section 1.1.1.4, have been utilised[15,16,70] to reveal the state of bonding of these groups with the metal ion. The bonding in the NTA with metal ion has been found to be similar to those found in metal-acetic acid[71],metal-diethylenetriamine pentacetic acid[72]and metal -EDTA complexes.[73,74]

However, a systematic investigation of chelation of nitrilotriacetic acid with metal ions, at various pH, has been carried out by Tomita et al.[16]The antisymmetric carboxyl stretching frequencies have been found to vary depending upon the pH of the solution. And, the chelation has been found to occur through oxygen atom at higher pH. In solution, it has also been concluded that NTA behaves as tetradentate ligand, with all carboxylate groups coordinated to the central metal ion.

The characteristic absorption bands observed[42]in case of metal NTA salts have been ~1680 cm^{-1} (-COOH), ~1620cm^{-1} (-COOM), ~1410 cm^{-1} ($-COO^{-}$crystal), ~1130 cm^{-1} (-CN) and the assignments are given in Table 1.6.

TABLE 1.6

Infrared Spectral Data (cm^{-1}) of Metal Nitrilotriacetate Hydrates

$M[N(CH_2COO)_3].xH_2O$ $Y = N(CH_2COO)_3$

Key M/x --> Assignement ↓	H_3Y	Mg x=3	Ca x=4	Sr x=4	Ba x=3	Zn x=2	Ni x=5
1. -OH	--	3520 2900vs	3525m 2930s 2875vs	3550w 3025s 2935vs	3500w 2925vs 2875vs	3350vs	2875vs
2. Unionised -COOH	1728 s	1720w 1660m	1710w 1660m	1700w 1680m	1725w 1680m	1745m 1680m	1730w 1665m
3. $\nu_{asym. stret}$ $-COO^-$	--	1595	1660w 1590	1565	1560	1585	1585
4. co-ordinate metal -COOM	--	1630s	1630s	1635s	1621s	1621vs	1625s
5. Stretching ν_{asym} COO^-	1434s	1425m 1408w	1440mr 1405mr	1412sr	1410mr 1445m	1432s	1432s 1400w
6. -CN	--	1150m	1160m 1145m	1165m	1155m	1125m	1120m
7. $-COO^-$	--	1075w	1045r	1050r	1050	1022m	1019m
8. ν_{C-C}	967m	975 s 930 s 910 s	970 s 960 s 910 s	975m 960s 910s	965m 940s 918s	962m 950s 906s	962 m 943 s 905 s
9. δ_{oco}	--	720 s	720 s	720 s	720 s	720 s	720 s

1.1.2.4 APPLICATIONS OF METAL-NITRILOTRIACETATE SALTS

Metal - NTA salts have wide variety of applications. Sodium salt of this acid, $Na_3[N(CH_2COO)_3]$ has been used as a detergent builder.[18,19] Metal NTA salts are extensively used in electronic industry. Most important use of these salts has been in the electrodeposition. Nickel-NTA salt added to gold bath in electroplating has been found to give hardness[75,76] to the gold deposit. Gold-ruthenium alloy has been deposited using ruthenium-NTA along with gold salt. With the NTA based solutions, deposition of gold alloy[78] containing zinc, nickel and indium was achieved. Metal NTA based baths were found to yield high rates[79] of deposition. Gold sulphite complex along with NTA was developed as a substitute[80] to cyanide bath in electroplating industry. Several other metals like palldium, molybdenum alloy, cadmium, copper etc. have been electrodeposited from NTA based baths. Recent[81] study has revealed that metal- NTA solutions can also be used for effective deposition of the metal by electroless plating process.

1.2.1 HYDRAZINE

Hydrazine is a colourless liquid, with the boiling point[82] of 114°C (m.p. 2°C) with a nasty ammonia like odour. Physically, it is similar to water, but chemically it is a strong reducing agent. Hydrazine is a varsatile compound with a molecular formula N_2H_4. It is an immensely important compound due to the presence of a potent N-N bond, four replaceable H atoms and two free pairs of electrons in it.

Commercially hydrazine is available as hydrazine hydrate ($N_2H_4.H_2O$), which has a m.p. of −51.7°C at one atomospheric pressure. Some of the properties of hydrazine are tabulated in Table 1.7

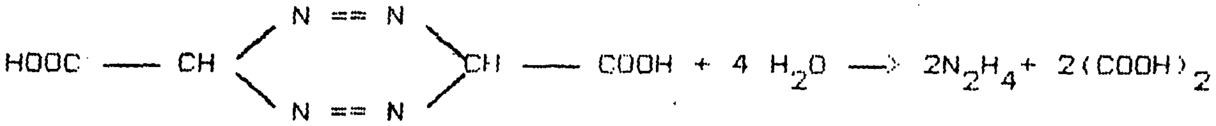
TABLE 1.7

Physical Properties of Hydrazine[83]

Property	
Molecular Weight	32.0453
Vapour Pressure	14.19 mm Hg
Density	1.0037
Viscosity	0.913
Surface Tension	0.6645 dyn cm^{-1}
Thermal Conductivity	7.86×10^{-5} cal $cm^{-1} K^{-1} S^{-1}$
Heat Capacity	3.0778 J $g^{-1} K^{-1}$
Heat of Foration	+50.434 KJ $mole^{-1}$
Dielectric Constant	51.7
Dipole Moment	1.84 debye unit
Refractive Index	1.4683

1.2.1.1 SYNTHESIS OF HYDRAZINE

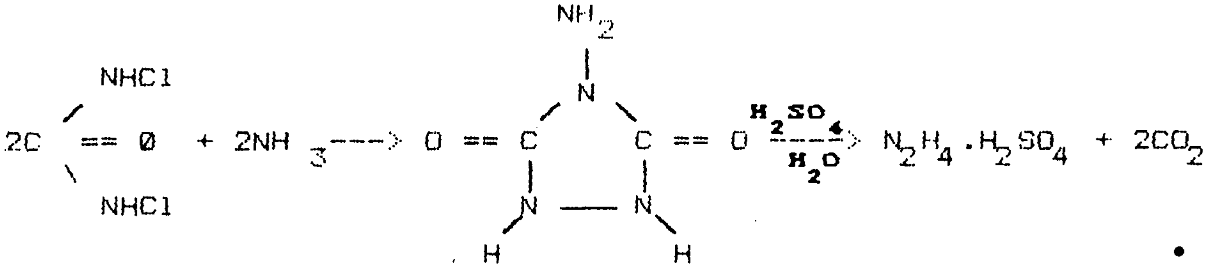
Hydrazine was first isolated by Curtius[84] in 1887 by hydrolysis of diazoacetic ester with alkali.



Commercially hydrazine is manufactured by two well known methods :

(i) the reaction between urea and sodium hypochlorite[85-88]

$$CO(NH_2)_2 + 2NaOCl \longrightarrow C(=O)(NHCl)_2 + 2NaOH$$



(ii) the reaction between ammonia and chloramine

$$NH_3 + NaOCl \longrightarrow ClNH_2 + NaOH$$

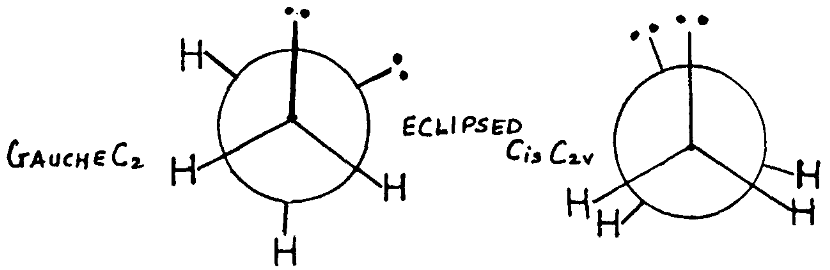
$$ClNH_2 + NH_3 + NaOH \longrightarrow N_2H_4 + NaCl + H_2O$$

In both these reactions, glue or gelatine is added to inhibit the catalytic decomposition of hydrazine, so formed, by the unreacted oxidant. Hydrazine synthesised by these methods is in the form of azeotropic mixture with water. Pure hydrazine (hydrate)is subsequently obtained by extractive distillation with aniline. Anhydrous N_2H_4 was subsequently prepared by DeBruyn[92] in 1895.

1.2.1.2 PHYSICO - CHEMICAL PROPERTIES OF HYDRAZINE

In hydrazine the N—N bond length has been found[93-95] to be 1.47 A^{o} and N—N—H angle equal to 112^{o}, suggesting sp^3 hybridization in nitrogen atoms. Hydrazine molecule has been found to have either gauche C_2 or Cis C_{2v} conformation in the solid state as revealed from the X-ray investigations.[96]

STRUCTURE



Hydrazine is athermally stable compound up to 250°C. On further increase in temperature, it decomposes exothermically releasing tremendous amount of energy. The bond[97] dissociation energies are (i) $D_{NH_2--NH_2} = 60.00$ K cal mole^{-1}

(ii) $D_{NH_2--H} = 75.00$ K cal mole^{-1}

and bond energy (iii) $E_{N-H} = 38.00$ K cal mole^{-1}

Hydrazine is a Lewis base and the reaction with water may yield either hydrazinium ion or hydrazonium ion.

$$N_2H_4 + H_2O \rightleftharpoons N_2H_5^+ + OH^- \qquad K_1 = 8.5 \times 10^{-7}$$

$$N_2H_5^+ + H_2O \rightleftharpoons N_2H_6^{2+} + OH^- \qquad K_2 = 8.9 \times 10^{-16}$$

Hydrazine has been known to be a powerful reducing agent, due to which, it has a variety of applications. Oxidation of hydrazine by oxygen is an exothermic[98] reaction in which enormous heat is liberated.

$$N_2H_4 + O_2 \longrightarrow N_2 + 2H_2O \; \ldots \; \Delta H_{298^\circ C} = 138.3 \text{ Kcal mole}^{-1}$$

Hydrazine reduces Nickel from solution in an alkaline medium, to metal nickel.[99]

$$2Ni^{+2} + N_2H_4 + 4OH^- \longrightarrow 2Ni + N_2 + 4H_2O$$

Due to the presence of two free electrons on the nitrogen atoms, hydrazine acts as a mono or bidentate bridge ligand,[100] especially with transition metal ion.[101]

1.2.1.3 SPECTRAL PROPERTIES OF HYDRAZINE

Studies on the infrared spectrum of hydrazine in solid[102-113] state have revealed the N—N bond distance to be 1.46°A. Corresponding to this, the bond stretching band• for N—N is observed at 884 cm^{-1}. The other characteristic absoprtion bands observed for N_2H_4 are 3310 cm^{-1} (weak H bonded N—H), 1650 cm^{-1} (NH_3^+ deformation), 1605 cm^{-1} (NH_2 bending), 1350 cm^{-1} (NH_2 wagging), 1130 cm^{-1} (NH_2 twisting) and 885 cm^{-1} (N—N stretching).

1.2.1.4 THERMAL PROPERTIES OF HYDRAZINE

The heat of formation[100] of hydrazine is +12 K cal $mole^{-1}$,

$$N_2\,(g) + 2H_2\,(g) \longrightarrow N_2H_4\,(l) \quad \Delta Hf^{\circ} = +\,12\ \text{K cal mole}^{-1}$$

This signifies that hydrazine is unstable, Yet it is quite stable at room temperature.

When heated, hydrazine decomposes to ammonia and nitrogen as the major products. But the decomposition[114] pattern varies depending upon the experimental conditions. Generally, the decomposition reaction can be written as,

$$3N_2H_4 \longrightarrow 4(1-x)NH_3 + (1+2x)\ N_2 + 6x\ H_2O$$

1.2.2 METAL HYDRAZINE SYSTEM

Hydrazine exists in various forms, such as N_2H_4, $N_2H_5^+$, $N_2H_6^{2+}$, $N_2H_3COO^-$ and N_2H_2. Depending on its nature, hydrazine forms various compounds or complexes. In metal salts, hydrazine may be present as a ligand (N_2H_4, $N_2H_5^+$, $N_2H_3COO^-$) or as a cation ($N_2H_5^+$ & $N_2H_6^{2+}$) or as an anion. ($N_2H_3COO^-$)

1.2.2.1 SYNTHESES OF METAL HYDRAZINE COMPOUNDS[83]

Aqueous hydrazine (aq N_2H_4) or hydrazine hydrate ($N_2H_4.H_2O$) or hydrazinium hydroxide (N_2H_5OH) forms simple salts when it is neutralised by an acid.

$$N_2H_5OH + HX \longrightarrow N_2H_5X + H_2O$$

Hydrazine has been found to react with metal salts to give either hydrazinates of the metal salts or double salts containing hydrazinium as one of the cation.

$$MX_2 + xN_2H_4.H_2O \longrightarrow M\,[N_2H_4]X_2$$

$$\longrightarrow (N_2H_5)M[X_3]$$

Hydrazine is also known to react with CO_2 to form hydrazido carboxylate in which hydrazine is present in the anionic species.

(i) $N_2H_4 + CO_2 \longrightarrow N_2H_3COOH$

(ii) $2N_2H_4 + CO_2 \longrightarrow N_2H_3COON_2H_5$

(iii) $N_2H_4.H_2O + CO_2 \longrightarrow N_2H_3COOH + H_2O$

Consequently, the aqueous mixture of hydrazine hydrate and metal salt exposed to atmospheric CO_2 has been found to yeild metal hydrazido carboxylate.

$$MX_2 + 4\ N_2H_4 + 2\ CO_2 \longrightarrow M\ [\ N_2H_3COO]_2 + 2N_2H_5X$$

All the reactions mentioned above could be in aqueous medium or heterogeneously with solid metal salts andliquid hydrazine hydrate.

By identical procedures mixed metal salts have also been synthesised by many investigators.[115-117]

1.2.2.2 SPECTRAL PROPERTIES OF METAL HYDRAZINE COMPOUNDS

Since the existence of hydrazine in the hydrazine based compounds has been known in various forms, it is very essential to study its nature in them. Infrared spectral study has been one of the important tools used to distinguish between the various forms of hydrazine. Along with it the complexation of the metal by hydrazine has also been investigated.[118-120]

The shift in N—N stretching freqeuncy occurs as a consequence of the different forms nature of hydrazine. This shift also depend on the physical state,[121] the bond length[122-124] and the field effect.[122]

Braibanti at al[119] have systematically studied the N—N streching band for various hydrazine compounds.

N—N stretching frequencies for various forms of hydrazine are given in Table 1.8

TABLE 1.8

N—N Stretching Frequency in Hydrazine

Hydrazine as	γ N–N Stretching Freq.
N_2H_2	1552 cm^{-1}
$N_2H_6^{2+}$	1023 cm^{-1}
$N_2H_3COO^-$	990–1015 cm^{-1}
$N_2H_5^+$	965 cm^{-1}
N_2H_4 (Unidentate)	~930 cm^{-1}
$H_4N_2 - N_2H_4$ (bridging)	948 – 900 cm^{-1}

1.2.2.3 THERMAL PROPERTIES OF HYDRAZINE BASED COMPOUNDS

Thermal decomposition of hydrazine is briefly described in section 1.2.1.4. Hydrazine decomposes to ammonia as a major product. Consequently, when heated, hydrazinium salts are found to decompose,[125-136] to ammonium salts. This has been experimentally confirmed by the detection of NH_4^+ as the intermediate product.

In thermal decomposition[137-142] of metal hydrazine complexes, the adduct hydrazine decomposes endothermically where as co-ordinated hydrazine decomposes exothermically.

For metal hydrazine complexes, wherever hydrazine decomposes at a fairly high temperature, which is nearer to the decomposition temperature of the corresponding salts, metal oxides (and/or metal) have been found to be the final residue in the decomposition.

The decomposition of hydrazine (whether in a simple molecule or in an ionic form) has been found[83] to be catalysed by metals such as Fe, Ni, Pt etc.. Therefore, it can be concluded that metal ion present in the metal hydrazine compound will influence its decomposition temperature.

1.2.2.4 APPLICATIONS OF HYDRAZINE AND ITS COMPOUNDS

Being varsatile hydrazine find a varity of applications[143-152] due to its unique structure and properties. It is used as a propellant in space rockets. Due to its reducing property, it is used as a corrosion inhibitor and in electroless plating[153-157] industry. It is also used in the synthesis of polymers, explosives etc. In the later, it is used due to its high exothermicity in decomposition.

The hydrazine based compounds are used as procursors[158-162] for the synthesis of material oxides, these compounds are found to yield fine powder oxides on decomposition.

1.3 PURPOSE AND SCOPE OF THE PRESENT INVESTIGATION

It is common knowledge that the effectiveness of detergent is considerably reduced when used with moderately hard water. This is due to the hardness components Ca and Mg, which react with detergent molecules, thereby, lowering its potency. Nowadays, nitrilotriacetic acid is widely used with detergent for the complexation of these components in order to overcome the retardation. It is noticed that the detergent solutions at higher temperatures are more effective in laundering. As such,it was interesting to study the effect of heat on complexation product viz calcium nitrilotriacetate and magnesium nitrilotriacetate salts. Subsequently, it was felt that the systematic study would be possible through the isolation of these salts in the solid form and by monitoring the effect of heat on these salts.

Secondly, NTA is widely used a complexing agent in the plating industry, especially electroplating. In electroplating of nickel on aluminium or mild steel, the working temperature of the plating baths is normally high. Consequently, Ni-NTA complex present in the plating bath is subjected to these high temperatures, thus affecting it stability. Therefore,it is essential to understand the thermal properties of this complex. This can be accomplished only by separating of this complex from the solution, in solid form,and carrying out its thermal studies.

NTA is also used as a complexing agent in electroless (EL) plating baths in which sodiumhypophosphite is used as the reducing agent for metal ion. Although many EL baths have been developed and patented with hydrazine[163-169] as the reducing agent, none of these baths make use of NTA as a complexing agent. Recent study on hydrazine-NTA for Nickel EL baths has shown that better quality deposits can be obtained on the substrate material. Further it was found out during the optimization of bath temperature that,higher efficiency can be achieved for electroless nickel when bath temperature is increased to about 85°C. Hence it was thought necessary to find out the nature of the product formed for Ni^{+2}—NTA— hydrazine system and also to investigate its thermoanalytical properties.

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CHAPTER TWO

CHAPTER TWO

EXPERIMENTAL

2. INTRODUCTION

The analytical procedures and the physico-chemical techniques employed in the present investigation are described in this chapter. These methods are used to characterise and to study the physical properties of the compound, isolated during the course of the investigation.

2.1 MATERIAL USED

Commercially available chemicals,(Analar or equivalent grade) are used without purification.

2.1.1 METAL COMPOUNDS

i) Magnesium Carbonate, $MgCO_3$, Sarabhai

ii) Calcium Carbonate, $CaCO_3$, (98 -100%) M & B.

iii) Strontium Carbonate, $SrCO_3$, Chemco.

iv) Barium Carbonate, $BaCO_3$, Loba-Chemie.

v) Zinc Carbonate, $ZnCO_3$, Loba-Chemie.

vi) Basic Nickel Carbonate, $NiCO_3.2Ni(OH)_2.4H_2O$, Loba-Chemie.

vii) Sodium Carbonate, Na_2CO_3, BDH.

viii) Potassium Carbonate, K_2CO_3, BDH.

ix) Ethylene Diamine Tetracetic Acid-Disodium salt, EDTA, BDH.

x) Potassium Iodate, KIO_3, BDH.

xi) Zinc Sulphate Heptahydrate, $ZnSO_4.7H_2O$, Qualigen.

xii) Hydrogen Peroxide, H_2O_2 (30 %), E.Merck.

xiii) Nitric Acid, Qualigen.

xiv) Hydrochloric Acid, Qualigen.

2.1.2 HYDRAZINE COMPOUNDS AND NTA

i) Hydrazine Hydrate, $N_2H_4.H_2O$, (99-100%) Qualigen.

ii) Hydrazine Sulphate, $(N_2H_5)_2\ SO_4$, Loba Chemie.

iii) Nitrilotriacetic Acid, $H_3[N(CH_2COO)_3]$, Loba-Chemie.

2.1.3 INDICATORS

i) Murexide.

ii) Eriochrome Black - T.

2.2 ANALYTICAL METHODS

Chemical analysis of the metal ion and hydrazine was carried out to fix the composition of product compounds.

2.2.1 ESTIMATION OF METAL

Known amount (approx 0.1g) of the compound was first decomposed[1], with 1 cc conc. HNO_3 and 3cc H_2O_2, by heating almost to dryness (on a sand bath). The residue was then extracted with 50cc of deionised water. This solution was then used as such for the estimation of metal ion.

A buffer solution with pH = 10 was prepared by using ammonium chloride and ammonium hydroxide.

A standard solution of 0.01 M EDTA[2-3] was prepared by weighing out the disodium salt of EDTA (3.7225 g per litre of solution) and dissolving it in deionised water. The solution was standardized by titrating with standard (0.01 M) zinc sulphate solution.

2.2.1.1 MAGNESIUM, CALCIUM AND ZINC ESTIMATION

The solution obtained after the decomposition of the product was maintained at pH = 10 using buffer solution and then titrated[2-3] against standard 0.01 M EDTA solution using Eriochrome Black - T indicator.

The end point was recorded when the colour of the solution changes from wine red to blue.

1 ml of 0.01 M EDTA = 0.0002432 g of Mg.
= 0.0004003 g of Ca.
= 0.0006538 g of Zn.

2.2.1.2 BARIUM ESTIMATION

Volume of the solution, after decomposition, was reduced to 25 cc by boiling and treated with about 10cc of 2N HCl. 15 cc of hot 2N H_2SO_4 was then added to precipitate Ba^{2+} as $BaSO_4$. The mixture was digested on a steam bath and filtered hot using Whatman No 40 filter paper. After washing $BaSO_4$ with warm water, it was dried and ignited in a crucible to weigh[2] as $BaSO_4$.

233.4 g of $BaSO_4$ ≡ 137.33 g of Ba.

2.2.1.3 NICKEL ESTIMATION

To the solution containing the nickel ion (2.2.1), after diluting to 75cc, about 0.05g of the indicator mixture (murexide + KNO_3) and 10 cc of 1M ammonium chloride was added. The pH of the mixture was increased to 10, by the addition of concentrated ammonia and then titrated against 0.01 M EDTA until colour changes from yellow to violet.[2-8] (the pH of the solution was further raised to 10 near end point, if required with concentrated ammonia).

2.2.2 ESTIMATION OF HYDRAZINE

Accurately weighed (0.04-0.06 g) compound was taken in a 250 cc reagent bottle. A mixture of 15 cc conc. HCl, 15 cc of deionised water and 5cc of CCl_4 was then added in it. Standard 0.025 M potassium iodate (5.350 g in one liter of the solution) was then added, with constant shaking of the stoppered bottle, until organic layer was just decolourised.[2]

1 ml of 0.025M KIO_3 ≡ 0.0008103 g of N_2H_4.

2.3 PHYSICO - CHEMICAL TECHNIQUES

The Physico-chemical techniques used in the present investigation include flame photometry, infrared spectrometry, magnetic susceptibility measurements, thermogravimetry (TGA), differential thermal analyis (DTA), etc.

2.3.1 DENSITY MEASUREMENTS

Pyknometer tube was used to determine the density of the samples. Mass of the displaced CCl_4 by the weighed amount of the solid sample in the tube was determined. By substituting the density of this liquid at ambient temperature, its volume was calculated which corresponds to the volume of the sample. The required density of the sample was then calculated using the expression $\rho = m/v$.

$$\rho_{\text{sample}} = \frac{\text{weight of the sample}}{(\text{Weight of the liquid displaced}) \div (\text{Density of the liquid})}$$

2.3.2 FLAME PHOTOMETRY

Flame photometry is the measurement[4] of the intensity of the emitted radiation by metal ions when sprayed into a flame. Intensity of emitted radiation is proportional to the amount of the ions sprayed. Hence this technique can be used for quantitative estimation of metal ions such as Na^{+}, K^{+}, Sr^{2+}, Cu^{2+} etc. in solution. The solution is sprayed on the flame with the help of the atomizer. ELICO CL 22D flame photometer was used in the present investigation.

2.3.3 INFRARED SPECTROPHOTOMETRY

Every molecule will have a number of fundamental vibrational frequencies, each of which may be associated with absorption of radiation of its own frequency. This principle[5] is followed in the infrared spectroscopy and absorption of frequencies is obtained in the form of spectrum, which are some times called "the finger prints".

The infrared spectra of solid samples were recorded by dispersing them in Nujol or fluorolobe (mull technique) and also in KBr disc (pellet technique).

TOSHNIWAL IR 408 Spectrophotometer was used to record the spectra in the range 4000 – 650 cm^{-1}. Calibration of the instrument was done with polystyrene[6] with its standard frequencies.

2.3.4 MAGNETIC SUSCEPTIBILITY MEASUREMENTS

Magnetic susceptibility may be defined as the extent to which a substance is susceptible to induced magnetisation. Paramagnetism is a type of magnetic behaviour which is exhibited by substances containing unpaired electrons. These substances are weakly attracted in the magnetic field.

Guoy method[7] is one of the simplest method of measuring the magnetic susceptibility. In this method, the sample in the form of uniform rod is suspended vertically in a strong non-homogeneous magnetic field generated by electromagnets. The force exerted on the rod is measured equivalent to weight difference by a conventional weighing technique.

Mercury tetrathiocyanato cobaltate [$HgCo(CNS)_4$] was used as the calibrant[8,9] for the tube, which was later on used for the solid samples. All the measurements were made at the ambient temperature. The molar susceptibility χ_m was first obtained and corrected for the diamagnetism using Pascal[10] constants. From corrected molar susceptibility χ_m, the effective magnetic moment was calculated by relation :

$$\mu_{eff} = 2.84 \sqrt{\chi_m \times T}$$

where T is the temperature in deg. Kelvin.

2.3.5 THERMOANALYTICAL TECHNIQUES

Thermal analysis techniques are those methods in which the changes in the physical and/or chemical properties of a substance is measured as a function of temperature. In these methods,[11-13] the substance is subjected to a controlled temperature, heating or cooling or constant temperature (isothermal). Most commonly used techniques, thermogravimetry and differential thermal analysis, are employed in the present investigation. Since single thermal analysis technique may not provide sufficient information, it is necessary to have the combination of the two techniques for reliability and complementary data. TG and DTA curves[14-16] are affected by various factors such as :

i) nature and shape of material used as sample holder,
ii) particle size of the sample,
iii) packing density of the sample,
iv) sample weight and its history,
v) surrounding atmosphere,
vi) sensitivity of the thermocouple.

Heating rate employed for TG/DTA was $5^{o}, 10^{o}, 20^{o}$ C min^{-1}, in air or nitrogen (20 ml min^{-1} as flow rate) or argon (same flow rate). About 10 mg of the sample in platinum cups was used for each experiment. Platinum – rhodium thermocouple was used as temperature detectors.

2.3.5.1 THERMOGRAVIMETRY

In thermogravimetry, mass of the sample under investigation is measured as a function of temperature, whilst the sample is subjected to a controlled temperature (heating, cooling or isothermal). The type of weight change observed in the TG and reaction is given in Table 2.1 .

The TG experiments were carried out using the instrument SHIMADZU THERMOBALANCE (model TD-30).

TABLE 2.1

The Reactions and the Observed Change in TGA.

Reaction	Adsorption or Absorption or Oxidation	Desorption or Decomposition or Reduction	Vapourisation or Sublimation or Dehydration	Solid state reaction
TG data	gain	loss	loss	gain or loss

2.3.5.2 DIFFERENTIAL THERMAL ANALYSIS

In DTA, sample and an inert material are simultaneously heated at a controlled heating rate. And the temperature difference between the two is recorded as a function of furnace temperature.

NETZSCH STA-409 Thermal Analyser was used to study the thermoanalytical properties of some of the compounds.

Table 2.2 gives different reactions and the corresponding DTA effect.

TABLE 2.2

The Reactions and the Observed Effects in the DTA

Reaction	Adsorption or Absorption	Vapourisation or Sublimation or Dehydration	Decomposition	Oxidative degradation
Thermal effect	exothermic (+)	endothermic (−)	exo or endo (+) or (−)	endo or exo (+) or (−)

2.3.6 X-RAY POWDER DIFFRACTION

The X-ray powder diffraction patterns were obtained using PHILLIPS X-Ray Diffractometer Mode PW 1840 using Cu$k\alpha$ radiation with nickel filter.

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CHAPTER THREE

CHAPTER THREE

SYNTHESIS, CHARACTERIZATION AND PROPERTIES OF METAL HYDRAZINIUM NITRILTRIACETATES

3 INTRODUCTION

The metal ions are known[1] to form salts with nitrilotriacetic acid which has three carboxylate groups. In the case of the transition metal ion, the complex formation in solution has been extensively studied,[2] both potentiometrically and colorimetrically. The knowledge of the stability of these complexes, especially that of nickel and copper, is important in formulation of plating bath.[3] Although these complexes have been isolated in the solid form by some workers [4], their properties in this physical state have not been thoroughly examined.

It is evident from the literature survey that a ternary system containing the NTA and hydrazine with metal ion has not been investigated. Interestingly, these three have been important components, albeit independent, in eletroles plating baths. Moreover, the reaction between hydrazine and metal NTA salt has not been studied with regard to product formation.

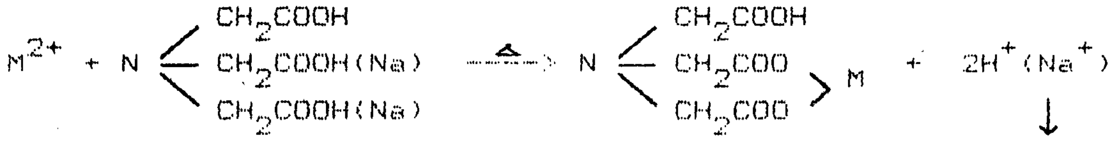
As such, the present investigation undertakes to study some of the physical properties of the metal NTA salts. Similarly, the reaction between hydrazine and these salts is studied by isolating of the products and characterizing them by chemical analysis as well as physico-chemical techniques. The findings of this investigation are presented in this chapter.

3.1 EXPERIMENTAL:SYNTHESIS OF METAL-NTA SALTS

Syntheses of metal nitrilotriacetates have been reported[1] in the literature. The three different methods which are standardized involve.

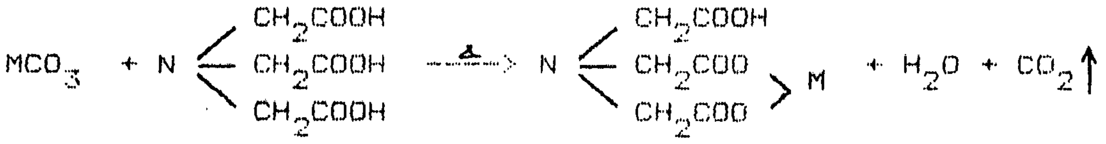
(i) reaction[4] between metal chloride (or sulphate) and sodium salt of NTA in aqueous medium.

(ii) reaction[1] between metal chloride (or sulphate) and warm aqueous suspension of NTA.



$$M^{2+} + N \left\langle \begin{array}{l} CH_2COOH \\ CH_2COOH(Na) \\ CH_2COOH(Na) \end{array} \right. \xrightarrow{\Delta} N \left\langle \begin{array}{l} CH_2COOH \\ CH_2COO \\ CH_2COO \end{array} \right\rangle M + 2H^+(Na^+)\downarrow$$

(iii) reaction[5] between metal carbonate and NTA in a warm aqueous suspension.



$$MCO_3 + N \left\langle \begin{array}{l} CH_2COOH \\ CH_2COOH \\ CH_2COOH \end{array} \right. \xrightarrow{\Delta} N \left\langle \begin{array}{l} CH_2COOH \\ CH_2COO \\ CH_2COO \end{array} \right\rangle M + H_2O + CO_2\uparrow$$

In the present investigation, last reaction was carried out to synthesize the salts. The product was recrtystallized in water and the yield was between 52-89 % depending on the salt.

3.1.1 SYNTHESES OF METAL-NTA HYDRAZINIUM SALTS

Metal NTA salt solutions were prepared by the method mentioned in the previous section. This solution (pH = 4.8) was treated with hydrazine hydrate - $N_2H_4.H_2O$ (stoichiometric $M:NTA:N_2H_4$ equal to 1:1:1 or excess for the last) and the product so obtained in solution was isolated under different conditions mentioned below.

<u>Method 1</u> : The solution was concentrated on a steambath to reduce the volume and allowed to stand for a few days in a vaccum dessicator The solid compound, so formed, was filtered and purified by recrystallization in water.

<u>Method 2</u> : The solution was treated with ethanol to precipitate out the compound. It was then purified by recrystallization.

<u>Method 3</u> : The solution was kept in freezing mixture to separate out the compound and then it was filtered and purified by recrystallization.

In the case of Mg, Ca, Sr and Zn colourless compounds were obtained, whereas Ni formed bluish green product.

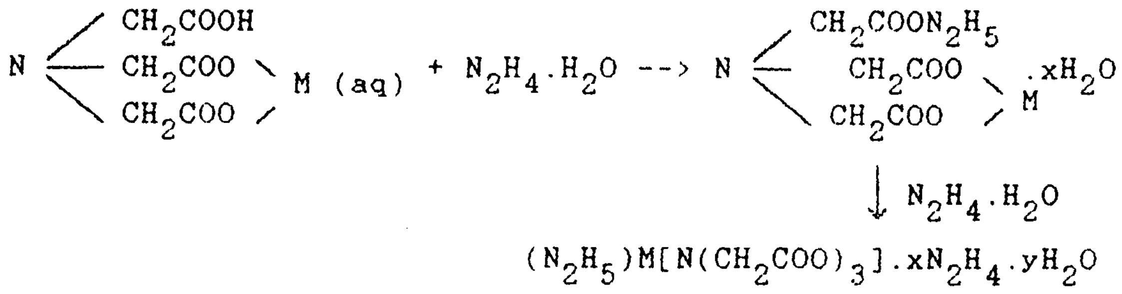
3.1.2 SYNTHESES OF NICKEL Na/K-NTA HYDRAZINATE SALTS

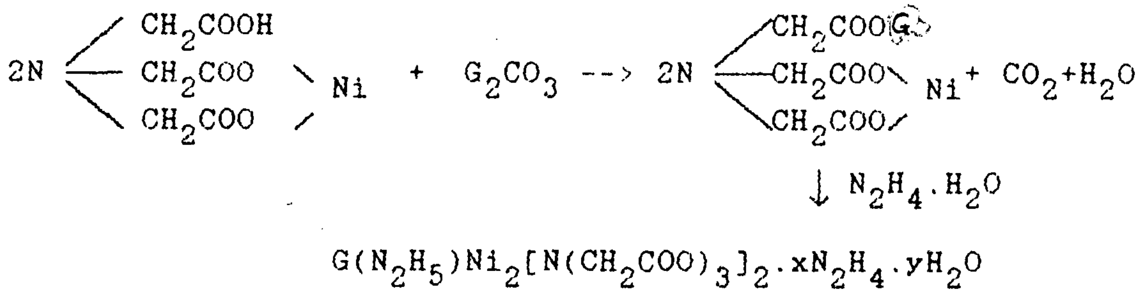
The mixed metal salt solution with nickel and sodium (or potassium was prepared by the addition of 0.05 m Na_2CO_3 (or K_2CO_3) from burette to the nickel - NTA solution until the pH of the solution was increased[5] to ~6.9. This solution was then treated with hydrazine hydrate and the product was isolated in the solid form by the different methods mentioned in section 3.1.1.

3.2 RESULTS AND DISCUSSION : CHARACTERIZATION OF THE SALTS

The chemical analysis of the compounds was carried out by methods described in Chapter Two. The metal contents in the metal - NTA salts are in agreement (Table 3.1)with those reported by Tomita and Ueno. All the salts are found to be hydrated.

Similarly, different chemical formulae are proposed (Table 3.1) on the basis of the metal and hydrazine contents in the hydrazine derivatives of the metal-NTA salts. It was observed that different compounds are formed depending on the method of isolation.





where G = Na or K

3.3 PHYSICAL PROPERTIES OF THE COMPLEXES

Pyknometric densities of the salts and the complexes were experimentally found out at the ambient temperature by the method described in Chapter Two. Comparison of the densities of the metal salts and the hydrazine derivatives, is given in (Table 3.2)

Code	Method Of Preparation
MG-1	(iii) in Sec 3.1
MG-3	(1) in Sec 3.1 (ratio 1:1:1)
MG-4	(1) in Sec 3.1.1 (Excess Hy.Hy.)
CA-1	(iii) in Sec 3.1
CA-3	(1) in Sec 3.1.1 (ratio 1:1:1)
SR-1	(iii) in Sec 3.1
SR-3	(1) in Sec 3.1.1 (ratio 1:1:1)
BA-1	(iii) in Sec 3.1
ZN-1	(iii) in Sec 3.1
ZN-3	(1) in Sec 3.1.1 (ratio 1:1:1)
NI-1	(iii) sec 3.1
NI-3	(3) in Sec 3.1.1 (ratio 1:1:1)
NI-4	(1) in Sec 3.1.1 (excess Hy.Hy.)
NI-5	(1) in Sec 3.1.1 (without conc.) 1:1:2
NI-6	(2) in Sec 3.1.1 (ratio 1:1:1)
NI-8	(2) in Sec 3.1.1 (excess Hy.Hy.)
NI-9	Sec 3.1.2
NI-10	Sec 3.1.2
NI-11	Sec 3.1.2
NI-12	Sec 3.1.2 (excess Hy.Hy.)

TABLE 3.1

Chemical Analysis Data of Metal Nitrilotriacetates and Their Hydrazine Derivatives

TABLE 3.1-A

Code	Metal Content %Obsd	Metal Content %Theor.	Hydrazine Content %obsd	Hydrazine Content %Theor.	Formula Assigned $Y = N(CH_2COO)_3$	Molecular Weight
MG-1	8.94	9.08	–	–	$HMg[Y].3H_2O$	267.45
MG-3	9.19	9.22	12.29	12.14	$(N_2H_5)Mg[Y].H_2O$	263.45
MG-4	8.55	8.63	12.58	11.36	$(N_2H_5)Mg[Y].2H_2O$	281.45
CA-1	15.00	15.11	–	–	$HCa[Y].2H_2O$	265.22
CA-3	12.77	13.48	10.72	10.76	$(N_2H_5)Ca[Y].2H_2O$	297.22
SR-1	24.9	25.12	–	–	$HSr[Y].4H_2O$	348.76
SR-3	27.07	26.81	10.18	9.79	$(N_2H_5)Sr[Y].H_2O$	326.76
BA-1	35.86	36.09	–	–	$HBa[Y].3H_2O$	380.47
ZN-1	22.40	22.50	–	–	$HZn[Y].2H_2O$	290.52
ZN-3	21.48	21.49	10.76	10.50	$(N_2H_5)Zn[Y].H_2O$	304.52
NI-1	17.36	17.37	–	–	$HNi[Y].5H_2O$	337.84
NI-3	16.15	16.68	8.91	9.09	$(N_2H_5)Ni[Y].4H_2O$	351.84
NI-4	14.07	14.60	15.74	15.92	$(N_2H_5)Ni[Y].N_2H_4.5H_2O$	401.84
NI-5	13.61	13.91	11.44	11.37	$(N_2H_5)Ni[Y].0.5N_2H_4.7H_2O$	421.84
NI-6	17.78	17.58	10.22	9.58	$(N_2H_5)Ni[Y].3H_2O$	333.84
NI-8	17.84	17.68	14.20	14.46	$(N_2H_5)Ni[Y].0.5N_2H_4.2H_2O$	331.84

TABLE 3.1-B

Code	Metal Content		Hvdrazine Content		Formula Assigned	Molecular Weight
	%Obsd	%Theor.	%Obsd	%Theor.	$Y = N(CH_2COO)_3$	
NI-9	18.08	18.46	15.19	15.10	$Na(N_2H_5)Ni_2[Y]_2.2N_2H_4.3H_2O$	635.68
NI-10	19.25	19.44	10.75	10.6	$Na(N_2H_5)Ni_2[Y]_2.N_2H_4.3H_2O$	603.68
NI-11	18.5	18.940	10.45	10.31	$K(N_2H_5)Ni_2[Y]_2.N_2H_4.3H_2O$	619.68
NI-12	18.3	18.01	14.98	14.73	$K(N_2H_5)Ni_2[Y]_2.2N_2H_4.3H_2O$	651.68

	Na Content			K Content	
	%Obsd	%Theor.		%Obsd	%Theor.
NI-9	3.55	3.61	NI-11	6.35	6.29
NI-10	3.81	3.8	NI-12	5.55	5.98

On hydrazination, the volume of the nitrilotriacetic salts of all the metals, except nickel, is reduced as seen from the increased density values. In the caseofnickel, however all the compounds formed after hydrazination, are found to be lighter than the nickel - NTA salt.

TABLE 3.2

Densities of Compounds Determined By Pyknometric Method.

Metal NTA salt density (ρ) g/cc code no. of sample	Metal-NTA-hydrazine density (ρ) g/cc code no. of sample
1.690 (MG-1)	1.73 (MG-3) 2.24 (MG-4)
1.6541 (CA-1)	1.95 (CA-3)
1.9727 (SR-1)	1.63 (SR-3)
1.6918 (BA-1)	-
1.566 (ZN-1)	1.8274 (ZN-3)
2.2825 (NI-1)	1.5249 (NI-3) 1.2344 (NI-4) 1.9223 (NI-5) 1.7008 (NI-6) 1.7596 (NI-8)
Ni/Na	1.4920 (NI-9) 1.1542 (NI-10)
Ni/K	1.6035 (NI-11) 1.5498 (NI-12)

When the nickel - NTA salt solution was conductometrically titrated with 5% $N_2H_4.H_2O$ solution, the conductance of the salt was found to increase initially, (upto $M:N_2H_4$ amount equal to one) and then remaining almost constant. This could be due to the neutraliziation of the third -COOH group by $N_2H_4.H_2O$ (or N_2H_5OH), which is a weak base. And the increased conductance is due to the ionic character of $N_2H_5^+$ ion.

The magnetic moments of nickel based NTA complexes are calculated from the magnetic susceptibility, measured at ambient temperature.

These values (Table 3.3) indicate that the complexes are of high spin variety.

TABLE 3.3

Magnetic Moments of the Complexes

	Complex $Y = N(CH_2COO)_3$	μ_{eff}
1	$HNi[Y].5H_2O$	3.6637
2	$(N_2H_5)Ni[Y].4H_2O$	3.8706
3	$(N_2H_5)Ni[Y].N_2H_4.5H_2O$	3.8565
4	$(N_2H_5)Ni[Y].0.5N_2H_4.7H_2O$	3.9137
5	$(N_2H_5)Ni[Y].3H_2O$	3.7790
6	$(N_2H_5)Ni[Y].0.5N_2H_4.2H_2O$	3.8588
7	$Na(N_2H_5)Ni_2[Y]_2.2N_2H_4.3H_2O$	7.5106
8	$Na(N_2H_5)Ni_2[Y]_2.N_2H_4.3H_2O$	5.0204
9	$K(N_2H_5)Ni_2[Y]_2.N_2H_4.3H_2O$	5.2031
10	$K(N_2H_5)Ni_2[Y]_2.2N_2H_4.3H_2O$	5.0515

3.4 SPECTRAL PROPERTIES OF THE SALTS

Tomita and Ueno[5] have studied the infrared spectra of the metal NTA salts both in solid state and in solution. The strong absorption bands for the three carboxyl groups in the NTA have been assigned to asymmetric and symmetric C-O stretching vibrations. However, in ionic carboxyl groups, band at ~1735 cm^{-1} has been found to disappear and a new band ~1680 cm^{-1} observed. Consequently these three regions have been studied to predict the possible structures of metal NTA salts. Also, the shifting[7] of band from 1730 to ~1580 cm^{-1} has been observed which is attributed to the loss of positive charge on nitrogen in NTA through the formation of Zwitter ion. Infrared spectral data of metal nitrilotriacetate salts are given in Table 1.6.

Presence of a weak band at 1720 cm^{-1} and a strong band ~1620 cm^{-1} have been assigned to the presence of one undissociated and two ionic carboxylic groups. And the difference between these two wave numbers have been found useful[8] to get the knowledge on oxygen metal bond.

In the present investigation, infra red spectra of solid metal NTA salts show typical absorption bands as observed by Tomita et al. For compounds obtained after hydrazination, no absorption is observed ~1730 cm^{-1} suggesting that the third -COOH in the salt is neutralized by the hydrazinium hydroxide, ($N_2H_4{\cdot}H_2O$), a weak base. This gives rise to an additional band ~945 cm^{-1} due to $N_2H_5^+$, hydrazinium ion, since N-N stretching is known[9] to occur in that region. Most of the characteristic carboxylate absorption overlap those of hydrazinium ion hence broad bands are observed[10,11] for the compounds in the region ~1640 (-COOM and $-NH_2$ bending), 1560(ν_{asym} COO^- stretching and bending of $-NH_3^+$), 1150 (-CN and $-NH_2$ twisting), and 980 cm^{-1} (νC-C and νN-N stretching).

Infrared spectral data of the hydrazine based metal nitrilotriacetate salts is presented in Table 3.4. The comparison of the infrared spectrum obtained for the metal-NTA salts and their hydrazine derivatives is demonstrated in Fig. 3.1 to 3.11.

TABLE 3.4

TABLE 3.4-A

Infrared Spectral Data (cm^{-1}) of $(N_2H_5).M[N(CH_2COO)_3].xH_2O$

Key M/x --> Assignement ↓	Mg/1	Mg/2	Ca/2	Sr/1	Zn/1
1. -OH	3425 2900 s	3400 m 2900 s	3475 m 2900 s	3400 m 2900 s	3420 2940
2. Unionised -COOH	--	--	--	--	--
3. -COOH	1670 1630	1660	--	--	1662
4. co-ordinated -COOM	1630	1630	1605	1625	1625
5. Stretching ν_{asym} COO^-	1585	1570	1585	1585	1590
6. Stretching ν_{sym} COO^-	1425	1430	1470 m 1440s,r	1440 1415	1450
7. $-COO^-$	1310	1370 1305	1370 s 1310 m	1325	1305
8. C-N	1155 1125	1115	1120	1125	1122
9. $-COO^-$	1020	1020	1012	1018s,r	1015
10. C-C	970 910	985 905	990 m,r 930 s,r	992 r 922s,r	980 905
11. Stretch. ν_{N-N}	940	950	960 m	950	945
12. $-COO^-$	720	730	720s,r	712	725

TABLE 3.4-B

Infrared Spectral Data (cm^{-1}) of

$(N_2H_5).Ni[N(CH_2COO)_3].xN_2H_4.yH_2O$

x= ---> y= Assignement ↓	NiNTA (Table1.6)	x=0 y=4	x=1 y=5	x=0.5 y=7	x=0.5 y=2	x=0 y=3
1. -OH	3520	3575 m 3350 s	3500 m 3300 s	3500 m 3340 s	3600m 3375s 3200m	3500m 3250s
2. Unionised -COOH	1730	---	---	---	---	---
3. -COOH	1665 s	1680m	1770m	1680m	1675m	1680m
4. co-ordinated -COOM	1625 s	1620s	1620s	1620s	1620m	1620m
5. Stretching ν_{asym} COO^-	1585 s	1580s	1570s	1590s	1590s	1580s
6. Stretching ν_{sym} COO^-	1432 s	1422s	1420s	1440s	1425s	1420
7. $-COO^-$	1317m	1365m 1310s	1320m	1345 1300m	1365m 1310s	1330m 1310m
8. C-N	1120m	1150s 1130s	1170s 1130s	1170s 1130s	1150s 1130m	1170s 1135sr
9. $-COO^-$	1010m	1018m,r	1018m,r	1020m	1015m,r	1025s,r
10. C-C	970m 912m	995m,r 918s,r	990m,r 920s,r	995m 925s,r	990s,r 920s,r	990s,r 918
11. Stretch ν_{N-N}	--	950m	950 m	950m	950m	945m
12. $-COO^-$	720	740 s	750s	755s	730s	750s

TABLE 3.4-C

Infrared spectral Data (cm^{-1}) of $G(N_2H_5).Ni_2M[N(CH_2COO)_3]_2xN_2H_4.yH$

Assignement ↓	G=Na x=2 y=3	G=Na x=1 y=3	G=K x=1 y=3	G=K x=2 y=3
1. -OH	3500 m 3300 s	3500 m 3250 s	3500 m 3250 s	3500 m 3300 s
2. Unionised -COOH	--	--	--	--
3. -COOH	1670s	1670 m	1675 m	1665 m
4. co-ordinated -COOM	1610 s	1620 s	1620 s	1625 s
5. Stretching ν_{asym} COO^-	1585 s	1580 s	1590 s	1580 s
6. Stretching ν_{sym} COO^-	1425 s	1410 s	1420s,r	1425 s
7. $-COO^-$	1325 m	1320 m 1300 m	1330 m 1308 m	1330 m
8. C-N	1130 m	1130 m	1170 m 1135 m	1170 s 1130 m
9. $-COO^-$	1020 m	1020 m	1023 m	1020
10. C-C	990 s,r 920	980 s,r 915	985 s 918 s,r	990 m 920s,r
11. Stretch ν_{N-N}	948 m	950 m	950 m	950w
12. $-COO^-$	750 s	750 s	750 s	750 m

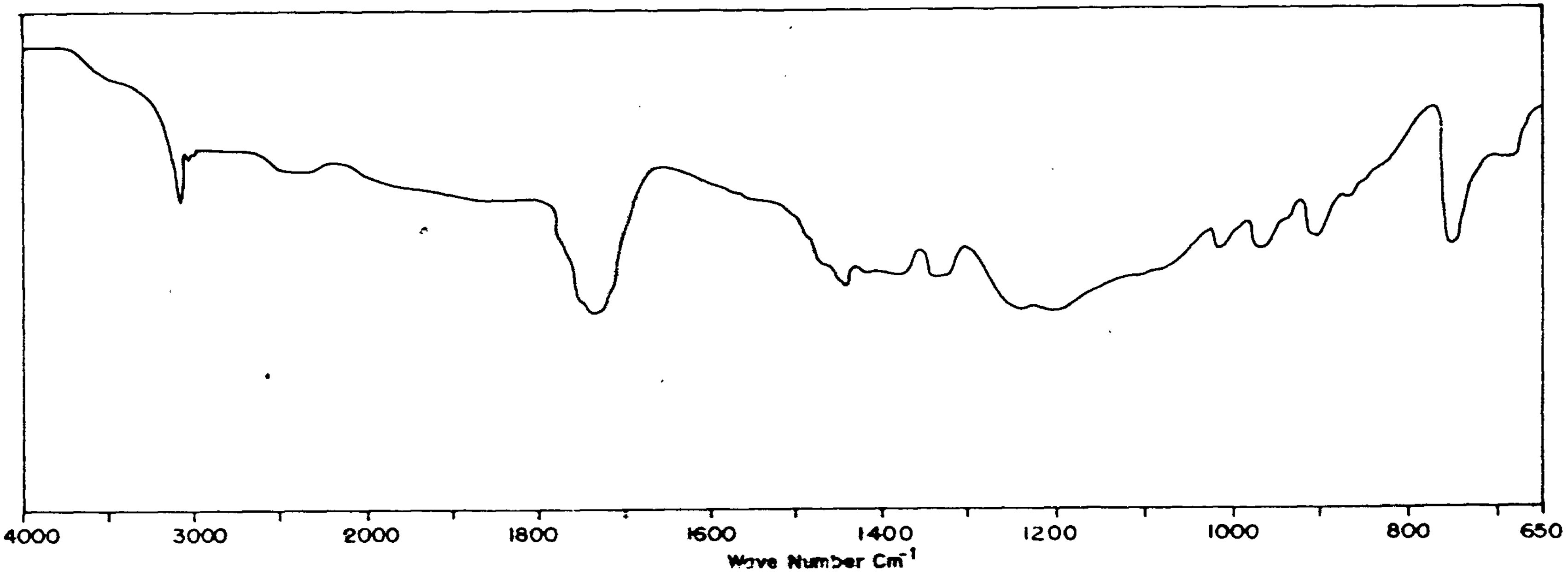


Fig.3.1 IR of H_3 $N(CH_2COO)_3$ Nitrilotriacetic Acid

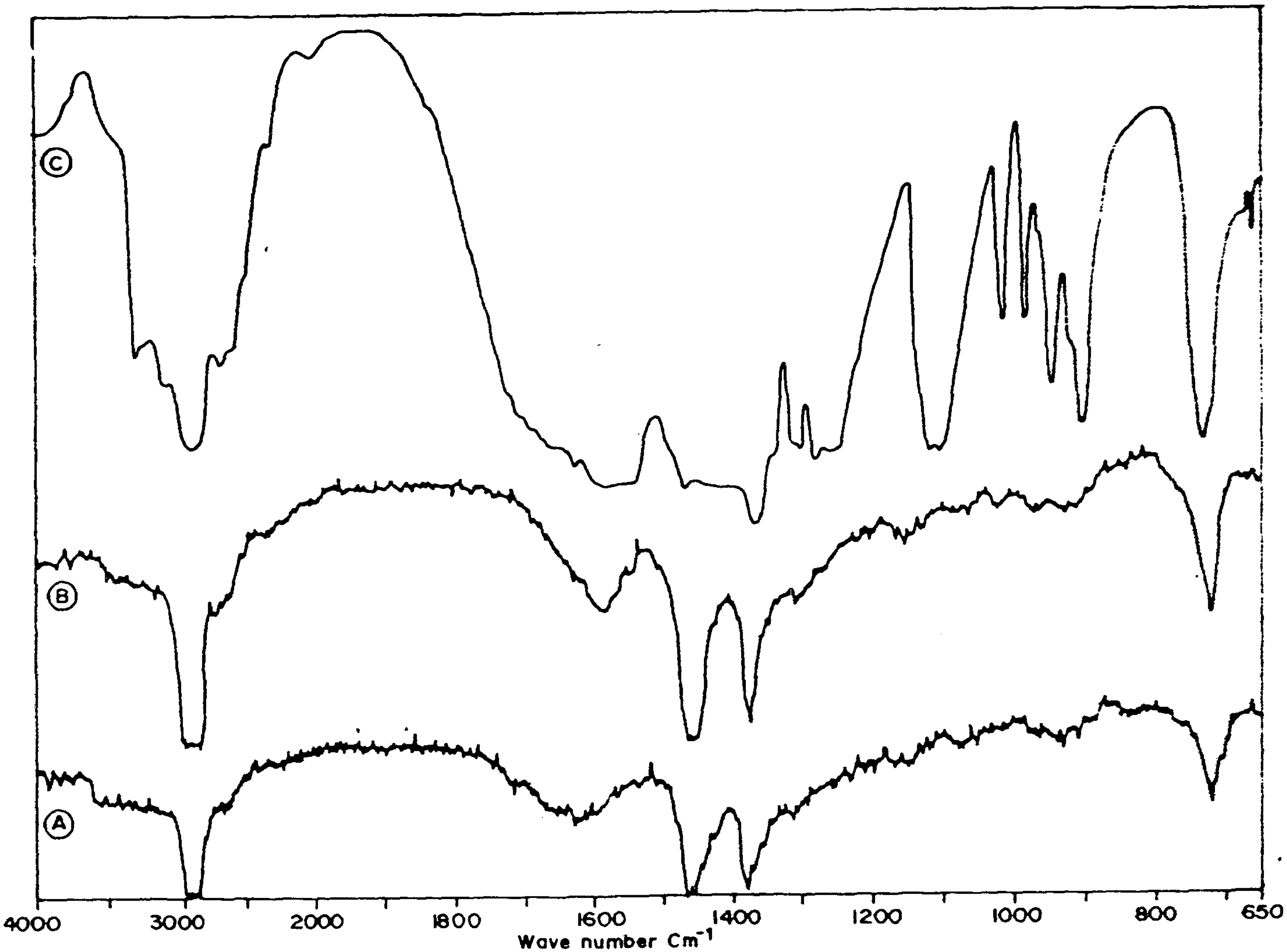


Fig.3.2 IR of A- HMg N $(CH_2COO)_3 \cdot 3H_2O$, B- $(N_2H_5)MgN(CH_2COO)_3 \cdot H_2O$, C- $(N_2H_5)MgN(CH_2COO)_3 \cdot 2H_2O$

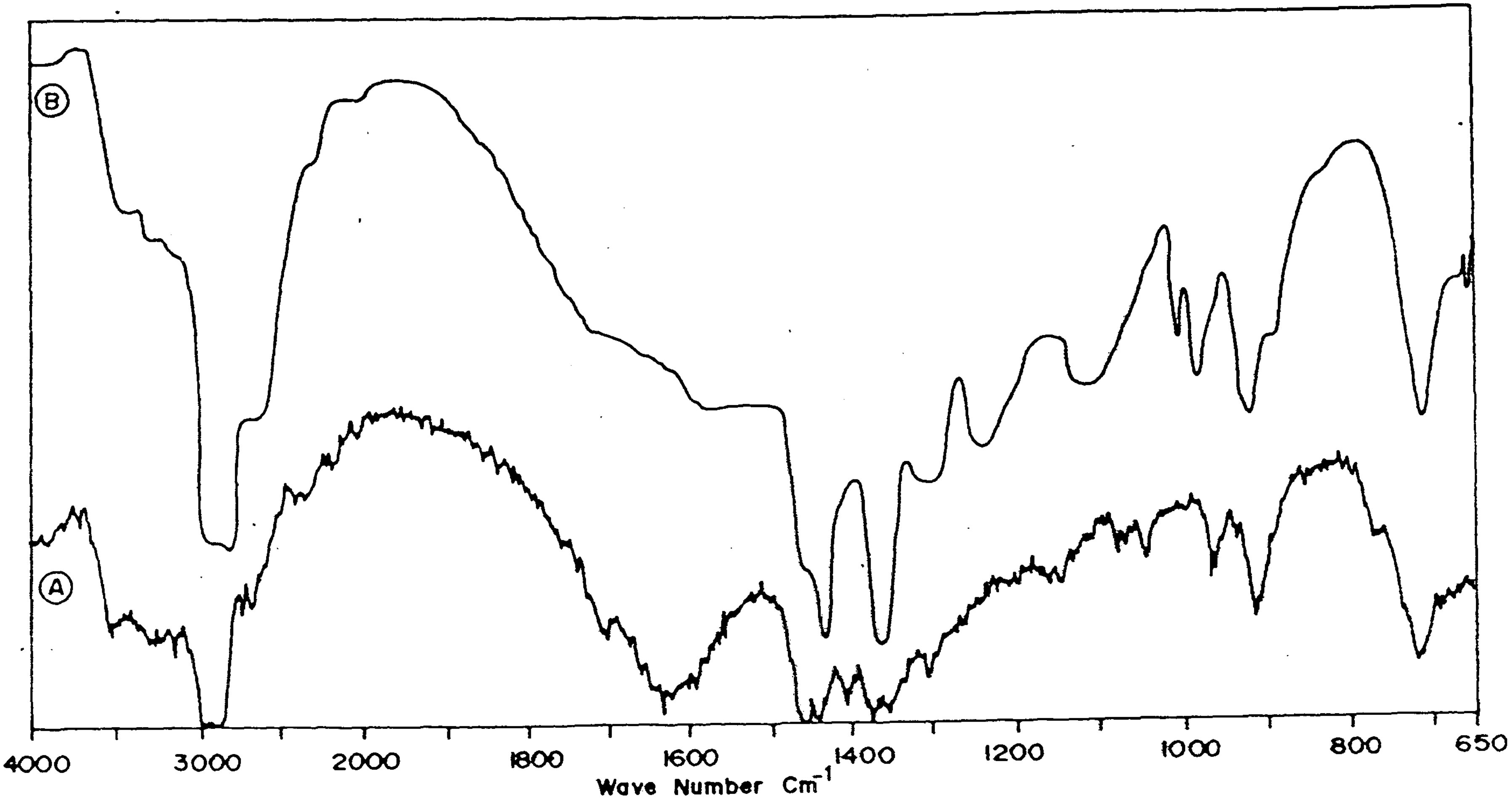


Fig.3.3 IR of A - $HCaN(CH_2COO)_3 \cdot 2H_2O$, B - $(N_2H_5)CaN(CH_2COO)_3 \cdot 2H_2O$

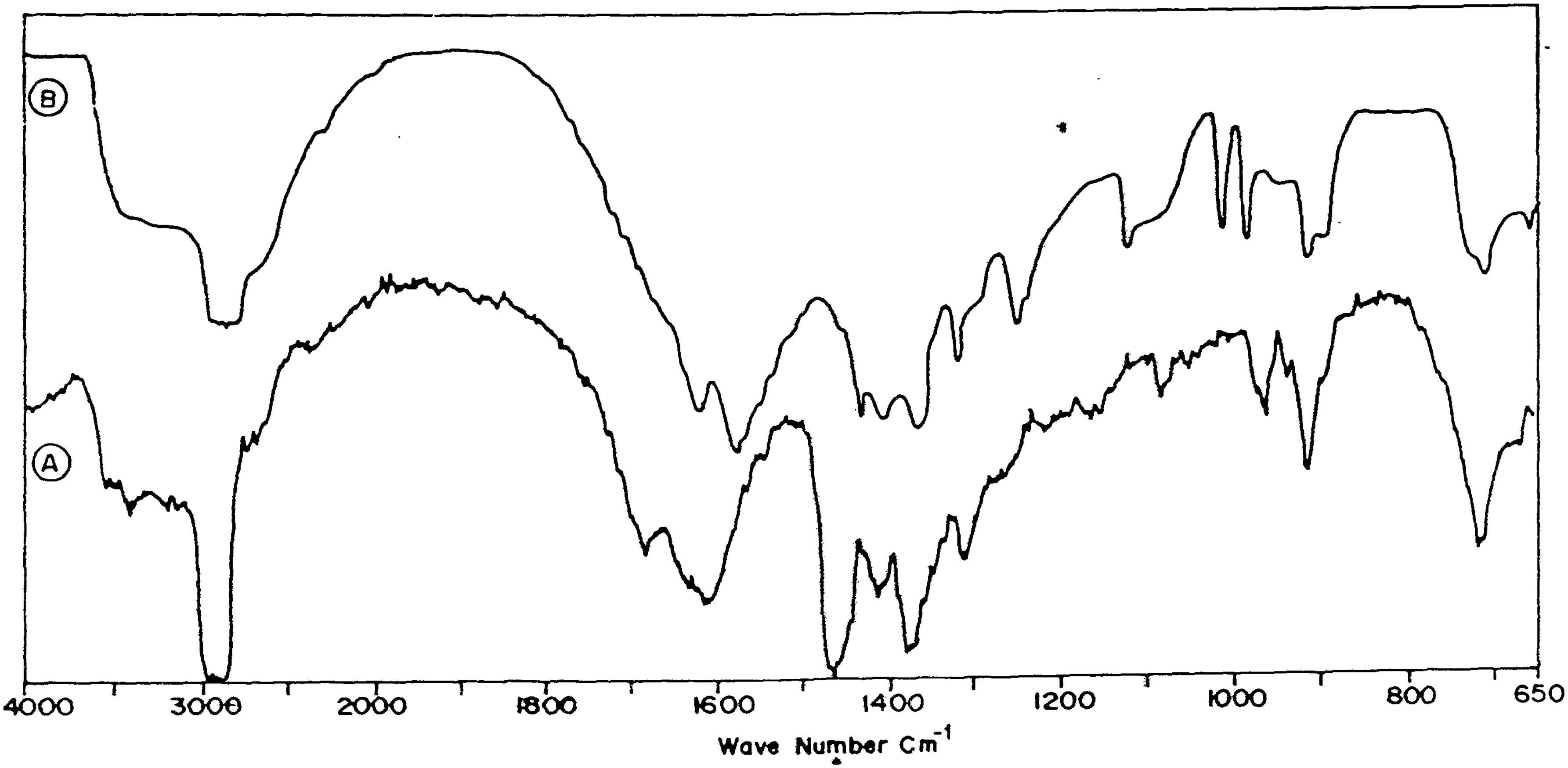


Fig.3.4 IR of A - $HSr\ N\ (CH_2COO)_3 \cdot 4H_2O$, B - $(N_2H_5)\ Sr\ N\ (CH_2COO)_3 \cdot H_2O$.

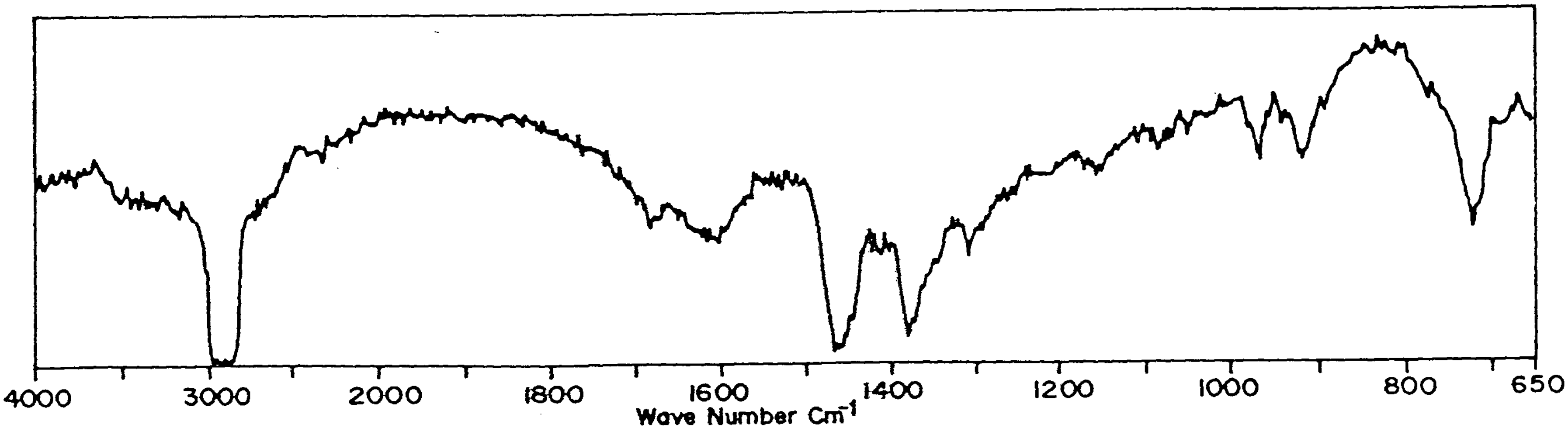


Fig.3.5 IR of HBaN $(CH_2COO)_3 \cdot 3H_2O$

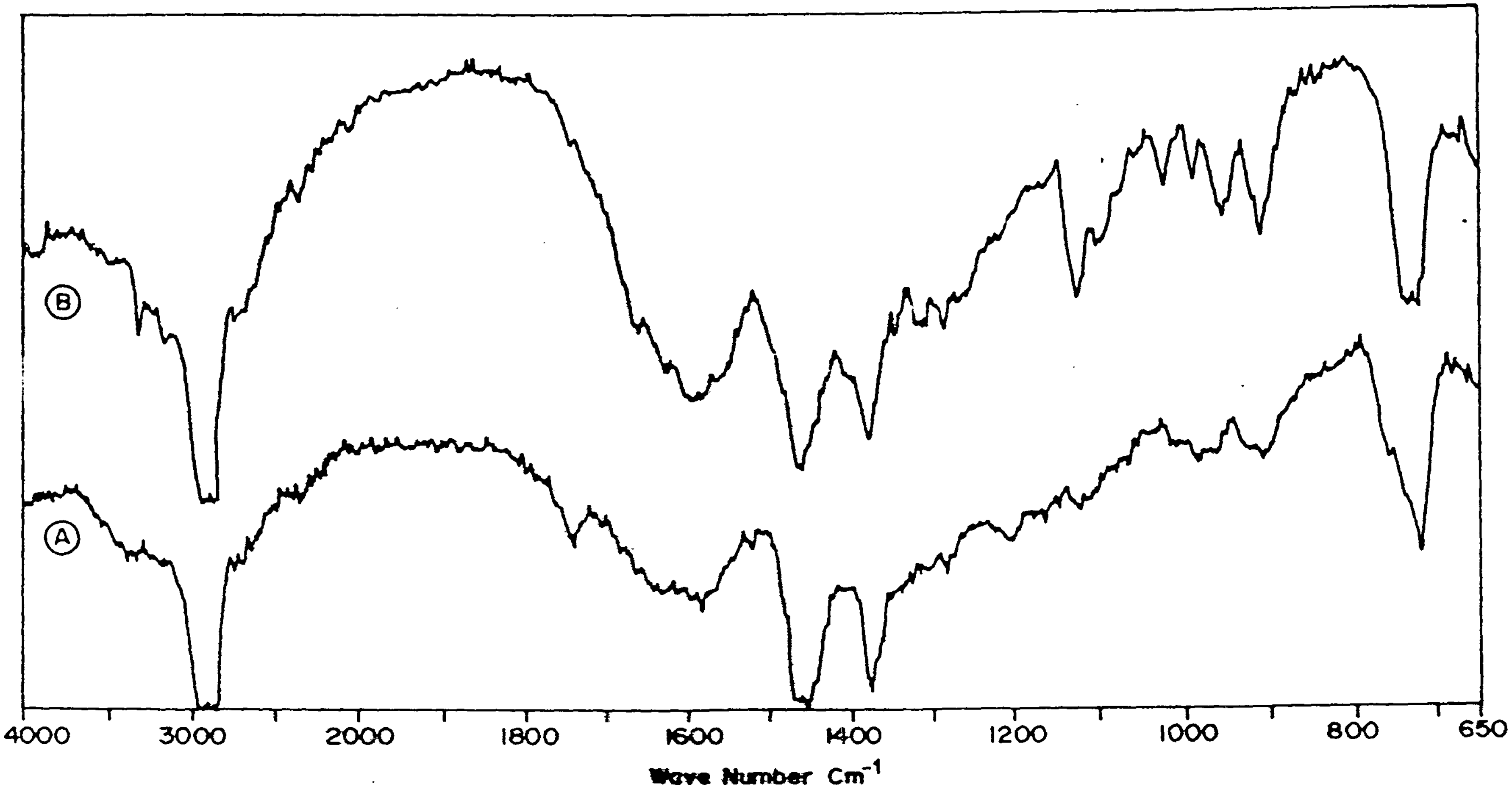


Fig.3.6 IR of A – $HZn\,N\,(CH_2COO)_3 \cdot 2H_2O$, B – $(N_2H_5)\,Zn\,N\,(CH_2COO)_3 \cdot H_2O$.

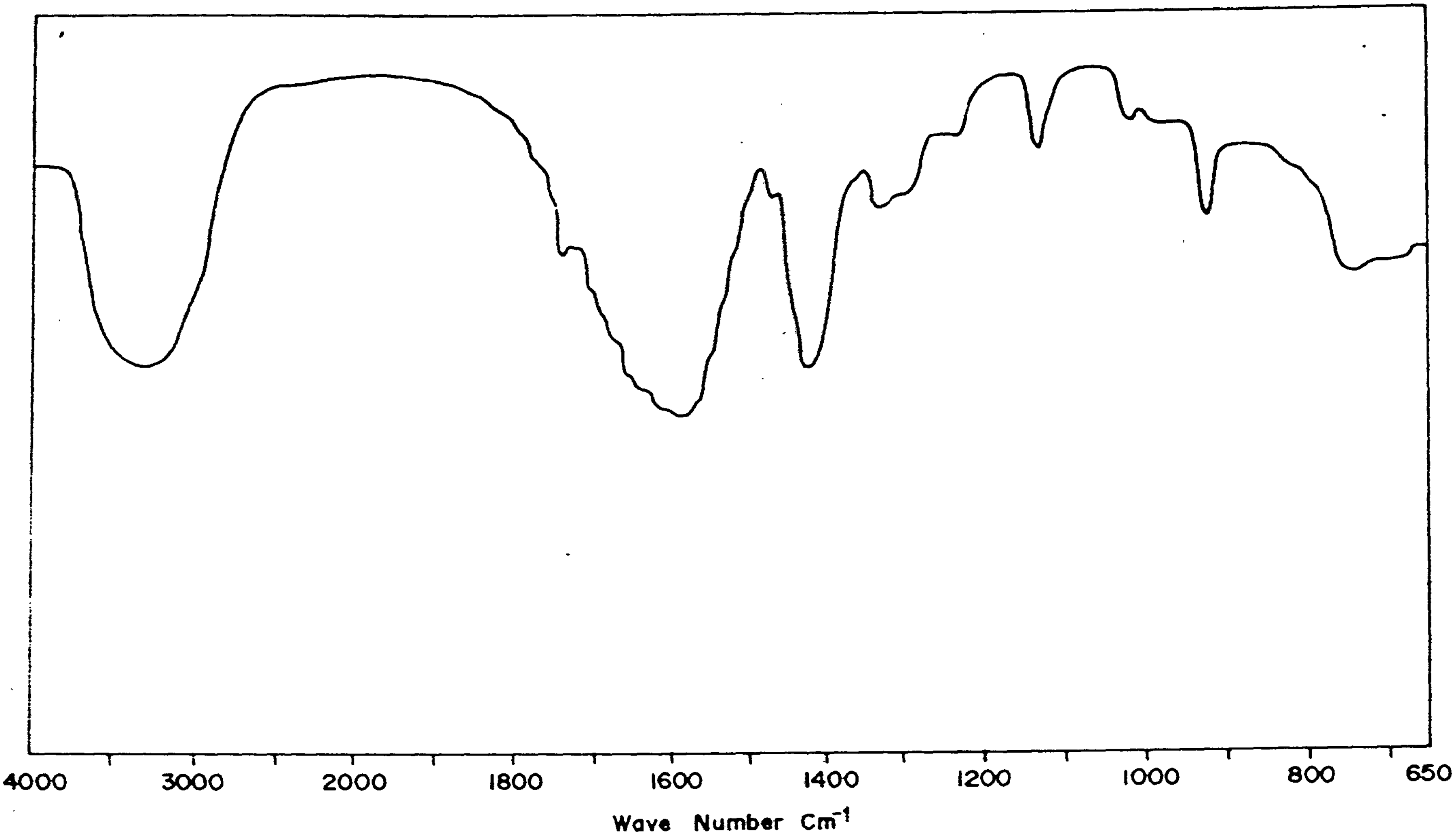


Fig. 3.7 IR of H Ni N $(CH_2COO)_3 \cdot 5H_2O$

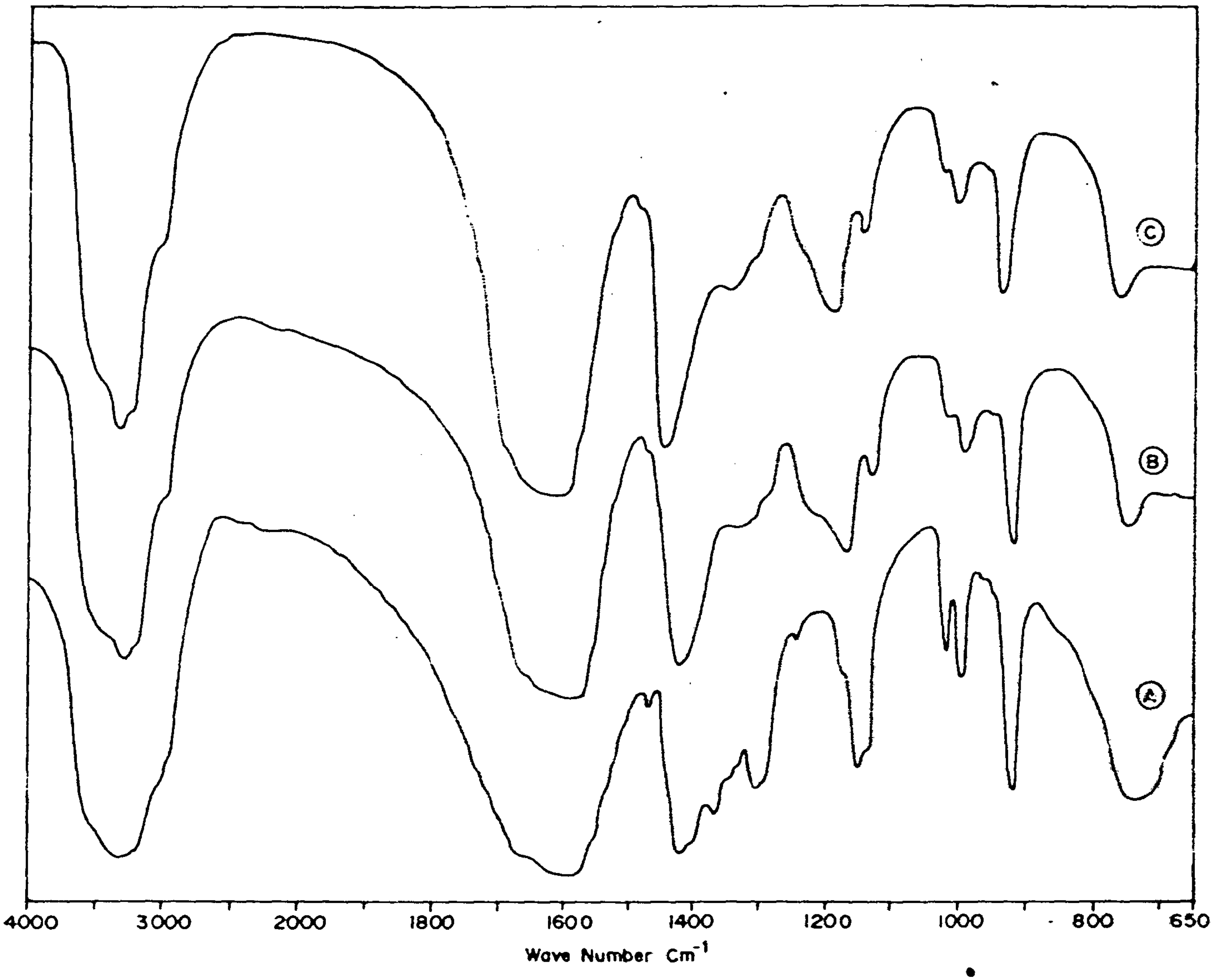


Fig 3.8 IR of A-$(N_2H_5)NiN(CH_2COO)_3 \cdot 4H_2O$, B-$(N_2H_5)NiN(CH_2COO)_3N_2H_4 \cdot 5H_2O$, C-$(N_2H_5)NiN(CH_2COO)_3 \cdot 0.5N_2H_4 \cdot 7H_2O$

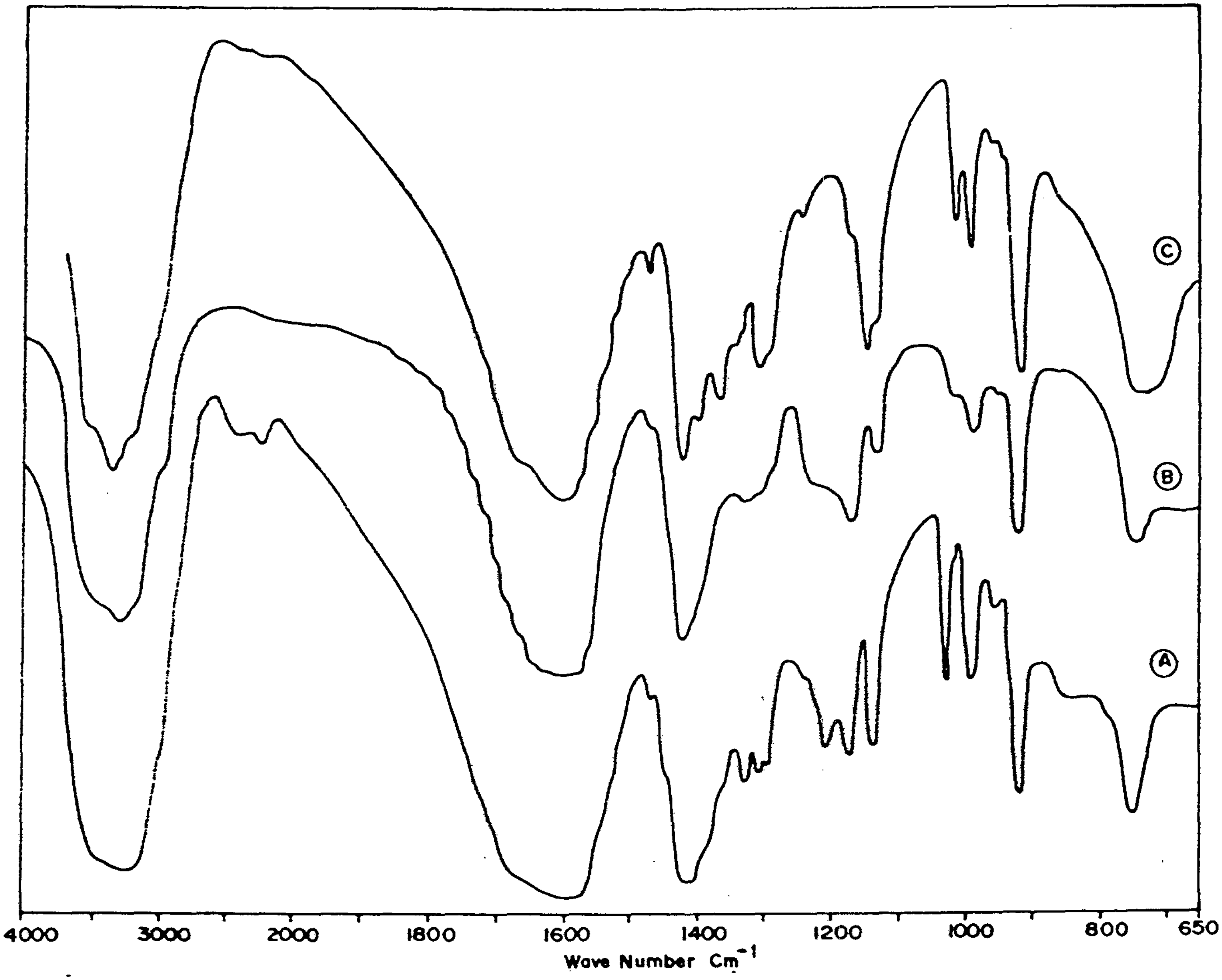


Fig. 3.9 IR of A-$(N_2H_5)Ni(N(CH_2COO)_3)\cdot 3H_2O$, B-$(N_2H_5)Ni(N(CH_2COO)_3)\cdot 0.5N_2H_4\cdot 1.5H_2O$, C-$(N_2H_5)Ni(N(CH_2COO)_3)\cdot 0.5H_2O\cdot 2H_2O$

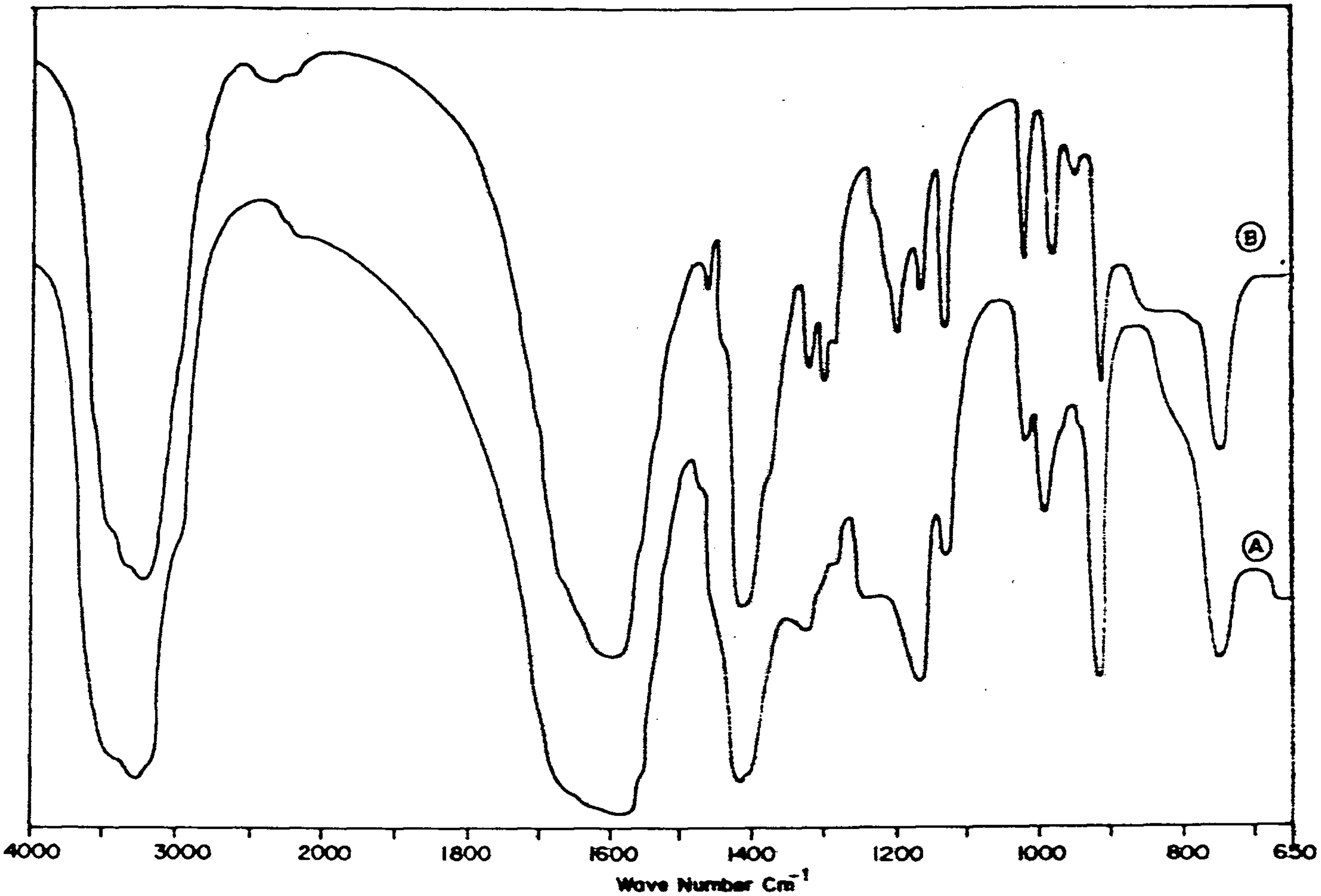


Fig 3.10 A - $Na(N_2H_5)Ni_2[N(CH_2COO)_3].2N_2H_4 \cdot 3H_2O$, B - $Na(N_2H_5)Ni_2[N(CH_2COO)_3]_2.N_2H_4 \cdot 3H_2O$

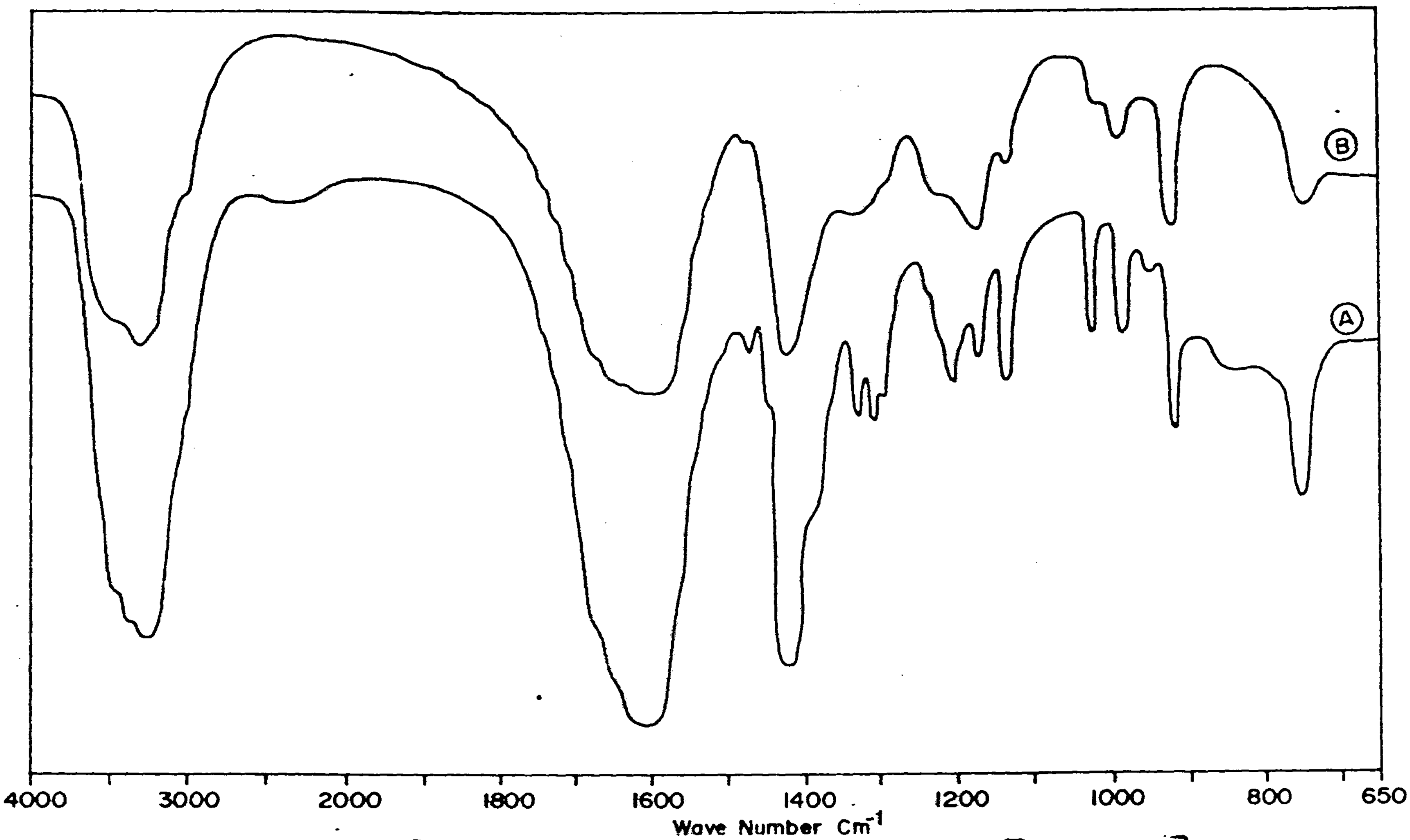


Fig.3.11 A-$K(N_2H_5)Ni_2[N(CH_2COO)_3]$. $N_2H_4.3H_2O$, B-$K(N_2H_5)Ni_2[N(CH_2COO)_3]_2.2N_2H_4.3H_2O$

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CHAPTER FOUR

CHAPTER FOUR

THERMAL STUDIES OF METAL-NTA SALTS AND THEIR HYDRAZINE DERIVATIVES

4. INTRODUCTION

Although some of the properties[1-4] of metal nitrilotriacetates have been extensively investigated, literature survey indicates that, the thermoanalytical properties of these salts have not been studied. NTA, like EDTA, is an amino derivative of an organic acid that has been found to co-ordinate with the metal ion through both nitrogen and oxygen in its salts. Since thermal study has been one of the analytical tools which can be used to investigate the bonding in metal salts or complexes it was thought worthwhile to carry out this investigation. More over, the knowledge of the thermal stabilities of metal-NTA salts are also useful due to the specific application of these salts as mentioned in Chapter One.

As such the thermal properties of metal-hydrazinium salts and hydrazinates of metal salts have been exhaustively studied[5-7] These various salts or complexes include those containing cl^-, No_3^-, SCN^-, $N_2H_3COO^-$ as univalent anion or SO_4^{2-}, SO_3^{2-}, $C_2O_4^{2-}$ as divalent anion. The distinct property of these compounds is that, they yield oxides at much lower temperatures as compared to their corresponding simple salts. It was also observed in the course of these thermal studies, that the bigger the molecule, the finer are the oxide particles in its final residue. The hydrazine derivative of metal-nitrilotriacetates when heated could be envisaged to yield such a fine powder oxide.

NTA* and hydrazine° have been important components in many electroless plating baths. Most of these baths operate at higher temperatures. The thermal stability of the bath in deposition process is therefore important not only for better efficiency but also for better product. In the present investigation, the compounds isolated from metal-NTA-hydrazine system, metal nitrilotriacetates and their hydrazine derivatives were subjected to heating in the TG and DTA. The results of this investigation are presented in this chapter.

4.1 EXPERIMENTAL

Thermal studies of the metal-nitrilotriacetates, $HM[N(CH_2COO)_3].xH_2O$ where M = Mg, Ca, Sr, Ba, Zn and Ni were carried out by using instruments described in Chapter Two. These salts were separately heated, in air and in nitrogen atmosphere, to about 700°C. The heating rates of 5 deg min^{-1}, 10 deg min^{-1} and 20 deg min^{-1} were employed separately to have a better understanding ofthe thermal properties.

4.2 RESULTS AND DISCUSSION : METAL-NTA SALTS

These salts, which are hydrated, initially lose water of hydration, endothermically, in single or different stages to form the corresponding anhydrous salts. This dehydration step, for most of the salts occurs above 100°C (Table 4.1). Generally, this decomposition reaction can be written as,

$$HM[N(CH_2COO)_3].xH_2O \xrightarrow{\Delta} HM[N(CH_2COO)_3] + xH_2O$$

The anhydrous salts, on further heating decompose to the acetate salts of the corresponding metals, along with large amount of gases CO_2, H_2O, NH_3 (vapour). Acetone was detected as one of the gaseous product. The non stoichiometric reaction could be written as :

$$HM[N(CH_2COO)_3] \xrightarrow{\Delta} M(CH_3COO)_2 + G.P.$$

$$G.P. = \text{Gaseous products} = aCO_2,\ bH_2O,\ cNH_3$$

The final residue, at about 600°C was found to contain oxycarbonate compound of the metal and metal itself. In the case of magnesium salts, the final residue at this temperature was MgO.

$$2M(CH_3COO)_2 \xrightarrow{\Delta} xMO.y.CO_2 + 2CH_3COCH_3 + (2-x)M + (2-y)CO_2 + (1-x/2)O_2$$

Metal acetates are known[10] to decompose to yield acetone as one of the gaseous products. Nitrilotriacetate also seems to decompose in a similar manner. In addition, the metal acetates are also known to decompose through oxycarbonates[10] $xMO.yCO_2$ as intermediates. The decomposition temperature for the oxycarbonate compounds is higher in comparison with that of the simple carbonate. For example, the oxycarbonate of zinc was found to be stable even at 600°C even though $ZnCO_3$ decomposes ~350°C.

Oxycarbonate, $xMO.yCO_2$, formed after the decomposition of metal acetate, further undergoes degradation by partial loss[11] of CO_2; this appears as weight loss in the TG. However, the changed or increased x:y ratio could not be definitely evaluated since it was not possible to estimate the metal contents along with the oxycarbonate at the completion of this step in the TG.

Along with the metal oxycarbonate, the residue at about 600°C was found to contain thecorresponding metal with almost 1:1 molar proportion. Such an observation has been made by Patil et al[10] in the decomposition of copper acetate. Presence of metal was further confirmed by the gain in weight seen as the last step in the TG, for almost all salts. This is perhaps due to the oxidation of the metal to its oxide.

The Differential thermal analyses of these salts show endothermic dehydration. The anhydrous nitrilotriacetate salt decomposes exothermically to acetates and further to oxicarbonates. However a sharp endotherm is also observed between these two steps. This is probably due to the free radical reaction occuring therein which could not be resolved. And The free radical reaction results in formation of acetone in the vapour state.[10]

The thermal properties of the salts mentioned above are individually discussed below :

4.2.1 THERMAL ANALYSIS OF $HMg[N(CH_2COO)_3].3H_2O$

This trihydrate salt of magnesium loses two H_2O molecules between 137-217°C (Fig 4.1) in N_2 atmosphere (heating rate 10 deg min^{-1}). On further heating, the monohydrate salt decomposes to magnesium acetate in the range 222-384°C. Magnesium acetate so formed decomposes at ~385°C to oxycarbonate.[12] This decomposition is complete at 480°C. On further heating, at about 620°C, Magnesium oxide is formed. Complementary peaks were observed in the DTA (MG-1 in Table 4.1)

Similar decompostion pattern (MG-2 in Table 4.1) was observed when this salt was heated in air to about 600°C and with the heating rate of 10°C min^{-1} (Fig.4.3).

4.2.2 THERMAL ANALYSIS OF $HCa[N(CH_2COO)_3].2H_2O$

Calcium nitrilotriacetate dihydrate is stable upto 40°C. The decomposition of the salt, through partial dehydration, is observed between 142-162°C with the weight loss of 3.6% indicating the loss of 0.5 H_2O. After further dehydration (175-219°C), the anhydrous calcium nitrilotriacetate decomposes, (231-439°C) to calcium oxycarbonate (CA-1 in Table 4.3) with loss of 45.1% when heated between 439 - 668°C, the oxycarbonate[13] lead to the formation of $CaCO_3$ or $CaO.CO_2$ with loss of 59.6% in weight (Fig. 4.2).

When the same salt was heated in Air (Heating rate 20°C/min), the first decomposition was similar to the one observed in the N_2 atmosphere in the temperature range 140-160°C (Fig. 4.4).

However, further decomposition of the salt in air occured at a comparatively higher temperature (268°C), and the total dehydration of the salt was completed at ~280°C. The anhydrous calcium NTA salt so formed decomposes (CA-2 in Table 4.3) between 280-420°C to calcium acetate and then further to stable CaO, within the temoerature range 415–595°C, with the weight loss of 40.5% in the TG. CaO is thus formed from oxycarbonate at much lower temperature compared to the decomposition of $CaCO_3$ to CaO which occurs ~600°C.

4.2.3 THERMAL ANALYSIS OF $HSr[N(CH_2COO)_3]\cdot 4H_2O$

Dehydration of this salt containing four H_2O molecules occured in two steps in N_2 atmosphere. Initially, it loses two H_2O molecules between 142–194°C, followed by the remaining two molecules between 215–388°C (Fig. 4.5). The weight loss in the two respective steps are 8.41% and 21.1%, which could be attributed to the formation of anhydrous salt. When heated further, it is decomposed to acetate with weight loss of 39.7% in the temperature range 389–419°C. The weight loss[14] in the last step indicated the formation of $SrO.2CO_2$ at ~540°C (SR-1 in Table 4.4).

Almost identical pattern of dehydration was observed when the salt was heated in air (Fig 4.7. The final residue at ~600°C was, similarly found to be oxycarbonate $SrO.2CO_2$ (SR-2 in Table 4.4).

4.2.4 THERMAL ANALYSIS OF $HBa[N(CH_2COO)_3].3H_2O$

Barium nitrilotriacetate trihydrate on heating in N_2 atmosphere lose one H_2O with the weight loss of 4.9% in the temperature range of 110–138.5° C. The dihydrate salt, so formed, is stable upto 323° C (Fig. 4.6). Beyond this temperature it further decomposes to $Ba(CH_3COO)_2$ and gaseous products as discussed earlier. The final residue at 700° C seems to be of oxycarbonate[15], $BaO.2CO_2$ (BA-1 in Table 4.5).

However decomposition in air yielded BaO (Fig. 4.8) at 600° C (BA-2 in Table 4.5)

4.2.5 THERMAL ANALYSIS OF $HZn[N(CH_2COO)_3].2H_2O$

This salt of Zinc (mol. wt. 281.52) undergoes dehydration in two steps when heated in N_2 gas 0.5 H_2O (3.16% wt. loss) and 1.5 H_2O (13.16 % wt. loss) are lost in two stages (Fig. 4.9). Further decomposition, as observed in the simultaneous TG-DTA, is similar to the other NTA salts. The sequence of decomposition is nitrilotriacetate --> (unhydrous) --> acetate --> oxycarbonate (Table 4.6:ZN-1).

Howerver, when this salt is decomposed in air at an increased heating rate (Table 4.6:ZN-2), the final residue in the TG was found to be ZnO (Fig. 4.10).

4.2.6 THERMAL ANALYSIS OF $HNi[N(CH_2COO_3)].5H_2O$

Nickel nitrilotriacetate pentahydrate is a pale green coloured compound and compared to alkaline earth nitrilotriacetates, it has lower thermal stability. In N_2 atmosphere when this salt is heated, it loses three H_2O molecules, (Fig. 4.11) as shown[16] by 16% weight loss in the TG in the temperature range of 62 - 370° C. The remaining two molecules of H_2O are lost along with the decomposition of the salt at ~380° C. (62 % weight loss).

On further heating, the salt decomposes to oxycarbonate (along with some metal). Presence of nickel is indicated by gain in weight observed beyond 490° C which can be ascribed to slow oxidation of nickel to NiO. The final residue, from the weight loss could be $2NiO.CO_2$ (Table 4.8)

Thermogravimetry of the salt was also carried out in argon atmosphere (Table 4.8 : NI-2). Total dehydration occured in the first step in TG. Also, the final loss in weight was different in comparison to decomposition in N_2.

4.3 TA OF HYDRAZINE DERIVATIVES OF M-NTA SALTS

Hydrazine derivatives of the metal nitrilotriacetate salts, prepared by different methods (Chapter Three), were decomposed in N_2 atmosphere upto 700° C.

4.3.1 TA OF $(N_2H_5)M[N(CH_2COO)_3].xH_2O$ WHERE M = Mg, Ca, Sr AND Zn

Hydrazine derivatives of alkaline earth metals nitrilotriacetate were prepared by treating aqueous M-NTA with $N_2H_4.H_2O$. These hydrated hydrazinium metal salts are thermally more stable than the corresponding simple salts. Initially, dehydration occurs in one or two steps depending upon number of molecules of water present.

After dehydration (Fig. 4.12 - 4.16), further degradation leads to the formation of simple metal-NTA salt as is evident from the weight loss in the TG. This further confirms the formulae assigned to the compounds.

Further decomposition pattern of these salts are similar to the corresponding metal nitrilotriacetates. However, the decomposition temperatures for different stages are lower in the case of salts under discussion.

In the final decomposition step, upto 700° C and in N_2 atmosphere, the salts yield oxycarbonates, though the temperatures of formation of oxycarbonate are lower.

TG data of these hydrazinium-metal NTA salts are given in Tables 4.2, 4.3, 4.4 and 4.7.

Complimentary peaks are observed in the DTA of the sample. Endothermic dehydration is followed by exothermic decomposition of the salt. A sharp endothermic peak which is seen immediately after exothermic is due to the free radical reaction as stated in Section 4.2.

4.3.2 THERMAL ANALYSIS OF $(N_2H_5)Ni[N(CH_2COO)_3].xN_2H_4.yH_2O$

As described in the Chapter Three, hydrazine derivatives of the nickel nitrilotriacetate were prepared under different preparative conditions. The general formula for this set of compounds can be written as $(N_2H_5)Ni[N(CH_2COO)_3].xN_2H_4.yH_2O$, where the value of x and y varied depending on the method of preparation.

Figures 4.18 to 4.23 represent the thermal behaviour of these complexes. Thermoanalytical data of the complexes is presented in Tables 4.9 to 4.11. All the complexes initially decompose endothermically with the loss of total or partial H_2O. This is followed by the loss of hydrazine and degradation of corresponding simple salt. The temperatures of these two step are very close hence the hydrazine decomposition appears as a shoulder (in the TG) to the subsequent degradation (Fig. 4.18 to 4.23). All the complexes yield nickel oxycarbonate after degradation similar to nickel-NTA salt (Sec. 4.2.6).

One of the complex was decomposed at two different heating rates (5 and 10°C min^{-1}). It is observed (Fig. 4.19 & 4.22) that the x:y ratio in $xNiO.yCO_2$ decreased with increase in the heating rate.

4.3.3 THERMAL ANALYSIS OF $Na(N_2H_5)Ni_2[N(CH_2COO)_3]_2.xN_2H_4.3H_2O$

These mixed metals complexes were obtained by treating nickel-NTA solution with aqueous Na_2CO_3, before adding of $N_2H_4.H_2O$. The hydrazine content varied depending on the amount of N_2H_4 added (Table 3-B). This reflected in the TG of the samples. The complex (from excess of hydrazine) with x=2 loses $2N_2H_4$ along with $3H_2O$ in a single step (Fig. 4.24).Where as the other, containing one N_2H_4 undergoes dehydration first followed by the decomposition of total N_2H_4 in the complex (Fig. 4.25). The single step, with weight loss of 17.0% is observed in the temperature range 50-175° C. In the case of the latter, 8.0% weight loss (85-150°C) and ~9.5 % weight loss (155-210° C) is seen in two different stages.

Further decomposition pattern for the complex was found to be almost similar to that of nickel hydrazinium nitrilotriacetates. The final residue at 700° C in the TG contained oxide mixture of the metals (NI-9,10 in Table 4.12).

4.3.4 THERMAL ANALYSIS OF $K(N_2H_5)Ni_2[N(CH_2COO)_3]_2.xN_2H_4.3H_2O$

Potassium mixed metal complex was also prepared by the two different methods as described in the previous section. In the initial stage, the decomposition pattern for the two samples, obtained by the two methods, were also similar. The single step in the TG for the loss of water and hydrazine molecules is seen (Fig. 4.27) in the temperature range 50-180° C (15 % weight loss). For the other complex prepared with limited amount of $N_2H_4.H_2O$ (Table 3-B) the weight loss of 7.0% (range 70-150° C), and of 10.0% (range : 155-210° C) was observed (Fig. 4.26) for

$3H_2O$ and $2N_2H_4$ (one from N_2H_5)respectively. The decomposition of the samples, finally at 700°C yielded mixture of oxides of nickel and potassium (NI-11,12 in Table 4.12).

TABLE 4

Thermoanalvtical Data Of The Samples

Key : (i) GP= gaseous products (ii) Y = N(CH$_2$COO)$_3$

TABLE 4.1

MG-1	In N$_2$	HMg[N(CH$_2$COO)$_3$].3H$_2$O			Fig. 4.1
Step No.	Thermogravimetry				DTA Peak Temp °C
	Temp. Range °C	Loss [Residue Left]	Weight Loss % obsd.	Weight Loss % calc.	
1	136.5-217.0	2H$_2$O [HMg.Y.H$_2$O]	15.0	13.5	180.7(-)
2	222-384.6	GP [Mg(AC)$_2$]	45.0	46.5	257.7(-) 392 (+)
3	384.6-480.1	GP [3MgO.2CO$_2$]	73.2	73.96	407 (-) 473.1(+)
4	481-620	2CO$_2$ [3MgO]	83.82	84.90	broad

MG-2	In Air	HMg[N(CH$_2$COO)$_3$].3H$_2$O			Fig. 4.3
Ste No.	Thermogravimetry				DTA Peak Temp °C
	Temp. Range °C	Loss [Residue Left]	Weight Loss % obsd.	Weight Loss % calc.	
1	136.5-217.0	2H$_2$O [HMg.Y.H$_2$O]	15.0	13.5	180.7
2	222-384.6	GP [Mg(AC)$_2$]	45.0	46.5	257.7
3	384.6-480.1	GP [3MgO.2CO$_2$]	73.2	73.96	473.1
4	481-620	2CO$_2$ [3MgO]	83.82	84.9	broad

TABLE 4.2

MG-3	In N_2		$(N_2H_5)Mg[N(CH_2COO)_3].H_2O$			Fig. 4.12
Step No.	Thermogravimetry					DTA Peak Temp. °C
	Temp. Range °C	Loss	[Residue Left]	Weight Loss %		
				obsd.	calc.	
1	210 - 300	(N_2+NH_3)	[HMgY]	20.0	18.97	293.3(-)
2	400 - 460		$[MgO.1.5H_2O]$	59.8	59.65	400 (+) 430.8(-)
3	460 -	1.5 CO_2	$[2MgO.CO_2]$	79.24	76.50	continous upto 700

MG-4	In N_2		$(N_2H_5)Mg[N(CH_2COO)_3].2H_2O$			Fig. 4.13
Step No.	Thermogravimetry					DTA Peak Temp. °C
	Temp. Range °C	Loss	[Residue Left]	Weight Loss %		
				obsd.	calc.	
1	160-280	H_2O	$[(N_2H_5)MgYH_2O]$	6.25	6.42	260(-)
2	400-460	H_2O + N_2H_4	[HMgY]	25.00	24.26	309(+)
3	403-580	GP	[MgO]	85.67	85.67	424.78(+)

TABLE 4.3

CA-1	In N_2 $HCa[N(CH_2COO)_3].2H_2O$				Fig. 4.2
Step No.	Thermogravimetry				DTA Peak Temp °C
	Temp. Range °C	Loss [Residue Left]	Weight Loss %		
			obsd.	calc.	
1	142.3-161.53	$0.5H_2O$ $[HCaY1.5H_2O]$	3.6	3.4	150
2	175.0-219.23	1.5 H_2O $[HCaY]$	13.12	13.57	203.8
3	230.8-290.38	-	-	-	-
4	390.4-438.46	GP $[CaO.2CO_2]$	45.1	45.71	400(-); 426.9(-)
5	439-665.38	CO_2 $[CaCO_3]$	59.6	62.3	513.5(+)

CA-2	In Air $HCa[N(CH_2COO)_3].2H_2O$				Fig. 4.4
Step No.	Thermogravimetry				DTA Peak Temp °C
	Temp. Range °C	Loss [Residue Left]	Weight Loss %		
			obsd.	calc.	
1	140.0-160.0	$0.5H_2O$ $[HCaY1.5H_2O]$	3.66	3.4	-
2	268.0-280.0	1.5 H_2O $[HCaY]$	12.6	13.57	-
3	280.0-420.0	GP $[Ca(AC)_2]$	40.5	40.43	-
4	424-595.0	GP $[CaO]$	79.0	78.9	-

CA-3	In N_2 $(N_2H_5)Ca[N(CH_2COO)_3].2H_2O$				Fig. 4.14
Step No.	Thermogravimetry				DTA Peak Temp. °C
	Temp. Range °C	Loss [Residue Left]	Weight Loss %		
			obsd.	calc.	
1	42.6-118	H_2O $[(N_2H_5)CaYH_2O]$	6.31	6.06	100(-)
2	280-351	$H_2O.N_2H_4$ $[HCaY]$	23.75	22.89	332.2(+)
3	400-423.5	- -	-	-	415.6(+)
4	423.5-491	GP $[CaO.CO_2$ or $CaCO_3]$	66.2	66.33	462.6(+)

TABLE 4.4

SR-1	In N_2	$HSr[N(CH_2COO)_3].4H_2O$			Fig. 4.5
Step No.	Thermogravimetry				DTA Peak Temp° C
	Temp. Range °C	Loss [Residue Left]	Weight Loss%		
			obsd.	calc.	
1	142.3-194.2	$2H_2O$ [$HSrY.2H_2O$]	8.41	10.34	176.9
2	215 -388.0	$2H_2O$ [HSrY]	21.1	20.69	broad
3	388.45-419.23	G P [$Sr(AC)_2$]	39.7	40.91	396.15(-) 411.5(-)
4	420-540	xH_2O + yCO_2 [$SrO.2CO_2$]	47.97	49.7	broad

SR- 2	In Air	$HSr[N(CH_2COO)_3].4H_2O$			Fig. 4.7
Step No.	Thermogravemetry				DTA Peak Temp °C
	Temp. Range °C	Loss [Residue Left]	Weight Loss%		
			obsd.	calc.	
1	183.0-250	$2H_2O$ [$HSrY.2H_2O$]	8.40	10.34	-
2	260 -419	G P [$Sr(AC)_2$]	42.5	40.91	-
3	419 -600	G P [$SrO.2CO_2$]	49.43	49.7	-

SR -3	In N_2	$(N_2H_5)Sr[N(CH_2COO)_3].H_2O$			Fig. 4.15
Step No.	Thermogravimetry				DTA Peak Temp. °C
	Temp. Range °C	Loss [Residue Left]	Weight Loss %		
			obsd.	calc.	
1	72.5-142.5	H_2O [$(N_2H_5)SrY$]	5.1	5.5	115(-)
2	142.5-195	N_2H_4 [HSrY]	13.8	15.33	180(+)
3	372.5-480	GP [$SrO.CO_2$ or $SrCO_3$]	51.03	54.82	442.5(+)

TABLE 4.5

BA-1	In N_2		$HBa[N(CH_2COO)_3].3H_2O$			Fig. 4.6
Step No.	Thermogravimetry					DTA Peak Temp °C
	Temp. Range °C	Loss	[Residue Left]	Weight Loss%		
				obsd.	calc.	
1	110 -138.5	$1H_2O$	$[HBaY.2H_2O]$	4.9	4.73	
2	323.1-417.3	GP	$[Ba(AC)_2]$	30.0	32.87	
3	417.3 -520	GP	$[BaO.2CO_2]$	35.8	36.55	

BA - 2	In Air		$HBa[N(CH_2COO)_3].3H_2O$			Fig. 4.8
Step No.	Thermogravimetry					DTA Peak Temp °C
	Temp. Range °C	Loss	[Residue Left]	Weight Loss %		
				obsd.	calc.	
1	370 - 438	GP	[--]	-	-	-
2	438 - 570	GP	[BaO]	60.3	59.31	-

TABLE 4.6

ZN-1	In N_2	$HZn[N(CH_2COO)_3].2H_2O$				Fig. 4.9
Step No.	Thermogravimetry					DTA Peak Temp °C
	Temp. Range °C	Loss	[Residue left]	Weight Loss % obsd.	Weight Loss % calc.	
1	210 - 260	0.5 H_2O	$[HZnY1.5H_2O]$	3.16	3.19	246.2 (-)
2	310 - 370	1.5 H_2O	[HZnY]	13.16	12.78	357.7 (-)
3	380 - 435	GP	$[Zn(AC)_2]$	33.0	34.96	394.2 (+)
4	380 - 435	GP	$[ZnO.2CO_2]$	44.21	39.84	419.2 (+)
5	435 - 560	CO_2	$[ZnO.CO_2]$	56.31	55.56	broad (+)

ZN-2	In Air	$HZn[N(CH_2COO)_3].2H_2O$				Fig. 4.10
Step No.	Thermogravimetry					DTA Peak Temp. °C
	Temp. Range °C	Loss	[Residue left]	Weight Loss % obsd.	Weight Loss % calc.	
1	30 - 130	0.5 H_2O	$[HZnY1.5H_2O]$	2.8	3.19	-
2	130 - 170	0.5 H_2O	$[HZnY1H_2O]$	5.5	6.38	-
3	170 - 250	0.5 H_2O	$[HZnY0.5H_2O]$	8.2	9.57	-
4	250 - 330	0.5 H_2O	[HZnY]	12.3	12.78	-
5	390 - 495	GP	[ZnO]	69.0	70.1	-

TABLE 4.7

ZN-3	In N_2	$(N_2H_5)Zn[N(CH_2COO)_3].H_2O$				Fig. 4.16
Step No.	Thermogravimetry					DTA Peak Temp. °C
	Temp. Range °C	Loss	[Residue Left]	Weight Loss %		
				obsd.	calc.	
1	220- 310	H_2O	$[(N_2H_5)ZnY]$	5.40	5.91	broad
2	310- 350	N_2H_4	$[HZnY]$	16.1	16.42	-
3	350- 650	GP	$[ZnO.CO_2]$	60.69	58.82	-

ZN-4	In Air	$(N_2H_5)Zn[N(CH_2COO)_3].H_2O$				Fig. 4.17
Step No.	Thermogravimetry					DTA Peak Temp. °C
	Temp. Range °C	Loss	[Residue Left]	Weight Loss %		
				obsd.	calc.	
1	70 - 300	H_2O	$[(N_2H_5)ZnY]$	5.1	5.91	-
2	300 - 380	-	-	22.5	-	-
3	390 - 480	GP	$[ZnO]$	71.2	73.27	-

TABLE 4.8

NI-1	In N_2	$HNi[N(CH_2COO)_3].5H_2O$				Fig. 4.11
Step No.	Thermogravimetry					DTA Peak Temp °C
	Temp. Range °C	Loss	[Residue Left]	Weight Loss% obsd.	Weight Loss% calc.	
1	62 -370	$3H_2O$	$[HNiY.2H_2O]$	16.0	15.99	broad
2	380 -440	GP	$[NiO.3CO_2 +Ni]$	62.0	60.74	434.5
3	440 -490	CO_2	$[NiO.2CO_2+Ni]$	67.75	67.25	455.75
4	500 -		$[2NiCO_3(2NiO.CO_2)]$	65.09	64.9	broad

NI-2	In Ar	$HNi[N(CH_2COO)_3].5H_2O$				-
Step No.	Thermogravimetry					DTA Peak Temp °C
	Temp. Range °C	Loss	[Residue Left]	Weight Loss obsd.	Weight Loss calc.	
1	62 - 420	5. H_2O	[HNiY]	25.71	26.62	-
2	420 - 450	GP	$[NiCO_3]$	65.0	64.9	-
3	450 - 572	CO_2	$[NiO.CO_2 + Ni]$	72.86	73.76	-
4	617 - 700		$[NiO.CO_2+NiO]$	71.42	71.39	-

TABLE 4.8

NI-3	In N_2	$(N_2H_5)Ni[N(CH_2COO)_3].4H_2O$			Fig. 4.18
Step No.	Thermogravimetry				DTA Peak Temp. °C
	Temp. Range °C	Loss [Residue Left]	Weight Loss %		
			obsd.	calc.	
1	90 - 150	$2H_2O$ $[(N_2H_5)NiY.2H_2O]$	10.5	10.23	-
2	160 - 280	$2H_2O$ $[(N_2H_5)NiY]$	20.0	20.46	-
3	290 - 410	N_2H_4 $[HNiY]$	28.50	29.55	-
4	420 - 500	GP $[Ni + NiO.1.5CO_2]$	70.0	71.67	-
5	510 - 660	XCO_2 $[Ni + 3NiO.CO_2]$	79.0	78.96	-
6	680 -	Gain $[NiO + 3NiO.CO_2]$	75.8	75.64	-

NI-5	In N_2	$(N_2H_5)Ni[N(CH_2COO)_3].1/2N_2H_4.7H_2O$			Fig. 4.20
Step No.	Thermogravimetry				DTA Peak Temp. °C
	Temp. Range °C	Loss [Residue Left]	Weight Loss %		
			obsd.	calc.	
1	60 - 190	$4H_2O[(N_2H_5)NiY0.5N_2H_4-3H_2O]$	17.00	16.71	-
2	200 - 340	$3H_2O/0.5N_2H_4$ $[(N_2H_5)NiY]$	33.00	35.05	-
3	335 - 425	GP $[Ni + NiO.1.5CO_2]$	76.00	76.85	-
4	425 - 540	xCO_2 $[Ni + \alpha NiO.\delta CO_2]$	84.25	-	-
5	550 - -	Gain $[NiO.CO_2 + NiO]$	76.00	75.85	-

TABLE 4.10

NI-4	In N_2	$(N_2H_5)Ni[N(CH_2COO)_3].N_2H_4.5H_2O$			Fig. 4.19
Step No.	Thermogravimetry				DTA Peak Temp. °C
	Temp. Range °C	Loss [Residue Left]	Weight Loss %		
			obsd.	calc.	
1	55 - 175	$4H_2O$ $[(N_2H_5)NiY.N_2H_4]$	17.00	17.91	-
2	210 - 328	H_2O/N_2H_4 $[HNiY]$	30.00	30.26	-
3	330 - 410	GP $[Ni+NiO.2.5CO_2]$	68.00	69.71	-
4	420 - 535	$1.5CO_2$ $[Ni + NiO.CO_2]$	76.5	77.92	-
5	535 - -	Gain $[NiO.CO_2]$	70.4	70.46	-

NI-7	In N_2	$(N_2H_5)Ni[N(CH_2COO)_3]N_2H_5.5H_2O$			Fig. 4.22
Step No.	Thermogravimetry H.R.: 10°C min^{-1}				DTA Peak Temp. °C
	Temp. Range °C	Loss [Residue Left]	Weight Loss %		
			obsd.	calc.	
1	50 - 150	$2H_2O$ $[(N_2H_5)NiY.N_2H_4.2H_2O]$	8.8	8.96	
2	160 - 340	$3H_2O$ $[(N_2H_5)NiY.N_2H_4]$	22.50	22.40	
3	340 - 410	GP $[2NiO.5CO_2]$	55.1	54.1	
4	- 700		55.0	55.0	

TABLE 4.11

NI-6	In N_2	$(N_2H_5)Ni[N(CH_2COO)_3].3H_2O$				Fig. 4.21
Step No.	Thermogravimetry					DTA Peak Temp. °C
	Temp. Range °C	Loss	[Residue Left]	Weight Loss %		
				obsd.	calc.	
1	55 - 145	$2H_2O$	$[(N_2H_5)NiY.H_2O]$	9.5	10.7	-
2	150 - 195	$1.5H_2O$	$[(N_2H_5)NiY]$	16.75	16.18	-
3	240 - 350	N_2H_4	[HNiY]	26.5	25.77	-
4	350 - 420	GP	$[NiO.3CO_2]$	68.0	67.6	-
5	415 - 432	xCO_2	[NiO]	77.25	-	-

NI-8	In N_2	$(N_2H_5)Ni[N(CH_2COO)_3].1/2N_2H_4.2H_2O$				Fig. 4.23
Step No.	Thermogravimetry					DTA Peak Temp. °C
	Temp. Range °C	Loss	[Residue Left]	Weight Loss %		
				obsd.	calc.	
1	90 - 160	$2H_2O$	$[(N_2H_5)NiY.0.5 N_2H_4]$	11.0	10.85	
2	165 - 272	N_2H_4	$[HNiY0.5N_2H_4]$	20.0	20.49	
3	305 - 405	$1/2N_2H_4$	[HNiY]	28.0	25.31	
4	436 - 505	GP	$[2NiO.3CO_2]$	69.5	69.96	
5	505 - 668	xCO_2	[4NiO.CO]	78.25	78.25	
6	668 -			gain		

TABLE 4.12

NI-9	In N_2	$Na(N_2H_5)Ni_2[N(CH_2COO)_3]_2.2N_2H_4.3H_2O$			Fig. 4.24
Step No.	Thermogravimetry				DTA Peak Temp. °C
	Temp. Range °C	Loss [Residue Left]	Weight Loss % obsd.	calc.	
1	50 - 175	$3H_2O$; $[Na(N_2H_5)Ni_2H(Y)_2]$ $2N_2H_4$	17.0	18.56	-

NI-10	In N_2	$Na(N_2H_5)Ni_2[N(CH_2COO)_3]_2.N_2H_4.3H_2O$			Fig. 4.25
Step No.	Thermogravimetry				DTA Peak Temp. °C
	Temp. Range °C	Loss [Residue Left]	Weight Loss % obsd.	calc.	
1	85 - 150	$3H_2O$ $[Na(N_2H_5)Ni_2(Y)_2$ $N_2H_4]$	8.0	8.94	-
2	155 - 210	$2N_2H_4$ $[NaHNi_2(Y)_2]$	10.0	10.6	-
3	at 700°C	GP $[NiO + Na_2O]$	76.0	-	-

NI-11	In N_2	$K(N_2H_5)Ni_2[N(CH_2COO)_3]_2.N_2H_4.3H_2O$			Fig. 4.26
Step No.	Thermogravimetry				DTA Peak Temp. °C
	Temp. Range °C	Loss [Residue Left]	Weight Loss % obsd.	calc.	
1	70 - 150	$3H_2O$ $[K\ (N_2H_5)Ni_2Y.$ $N_2H_4]$	7.0	8.71	-
2	155 - 210	$2N_2H_4$ $[K\ HNi_2Y]$	10.0	10.32	
3	at 700°C	GP $[NiO + K_2O]$	70.5		

NI-12	In N_2	$K(N_2H_5)Ni_2[N(CH_2COO)_3]_2.2N_2H_4.3H_2O$			Fig. 4.27
Step No.	Thermogravimetry				DTA Peak Temp. °C
	Temp. Range °C	Loss [Residue Left]	Weight Loss % obsd.	calc.	
1	50 - 180	$3H_2O.2N_2H_4$ $[K(N_2H_5Ni_2Y_2]$	15.0	18.1	-

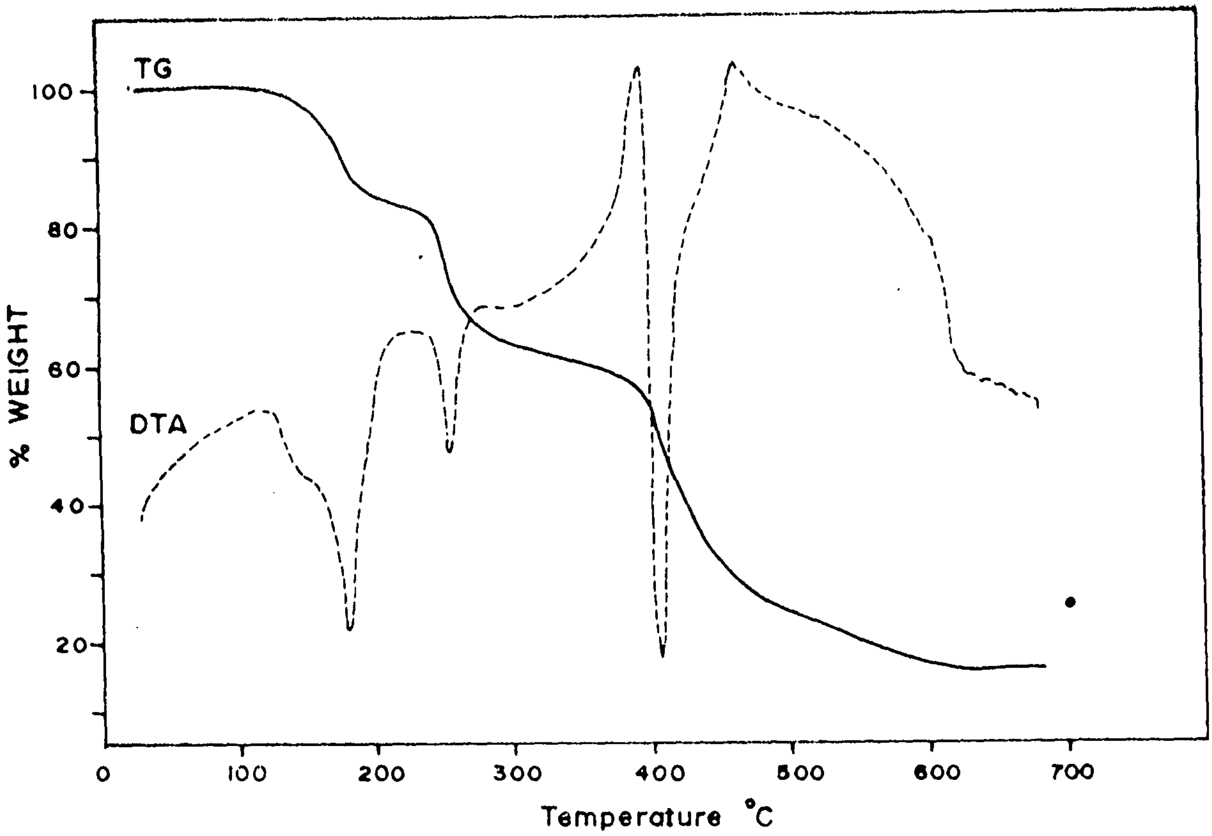

Fig. 4.1 TG, DTA of $HMg\,N(CH_2COO)_3 \cdot 3H_2O$

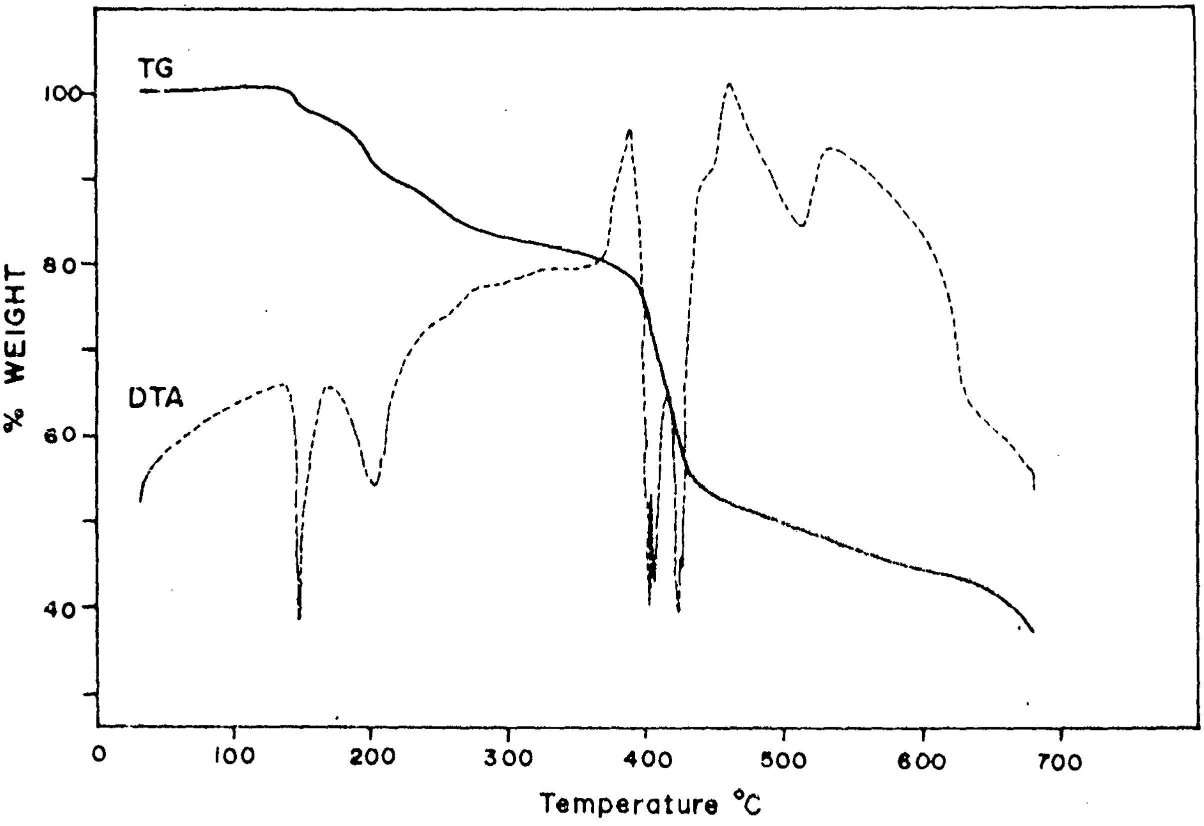

Fig. 4.2 TG, DTA of $HCa\,N(CH_2COO)_3 \cdot 2H_2O$

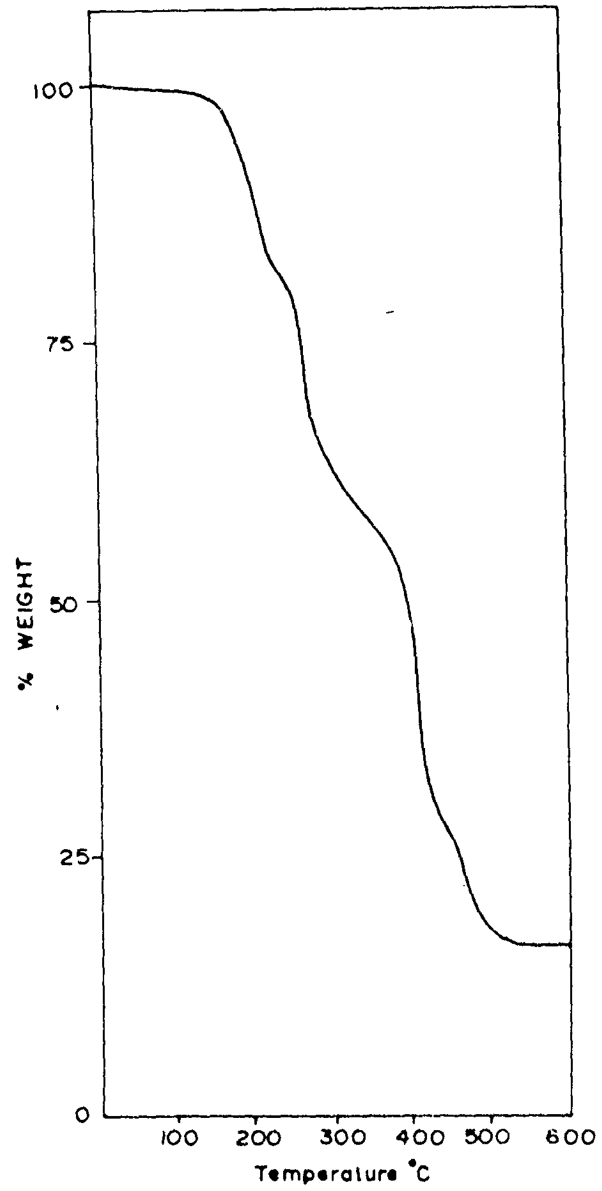

Fig. 4.3 TG of $HMg\,N(CH_2COO)_3{\cdot}3H_2O$

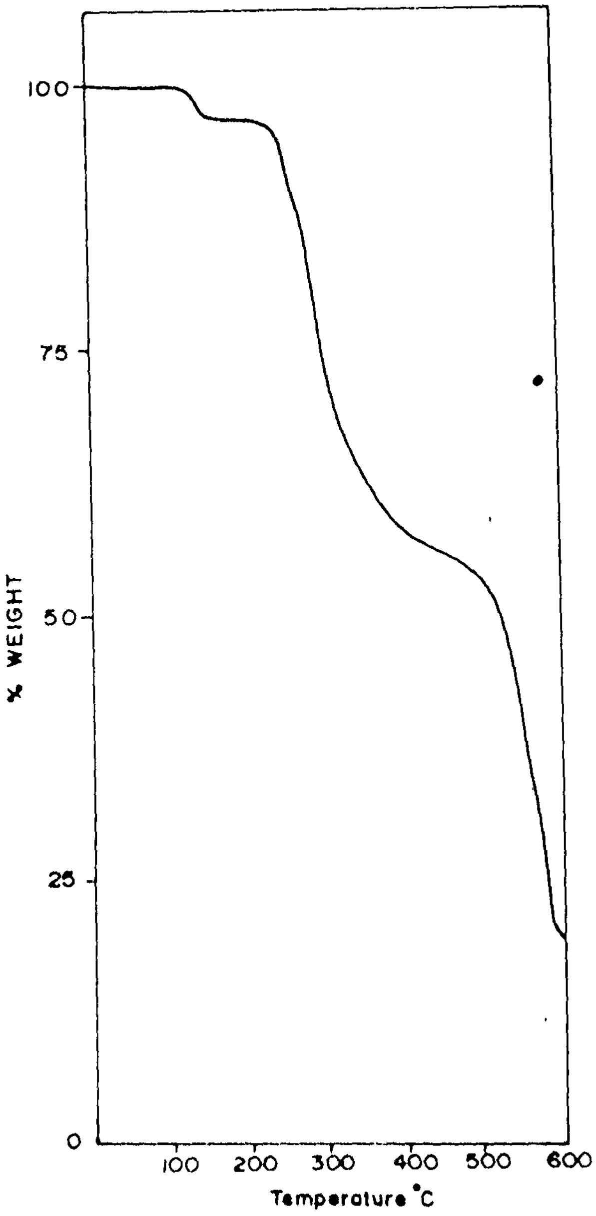

Fig. 4.4 TG of $HCa\,N(CH_2COO)_3{\cdot}2H_2O$

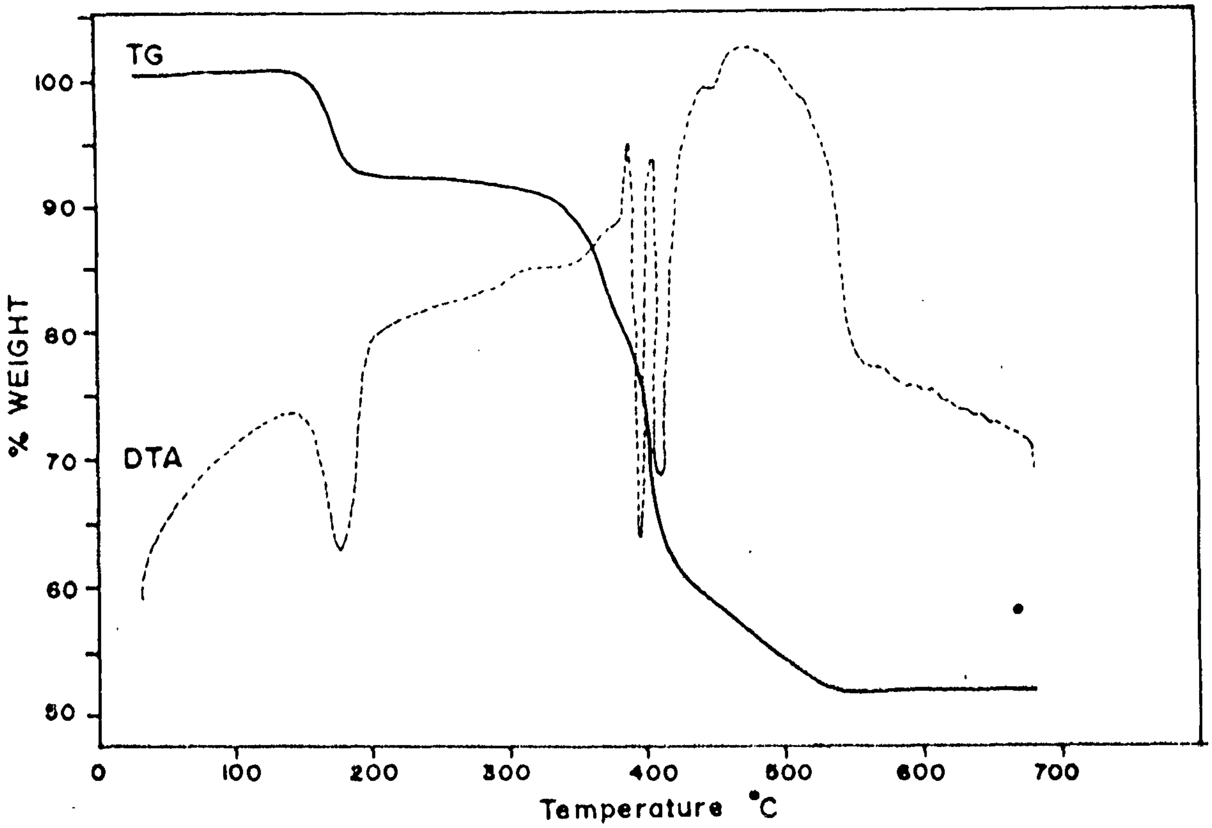

Fig. 4.5 TG, DTA of $HSrN(CH_2COO)_3 . 4H_2O$

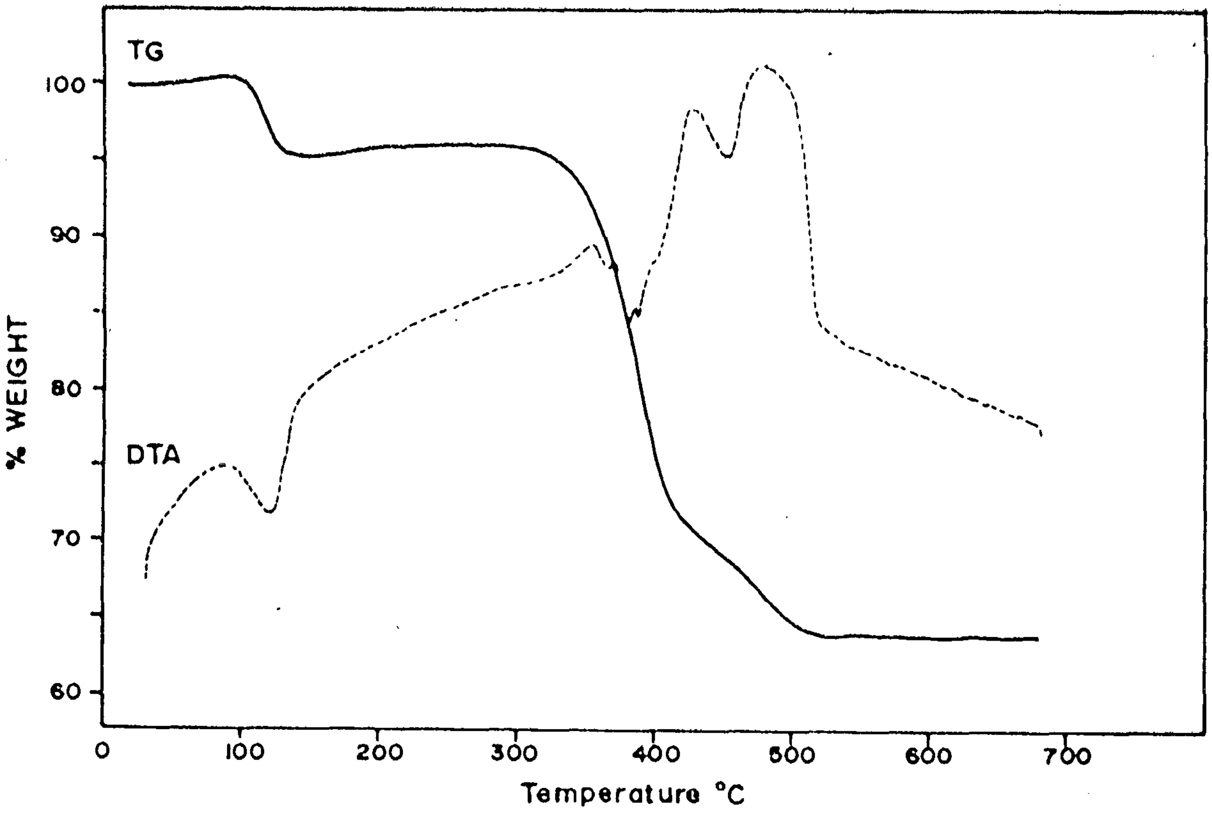

Fig. 4·6 TG, DTA of $HBaN(CH_2COO)_3 \cdot 3H_2O$

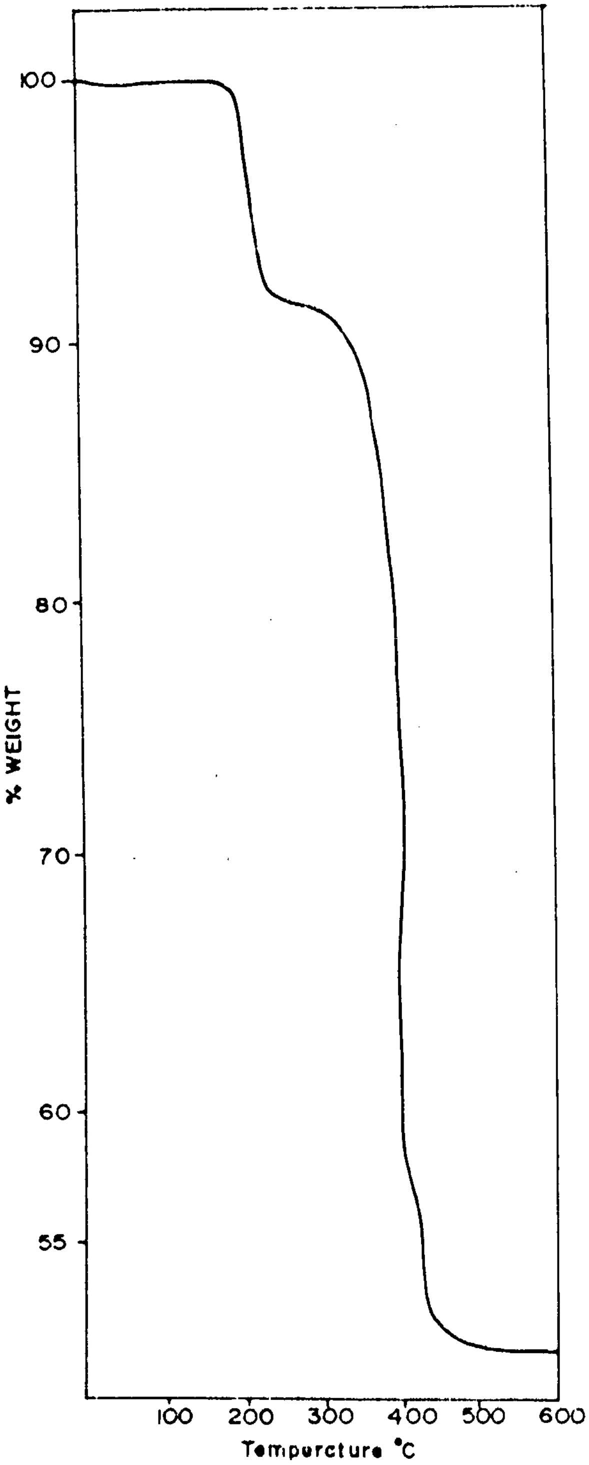

Fig. 4·7 TG of HSr N $(CH_2COO)_3 \cdot 4H_2O$

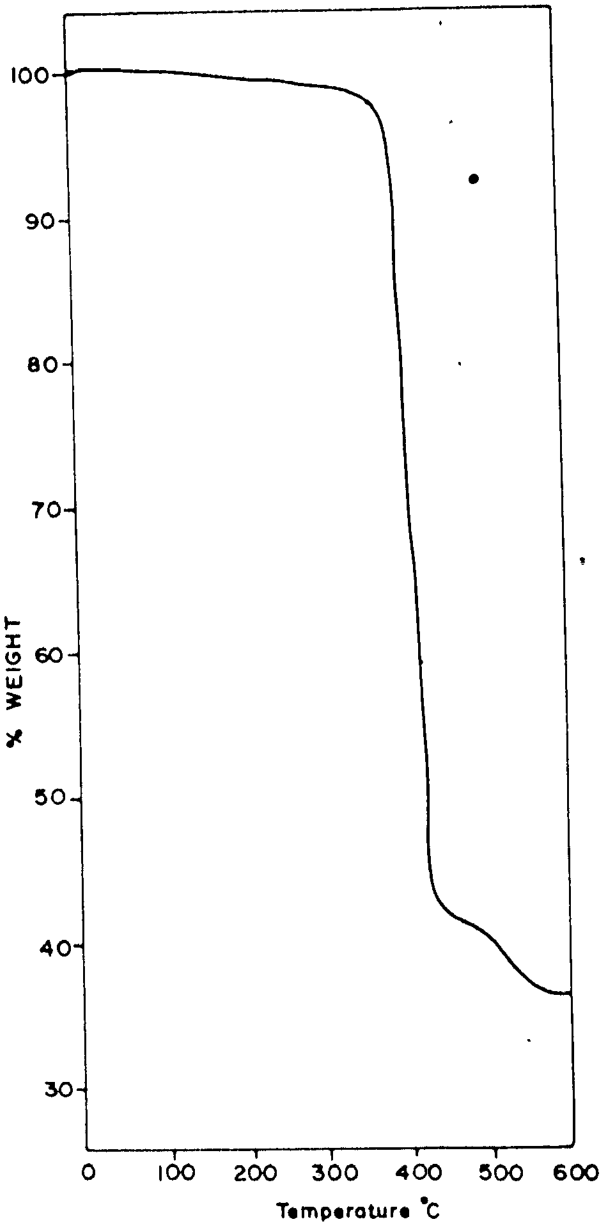

Fig.4·8 TG of HBa N $(CH_2COO)_3 \cdot 3H_2O$

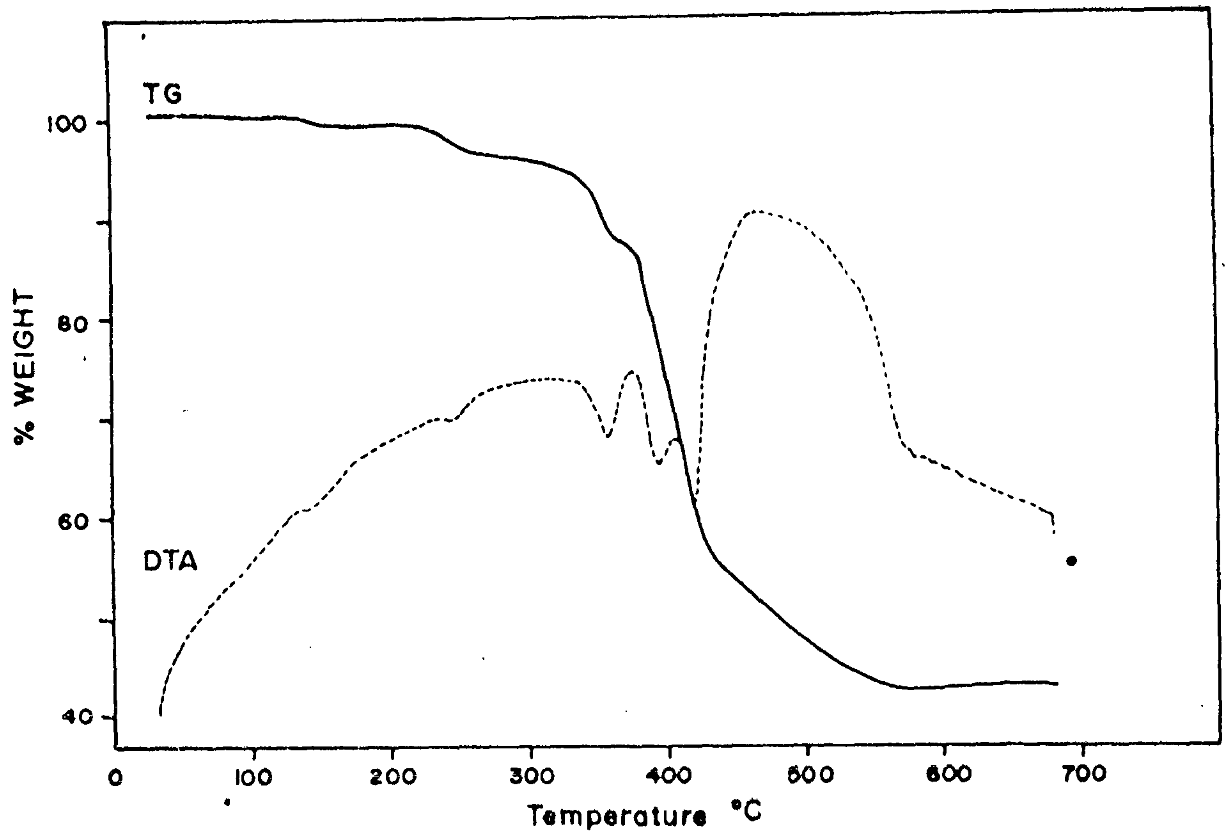

Fig. 4.9 TG DTA of HZn N $(CH_2COO)_3 \cdot 2H_2O$

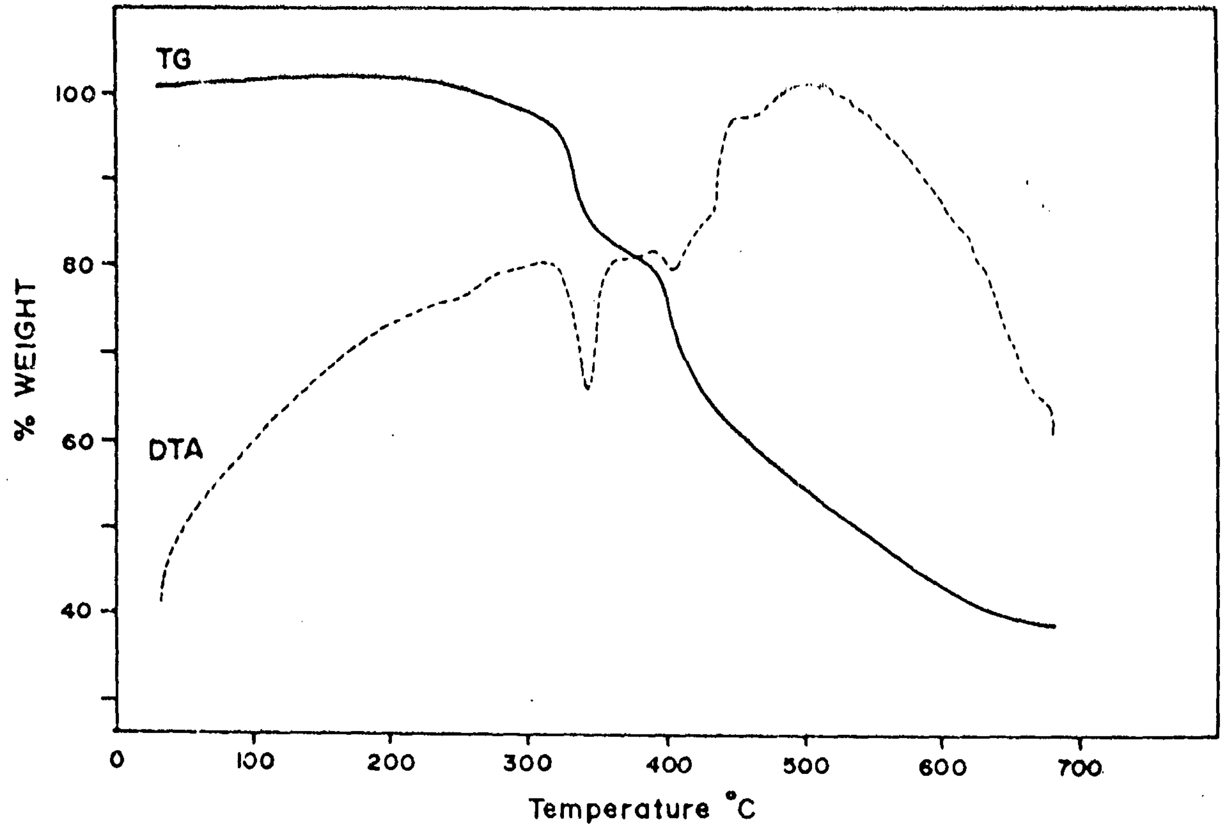

Fig. 4·16 TG, DTA of $(N_2H_5)ZnN(CH_2COO)_3 \cdot H_2O$

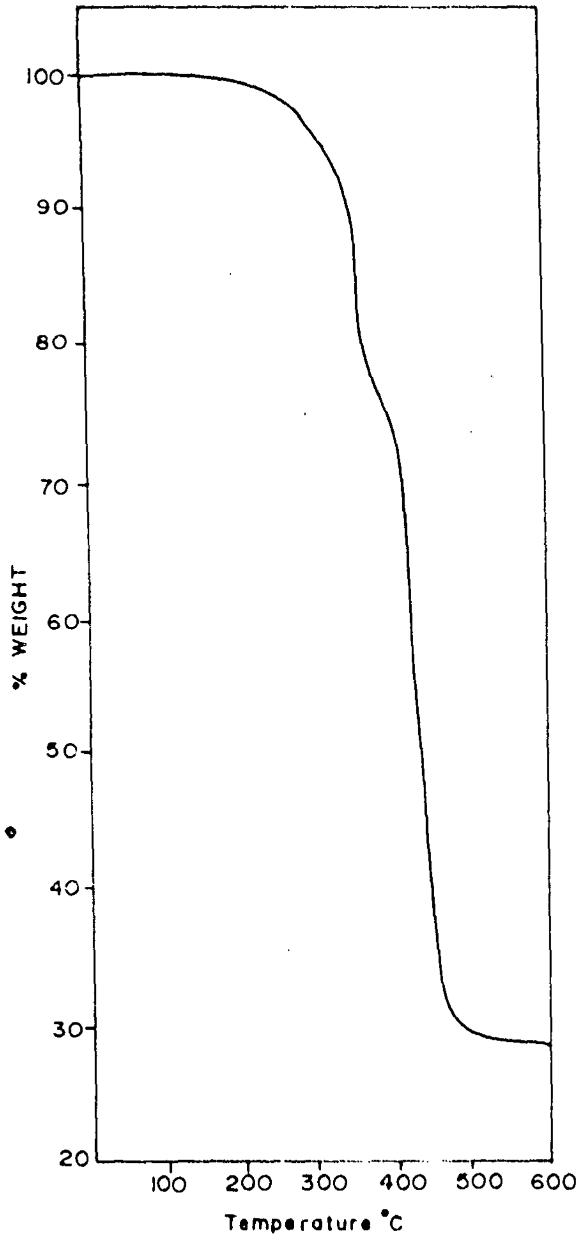

Fig.4·17 TG of $(N_2H_5)ZnN(CH_2COO)_3 \cdot H_2O$

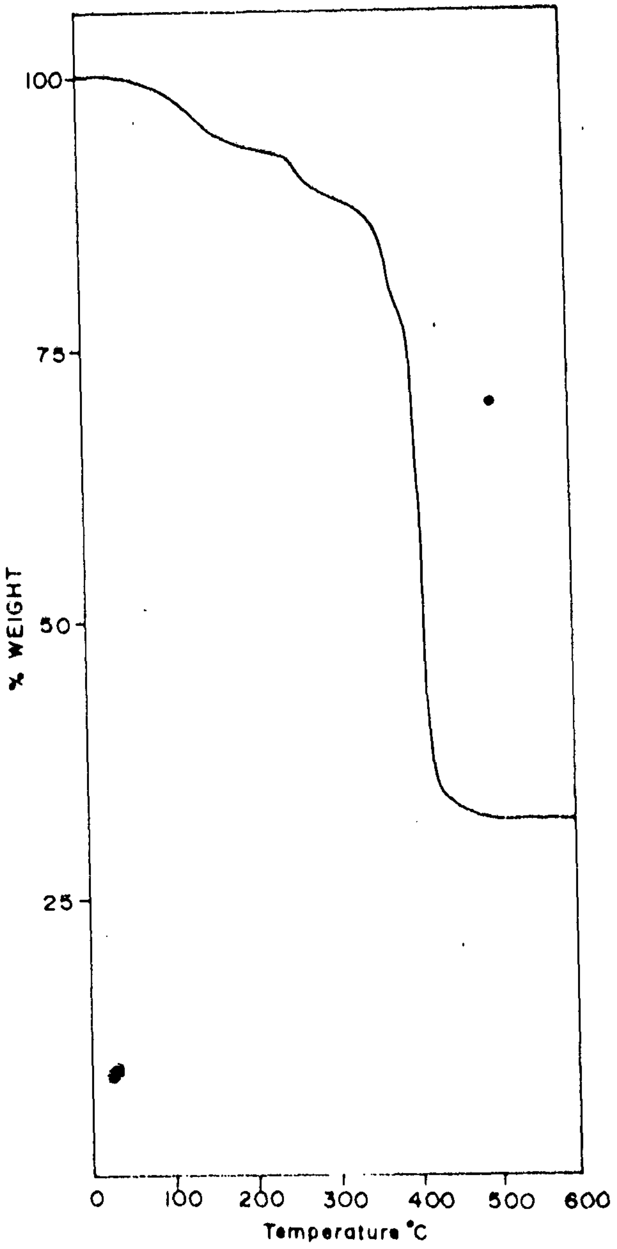

Fig.4·10 TG of $HZnN(CH_2COO)_3 \cdot 2H_2O$

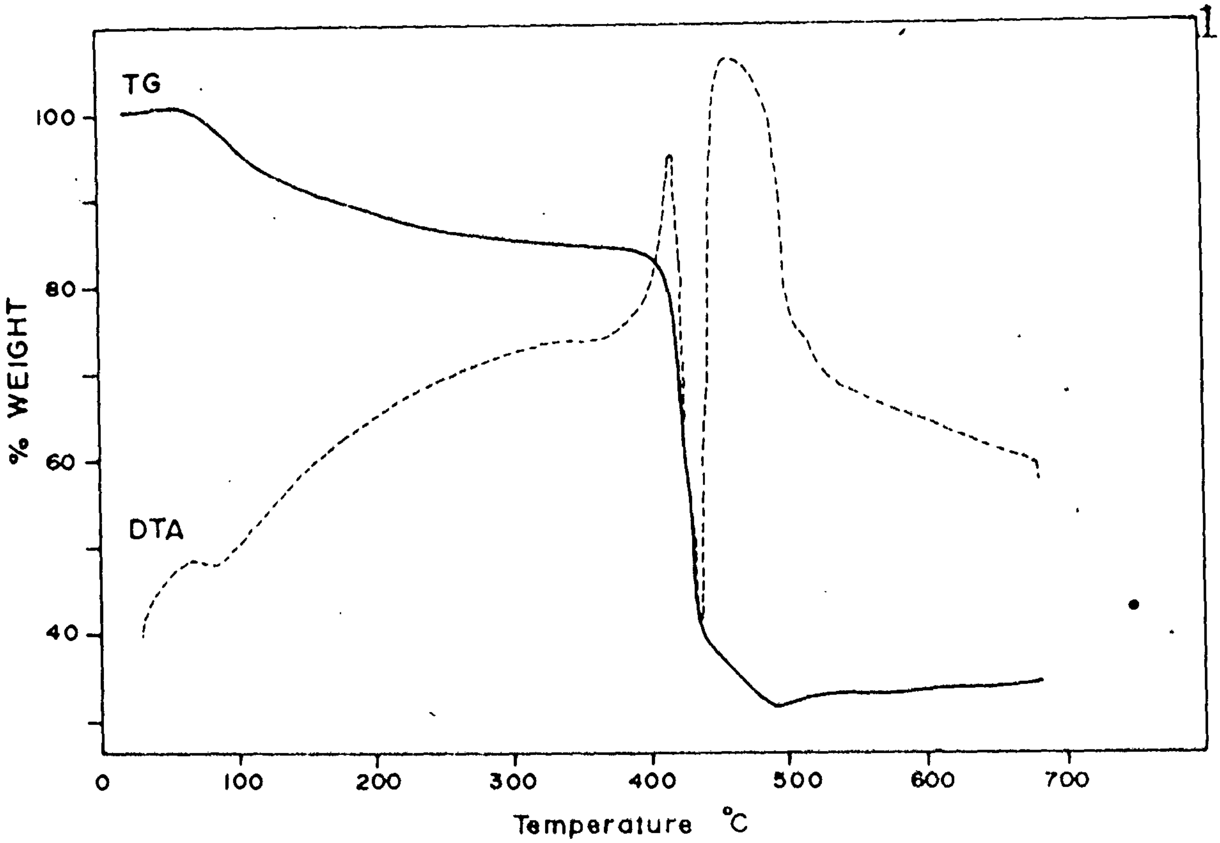

Fig. 4.11 TG, DTA of HNi N $(CH_2COO)_3 \cdot 5H_2O$

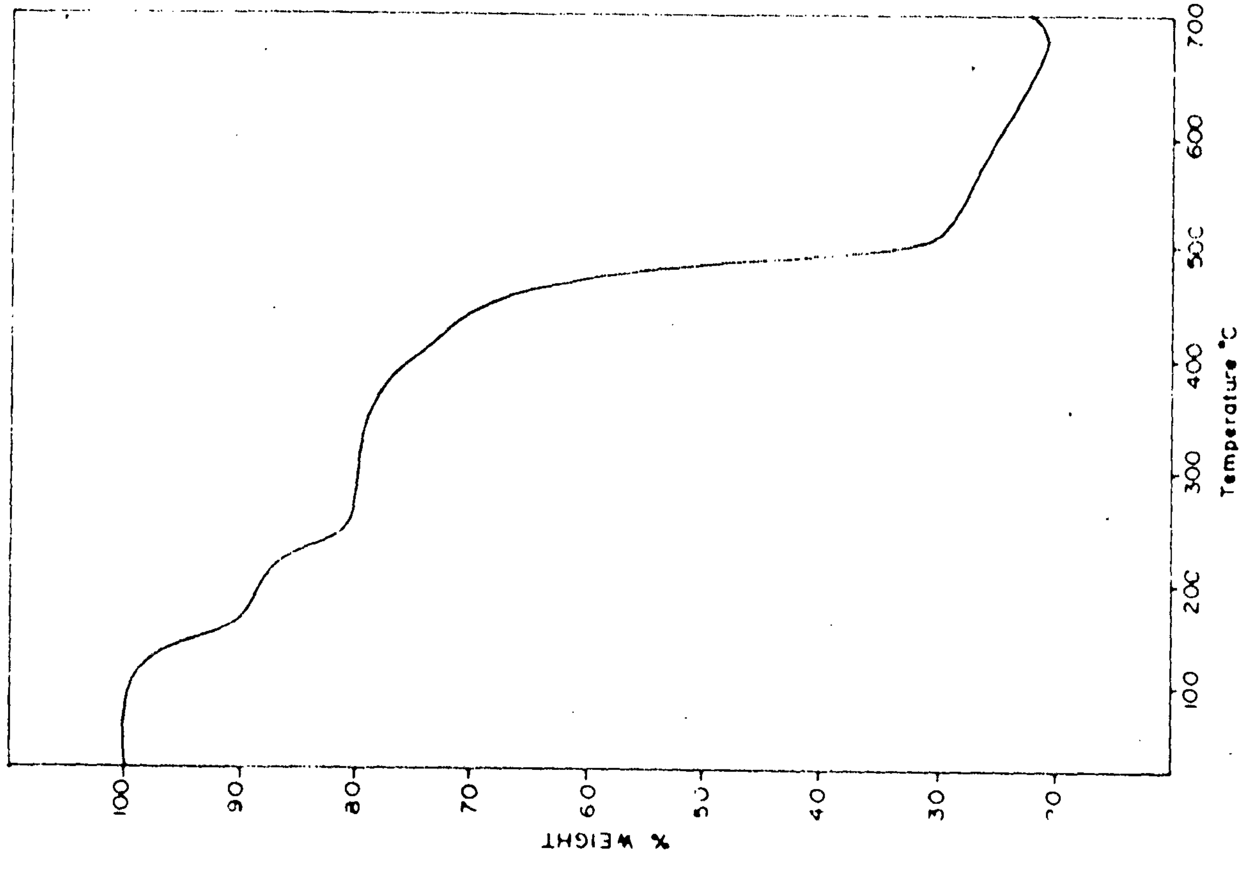

Fig 4.18 TG of (N_2H_5)Ni N $(CH_2COO)_3 \cdot 4H_2O$

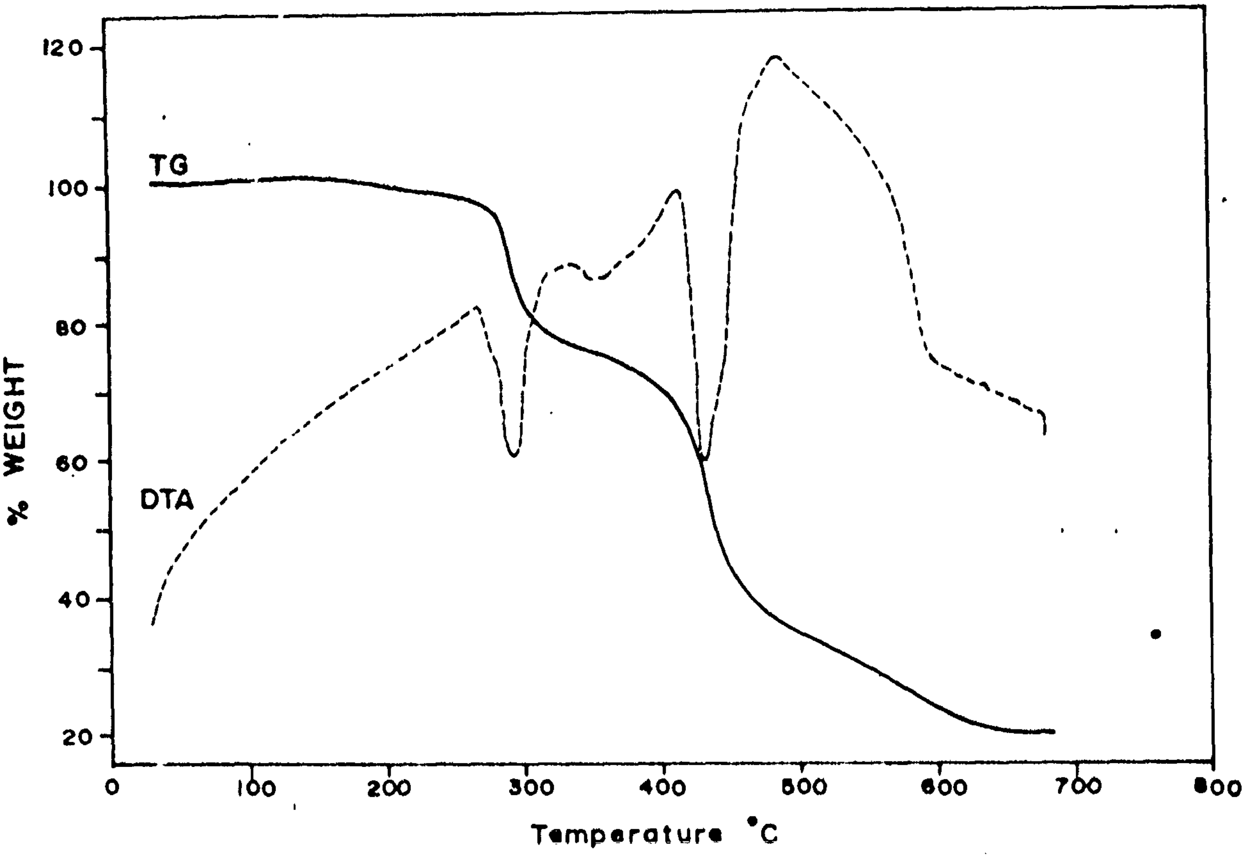

Fig. 4.12 TG, DTA of $Mg(N_2H_5)N(CH_2COO)_3 \cdot H_2O$

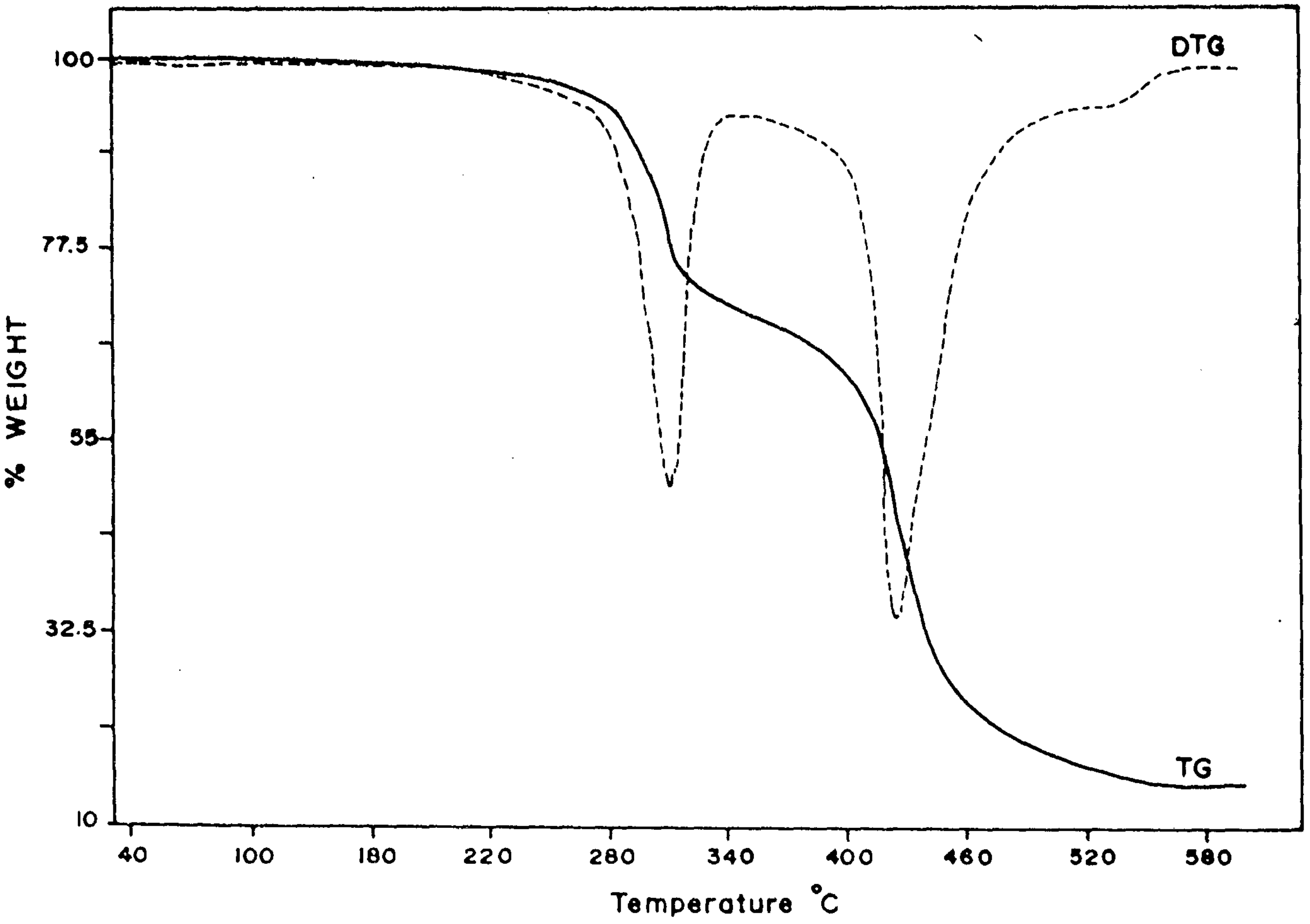

Fig. 4.13 TG, DTG of $Mg(N_2H_5)N(CH_2COO)_3 \cdot 2H_2O$

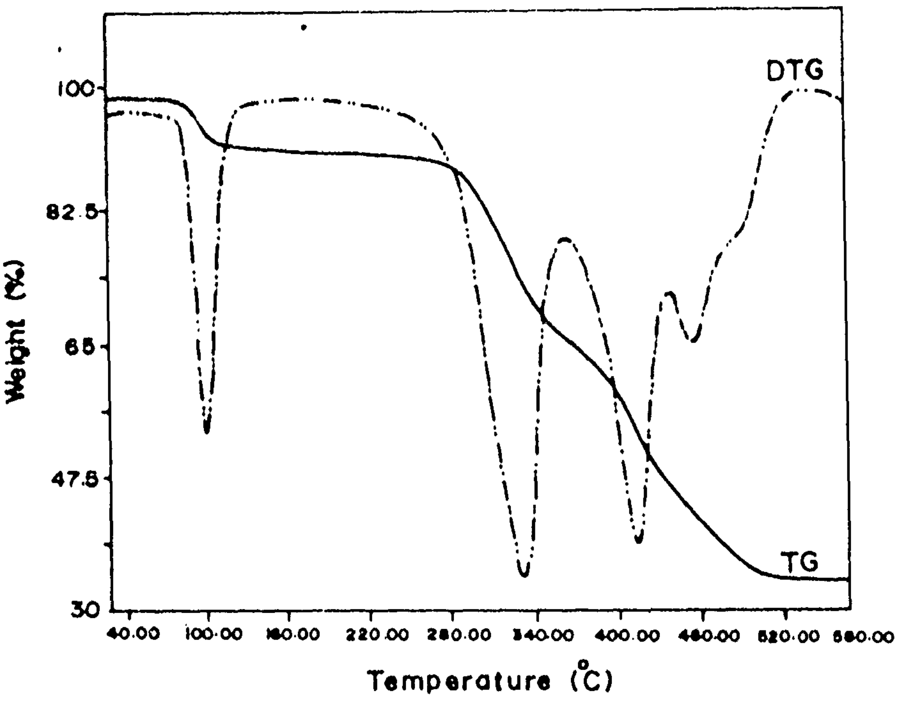

Fig.4.14 TG, DTG of $(N_2H_5)Ca\,N\,(CH_2COO)_3.2H_2O$

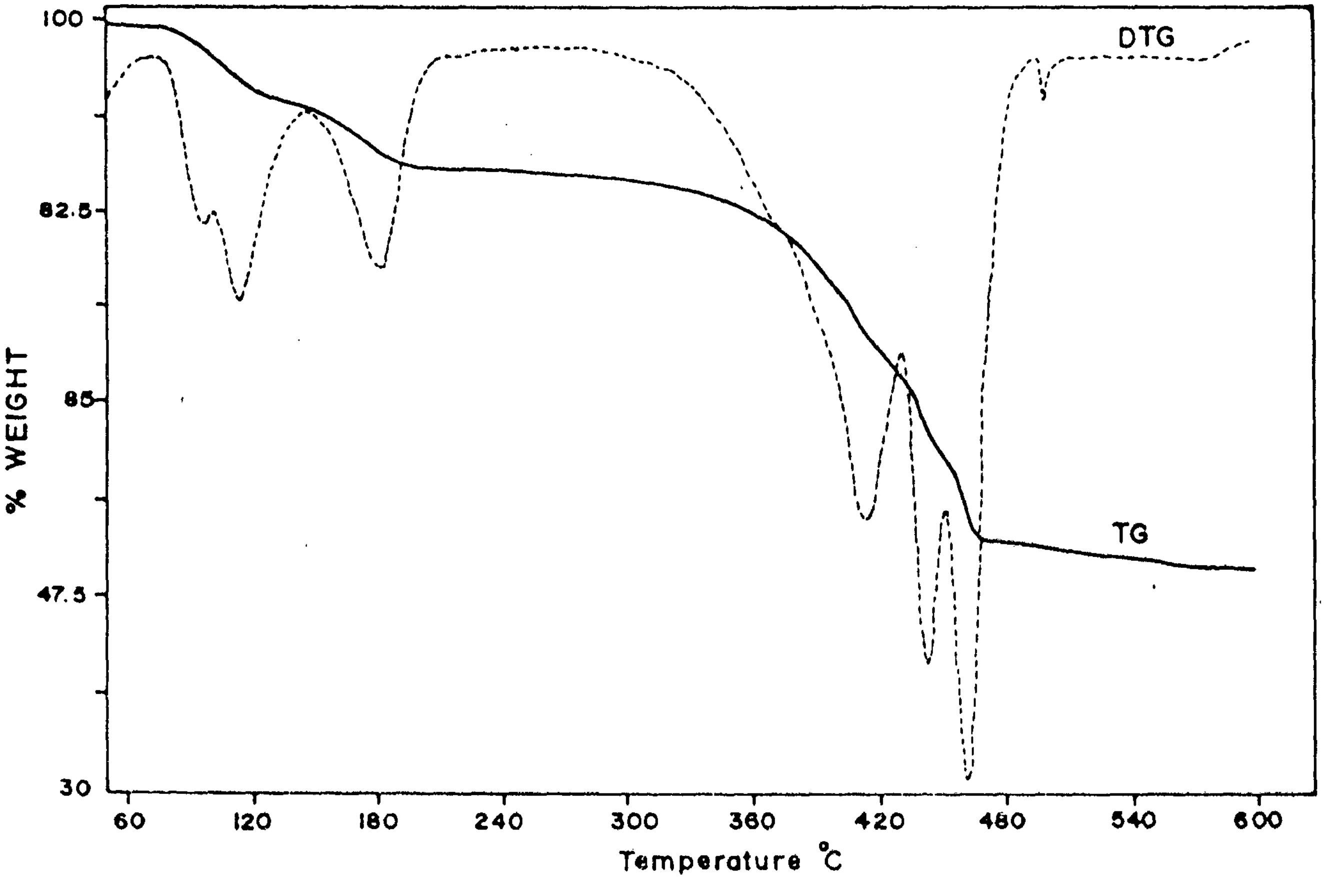

Fig.4.15 TG, DTG of $Sr(N_2H_5)N(CH_2COO)_3.1H_2O$

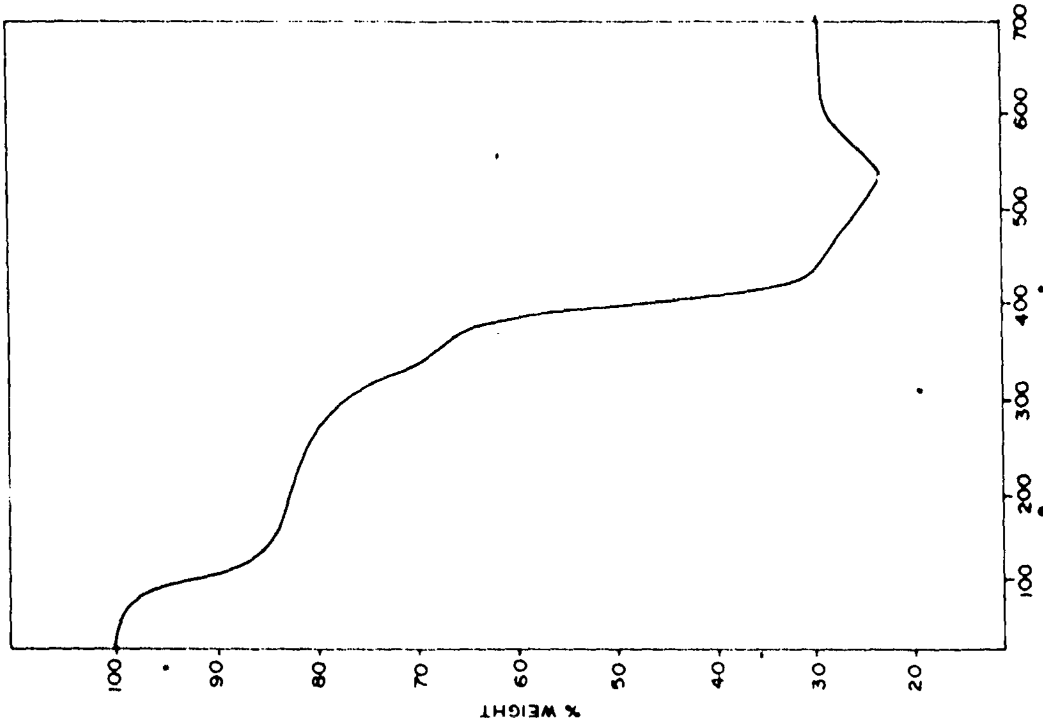

Fig 4.19 TG of $(N_2H_5)NiN(CH_2COO)_3 \cdot 5H_2O$

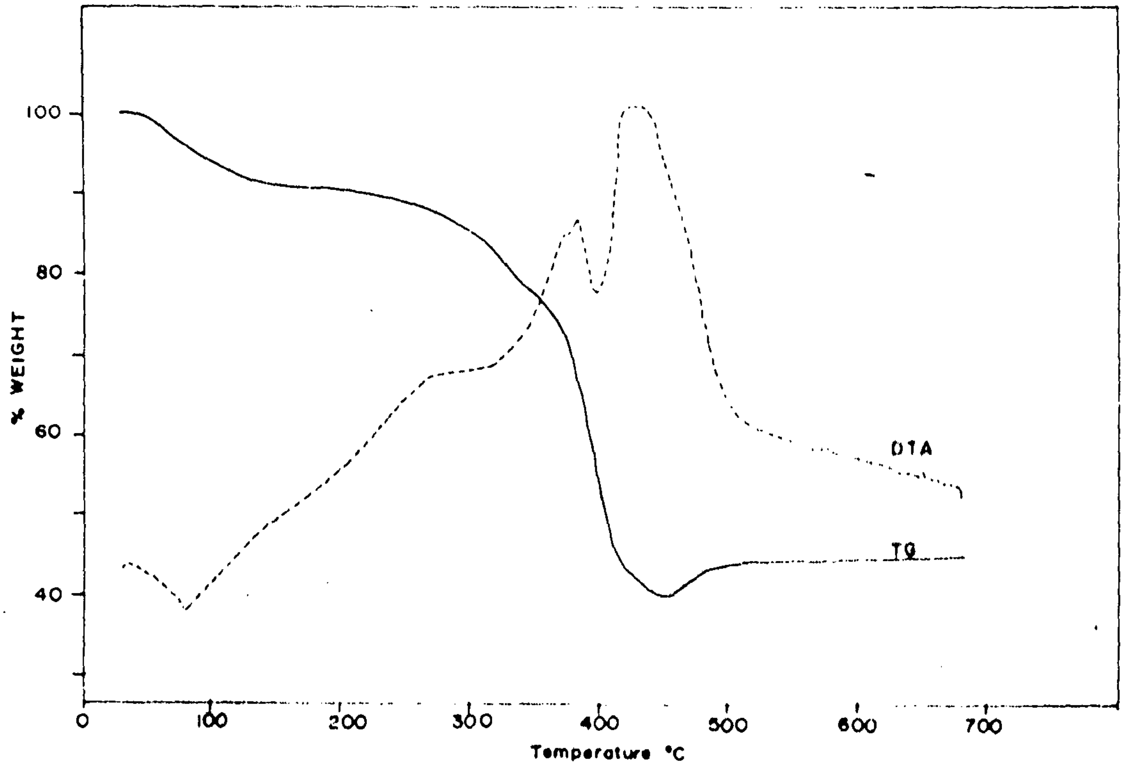

Fig.4.22 TG, DTA of $(N_2H_5)Ni\ N(CH_2COO)_3 \cdot N_2H_4 \cdot 5H_2O$

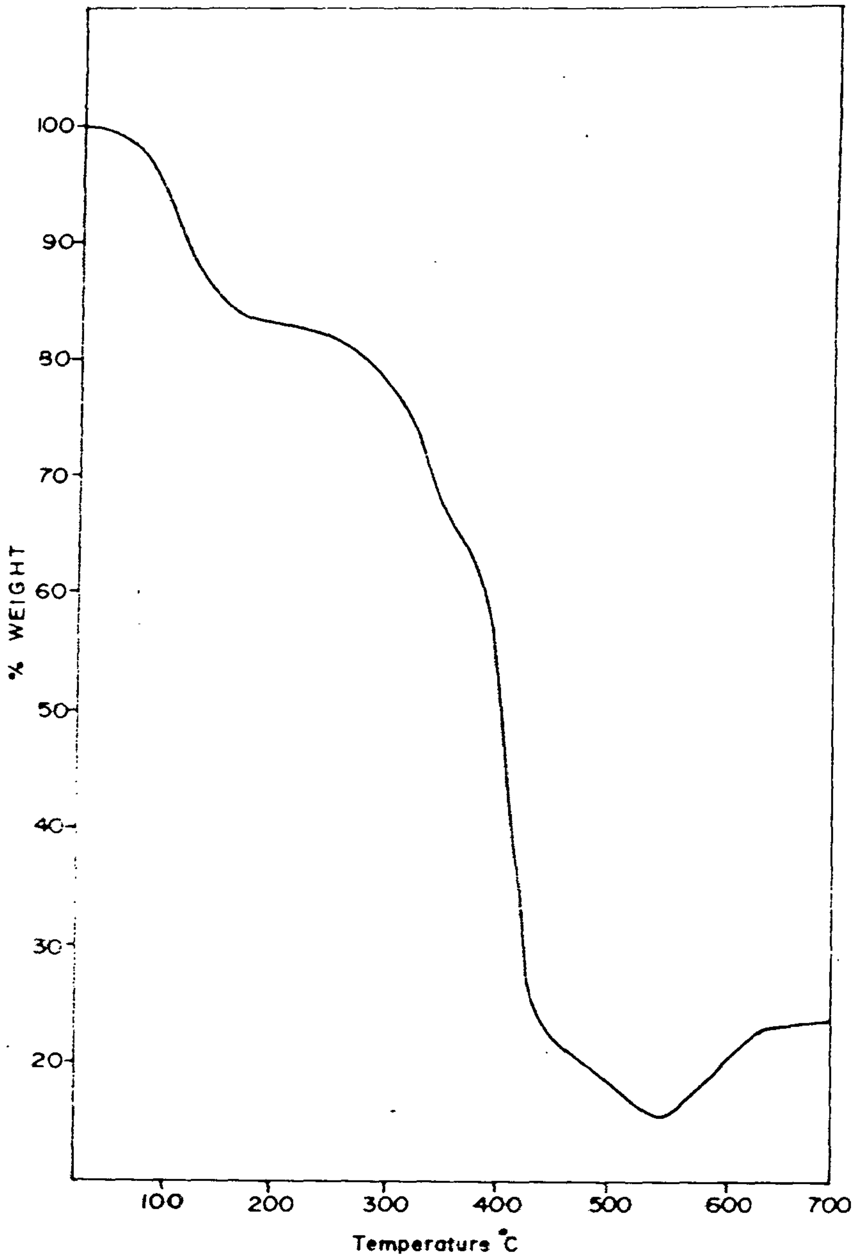

Fig 4.20 TG of $(N_2H_5)NiN(CH_2COO)_3 \cdot 0.5\ N_2H_4 \cdot 7H_2O$

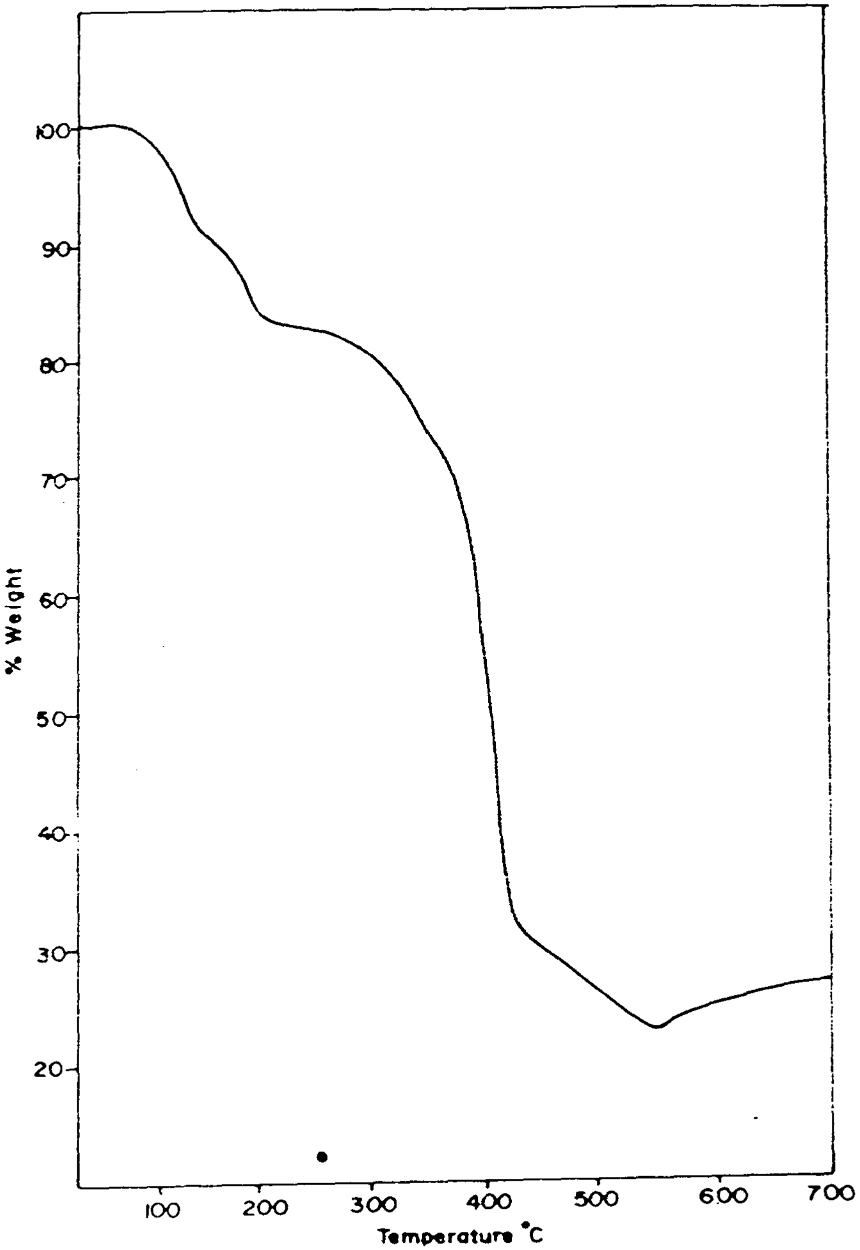

Fig.4.21 TG of $(N_2H_5)Ni\ N(CH_2COO)_3\ 3H_2O$

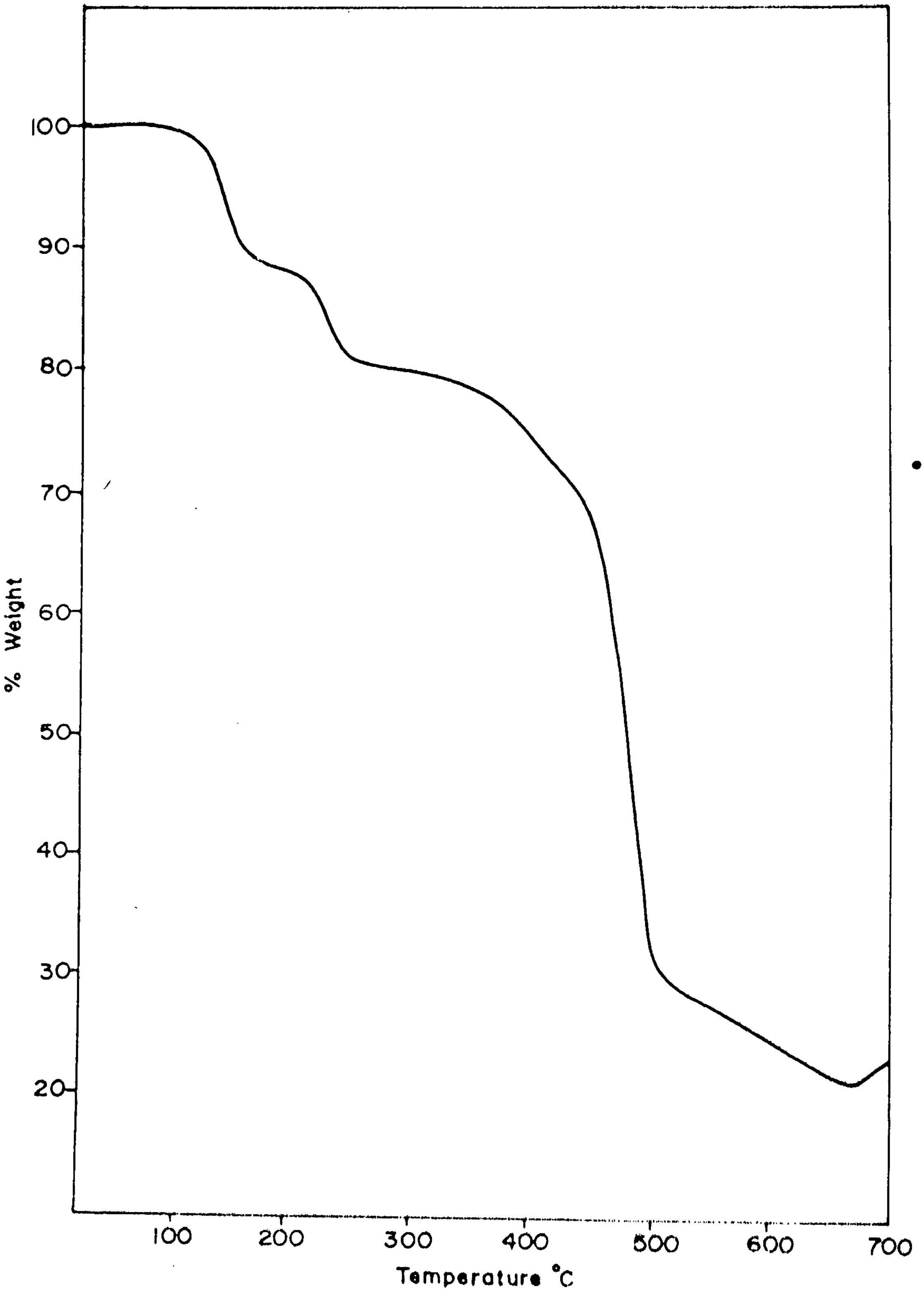

Fig.4.23 TG of $(N_2H_5)Ni\ N(CH_2COO)_3 \cdot 0.5H_2O \cdot 2H_2O$

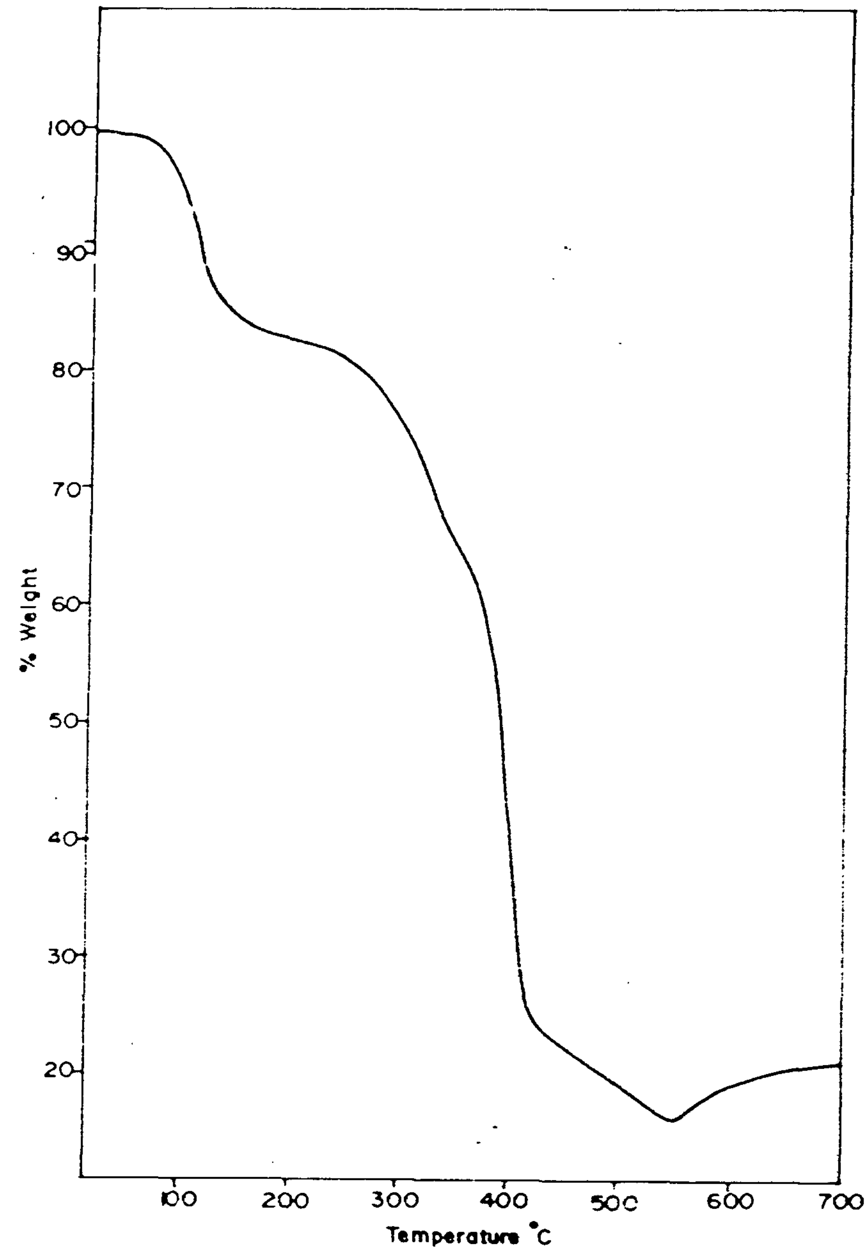

Fig. 4.24 $Na(N_4H_5)Ni_2[N(CH_2COO)_3]_2 \cdot 2N_2H_4 \cdot 3H_2O$

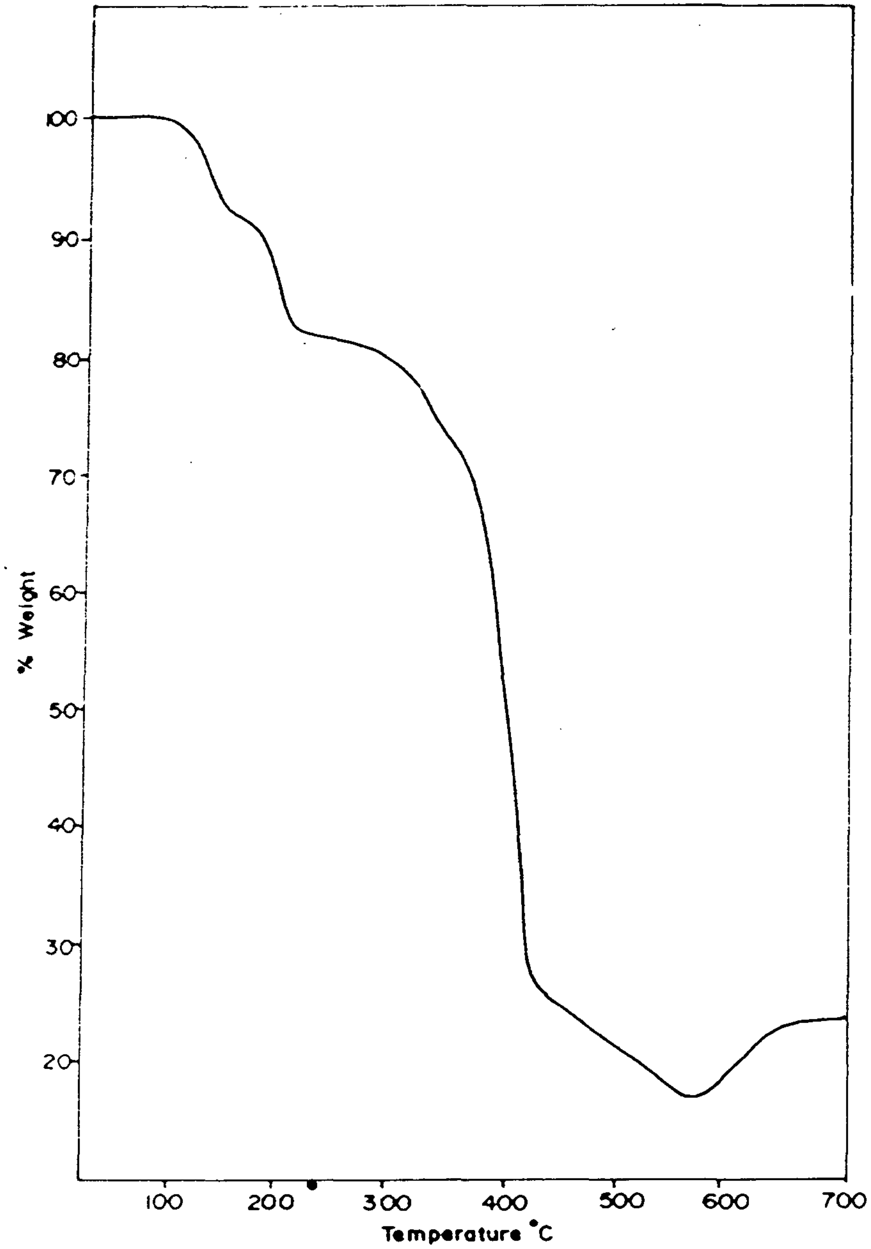

Fig 4.25 $Na(N_2H_5)Ni_2[N(CH_2COO)_3]_2 \cdot N_2H_4 \cdot 3H_2O$

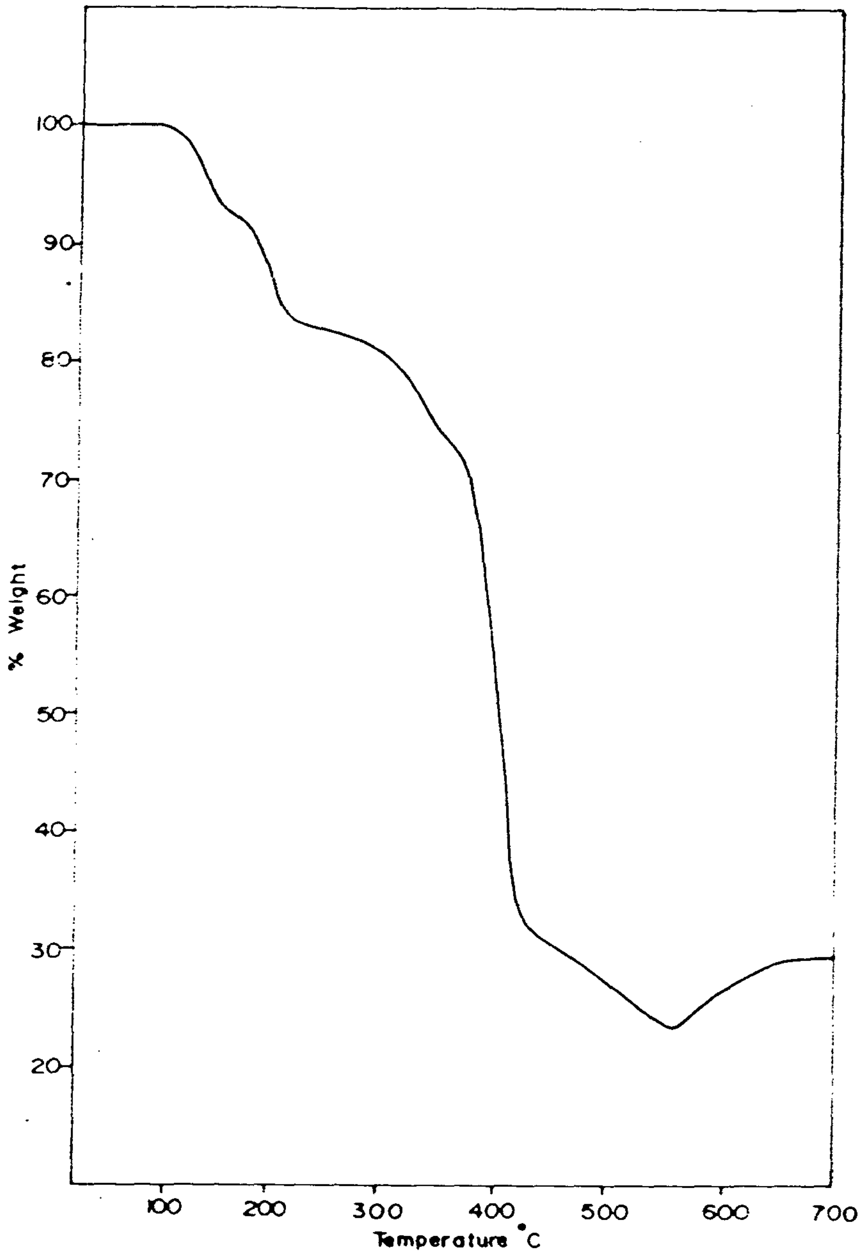

Fig. 4.26 $K(N_2H_5)Ni_2[N(CH_2COO)_3]_2 \cdot N_2H_4 \cdot 3H_2O$

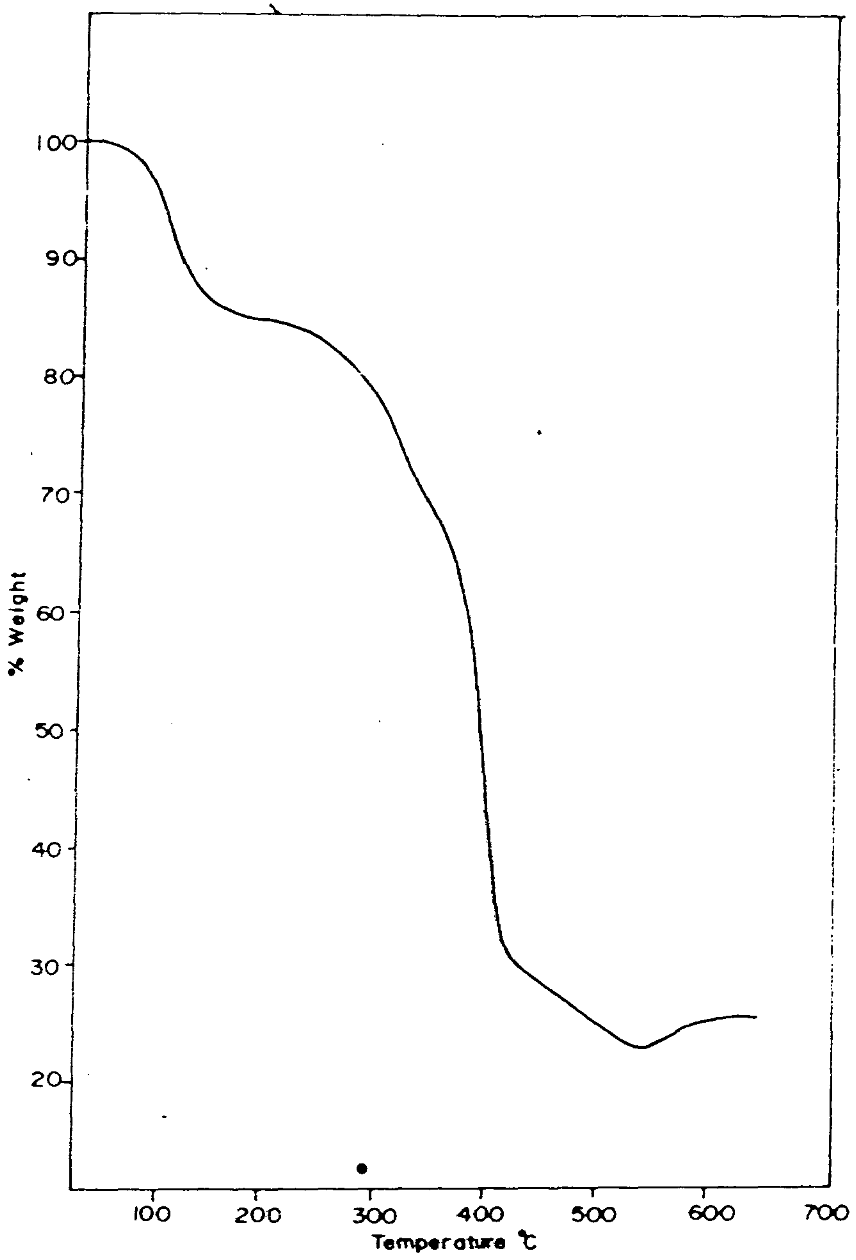

Fig.4.27 $K(N_2H_5)Ni_2[N(CH_2COO)_3]_2 \cdot 2N_2H_4 \cdot 3H_2O$

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CHAPTER FIVE

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THERMAL DECOMPOSITION KINETICS OF METAL-NTA SALTS AND THEIR HYDRAZINE DERIVATIVES

5. INTRODUCTION

Decomposition of a solid is a complicated reaction. A single and simple looking step is invariably associated with many other reactions occuring simultaneously.

They are,

(i) destruction of initial crystal lattice.

(ii) decomposition of one compound and the formation of the other,

(iii) formation of new crystalline centres for new compounds and their growth,

(iv) bond dissociation, resulting in the formation of the gaseous product(s).

(v) adsorption of gases on solid sample surface,

(vi) desorption of gaseous products,

(vii) diffusion of gaseous products, etc.

The reactions mentioned above, consequently the decomposition step, depends on the experimental conditions (section 2.3.5) adopted in the thermal method used. Thermoanalytical techniques are widely used to understand the thermal behaviour of variety of substances when subjected to heating. From among these tools, thermogravimetric analysis has found an important application in the kinetic study of the solid state reaction involving weight loss. This is because the shape of the curve in a particular step is determined by the kinetic parameters for that step. These parameters include energy of activation, order of reaction, frequency factor etc., and can be calculated from the proper assessment of the curve. Freeman and Carroll[2] have been pioneers to give the method of determination of kinetic parameters from the curve. Subsequently, based on the fundamental kinetic laws, other methods[3-8] have been developed to evaluate the parameters from thermogravimetric data. The weights of the sample at different temperatures, as seen on the TG curve have been used in the calculation of the kinetic parameters.

Computational methods have also been developed[9-12] on the basis of the procedures mentioned. In the present study, energy of activation and order of reaction for different steps in the thermal decomposition of the NTA based compounds are calculated. These kinetic parameter values are presented in this chapter.

5.1 EXPERIMENTAL : METHOD OF CALCULATING KINETIC PARAMETERS

In the present study kinetic parameters are calculated by using three methods, namely

i) Freeman and Carroll[2]
ii) Coats and Redfern[7]
iii) Horowitz and Metzger[6]

(These methods are also mentioned as FC,CR and HM respectively, in the ensuing discussion)

These three methods are based on the basic kinetic laws of the rate of reaction and the Arrehenius equation.

$-(dX/dt) = k\ X^n$ where X = mole fraction or amount of reactant

and $k = Ze^{-Ea/RT}$

k = Specific rate

n = order of reaction

Z = frequency factor

Ea = energy of activation

T = Temperature (deg.kelvin)

such that, $-(dX/dt) = Ze^{-Ea/RT}.\ X^n$ .... eq(i)

on the basis of this equation different methods, as mentioned above, have been designed.

5.1.1 FREEMAN AND CARROLL METHOD

Using equation(i), Freeman and Carroll have derived a method of evaluation of kinetic parameters in the solid state decomposition of reaction. In terms of moles of the reactants, eqn(i) has been modified such that,

$$-(dn_o/dt) = -[(n_o/w_o)(dw/dt)]$$

The advantage in this approach is that it relates the number of molecules of reactants to the weight.

The expression used to calculate the kinetic parameters in the FC method is

$$-(E_a/RT)\ \frac{D\ (1/T)}{D\ \log\ W_r} = -x + \frac{D\ \log(dw/dt)}{D\ \log\ W_r}$$

where $w_r = w_o - w$ w_o = weight loss at completion of reactions.

w = Total weight loss upto time t.

dw/dt is the rate of change in weight which can be equated to (dw/dT)q where q is the heating rate of the sample.

Therefore graph of $\frac{D \log[(dw/dT)q]}{D \log Wr}$ V/S $\frac{D\ (1/T)}{D \log Wr}$ woule give an intercept on the y-axis which is identified as the order of the reaction. And from the slope of the line, energy of activation can be calculated.

$$\text{slope} = -(E_a/RT)$$

In the present study the change in the sample weight with the temperature was obtained from the TG curve by going horizontally equal division on either side of a particular point of the curve and extending two vertical lines in opposite directions at these position to the curve. From the vertical difference in the percentages (or weights), and corresponding temperature difference for the two point of the curve, dw/dT value was calculated.

These plots were obtained on Computer using Lotus 1-2-3 R3.

5.1.2 COATS AND REDFERN METHOD

In this method the weight of the reaction is expressed in terms of the fraction (α) of the reactant decomposed.

$(d\alpha/dt) = K\ (1-\alpha)^n$ where α = fraction of the reactant decomposed

$\therefore K\ (1-\alpha)^n = Ze^{-Ea/RT}$ n = order of reaction

On the basis of this equation, an expression has been derived by Coats and Redern as,

$$\text{Log}\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \log\frac{AR}{E_a}\left[1-\frac{2RT}{E_a}\right] - \frac{E_a}{2.303\ RT}$$

and therefore the graph of $\log \left[\frac{1-(1-\alpha)^{1-n}}{T^2\ (1-n)} \right]$ ... Y-axis

and 1/T ... X-axis

should result in a straight line with the slope equal to −Ea/2.303R.

On the basis of this equation a program on computer in FORTRAN language was developed for instant calculation of Ea. for the best fitting "n" values which is given below.

```
        dimension a(25),t(25),alg(25),act(20),ord(20)
        open(7,file='input.n')
        read(7,*)nset
        do 19  iset = 1,nset
        act(iset) = 0.0
        ord(iset) = 0.0
        write(*,*)iset,nset
        read(7,*)npt
        read(7,*)(a(i),i=1,npt)
        read(7,*)(t(i),i=1,npt)
        do i =1,npt
        a(i)=1-a(i)
        t(i)= 1.0/t(i)
        enddo
 5      write(6,*)'nst,nnd,nstp'
        read(5,*)st,ed,nstp
        if(st.ge.2)goto 19
        ncrt = 0
        an = st
        nr = 0
 2      continue
        do i =1,npt
        var=(1-a(i)**(1-an))/(1-an)
        alg(i)=log10(var*t(i)*t(i))
        enddo
        var = enact(npt,alg,t,ea,corcof)
        if(ncrt.gt.0.and.nr.eq.0)then
        if(corcof.gt.ctt)then
        act(iset) = ett
        ord(iset) = ott
        write(*,*)'                    <-------------------->'
        nr = 1
```

```
        endif
        endif
        ctt = corcof
        ett = ea
        ott = an
        write(*,77)ea,corcof.an
        if(nr.eq.1)goto 19
77      format(1x,'Ea = ',f12.5,' coeffi. = ',f12.6,2x,f12.5)
        an = an + (ed-st)/nstp
        ncrt = ncrt+1
        if(ncrt.le.nstp)go to 2
        if(nr.eq.0)goto 5
19      continue
        close(7)
78      format(1x,i5,2x,'Ea = ',f12.5,5x,'n  = ',f12.5)
        open(7,file='output.n')
        do i = 1,nset
        write(7,78)i,act(i),ord(i)
        enddo
        close(7)
        stop
        end

        function enact(npt,y,x,ea,corcof)
        dimension x(25),y(25)
        enact = 0.0
        sx = 0.0
        sy = 0.0
        sxy = 0.0
        sxx = 0.0
        do i =1,npt
        sx = sx + x(i)
        sy = sy + y(i)
        sxy = sxy + x(i)*y(i)
        sxx = sxx + x(i)*x(i)
        enddo
        var = npt*sxx-sx*sx
        if(abs(var).le.1.0e-12)then
        write(*,*)'line parallel to y axis'
        return
        endif
        slp = (npt*sxy-sx*sy)/var
        cpt = (sy*sxx-sx*sxy)/var
        ea = -slp*1.987*2.303
        xmin = sx/npt
        ymin = sy/npt
        sxy = 0.0
        sxx = 0.0
        syy = 0.0
        do i =1,npt
```

```
      sxy = sxy + (x(i)-xmin)*(y(i)-ymin)

      sxx = sxx + (x(i)-xmin)**2

      syy = syy + (y(i)-ymin)**2
      enddo
      if(abs(sxx*syy).le.1.0e-24)stop
      corcof = sxy/((sxx*syy)**(0.5))
      return
      end
```

5.1.3 HOROWITZ AND METZGER METHOD

This method makes use of the equation

$$\ln.\ln[(W_o-W_f)/(W_t-W_f)] = (E_a/RT_s^2)\theta$$

Where W_T = the weight remaining at the given temp.

W_o = initial weight

W_f = final weight

θ = T - Ts where Ts is the peak temperature

The graph of the values on the left hand side in above equation (Y-axis) and θ (X-axis) is a straight line. The energy of activation is then calculated by using the slope and the expression E_a/RT_s^2

$$\text{slope} = E_a/RT_s^2$$

These plots were obtained on a Computer using Lotus 1-2-3 R3.

5.2 RESULTS AND DISCUSSION : KINETIC PARAMETERS IN THE DECOMPOSITION

There are four Principle steps in the decomposition of metal nitrilotriacetate hydrates salts and their hydrazinates. The reactions in the sequence being

i) dehydration (total or partial in two or more stages) and dehydrazination,

ii) decomposition of metal nitrilotriacetate (which is also associated with the free radical decomposition) leading to the corresponding metal acetate,

iii) decomposition of metal acetate to metal oxycarbonate, and

iv) decomposition of the metal oxycarbonate involving partial loss of carbon dioxide.

These steps in the TG are analysed by using the three methods described in Section 5.1. The values of the kinetic parameters obtained by means of Coats-Refern and Freeman-Carroll methods are in good agreement. Although the values obtained by the Horowitz-Metzger method are on the higher side, for some of the steps (Table 5.1), the variation is within 10%.

The activation energy for the dehydration step is between 4.5 to 13.5 K Cal mole^{-1} depending on the number of moles of H_2O lost in the step. The decomposition of the salt from nitrilotriacetate to the acetate form is associated with the activation energy of ~30 K Cal mole^{-1}.

The metal acetates decompose to the corresponding oxycarbonates due to the concentrated atmosphere of carbon dioxide surrounding the sample holder. Obviously, this is due to the decomposition of the organic nitrilotriacetate ion From the activation energy value for the loss of partial carbon dioxide from the oxycarbonate (step iv above), it can be concluded that carbon dioxide is losely bonded to the metal oxide. The hydrazine derivatives of nitrilotriacetate salts on heating in air and in an open crucible, decompose to the corresponding metal oxide(s). The percentage weight loss in this decomposition substantiate the observation.

Nickel hydrazinium nitrilotriacetate complexes, $(N_2H_5)Ni[N(CH_2COO)_3].xN_2H_4.yH_2O$, were heated (in air) to about 700°C. The X-ray powder diffraction patterns of these residues, thus obtained, were determined by using the instrument mentioned in Section 2.3.6. These patterns indicate that the complexes decompose, in combustion, to nickel oxide (with traces of metal nickel).

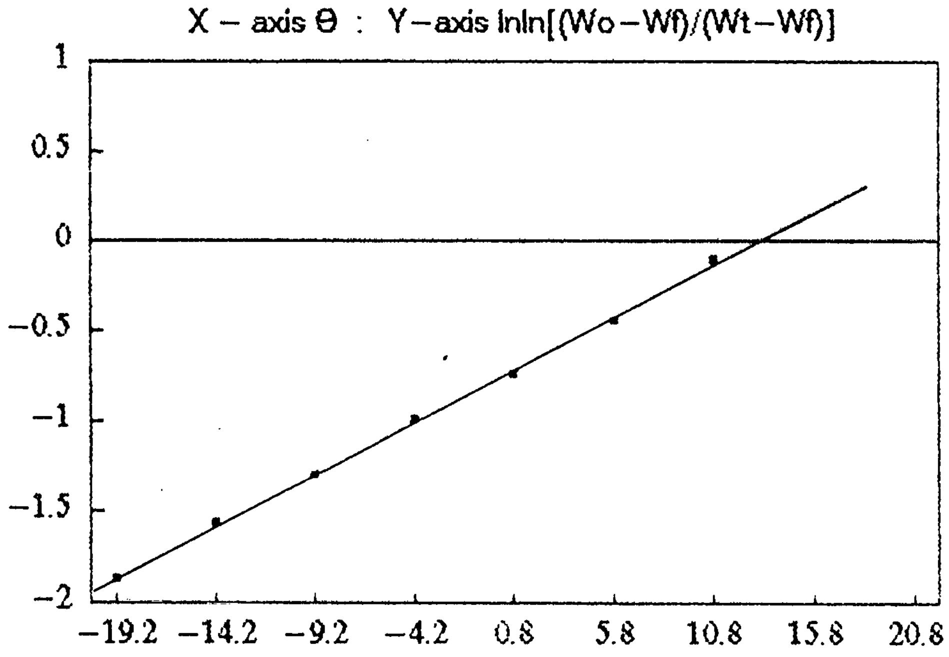

Fig. 5.1.1 HM Plot for Step I in the TGA of sample MG–1

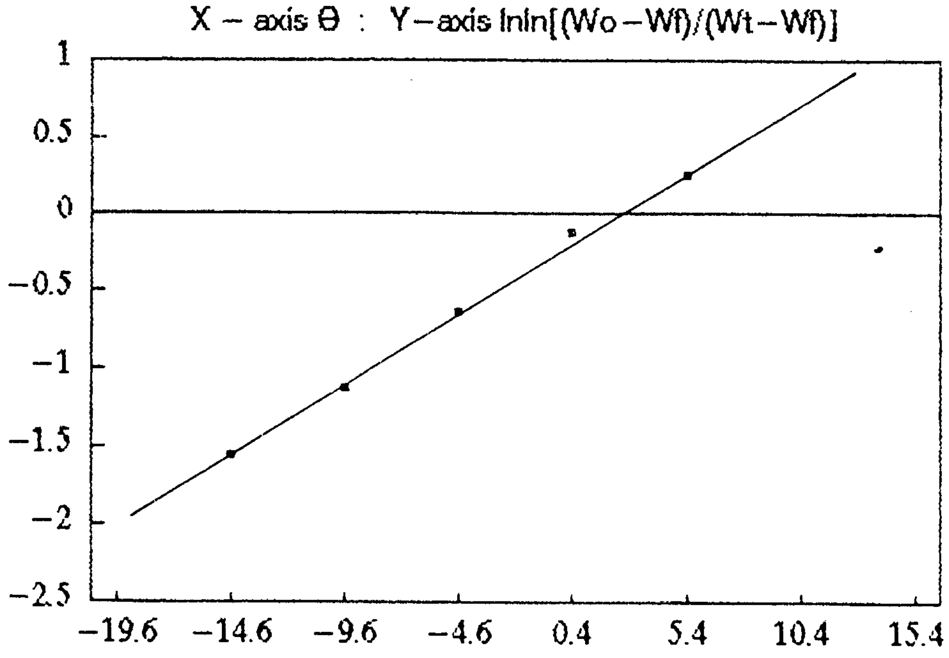

Fig. 5.1.2 HM Plot for Step II in the TGA of sample MG–1

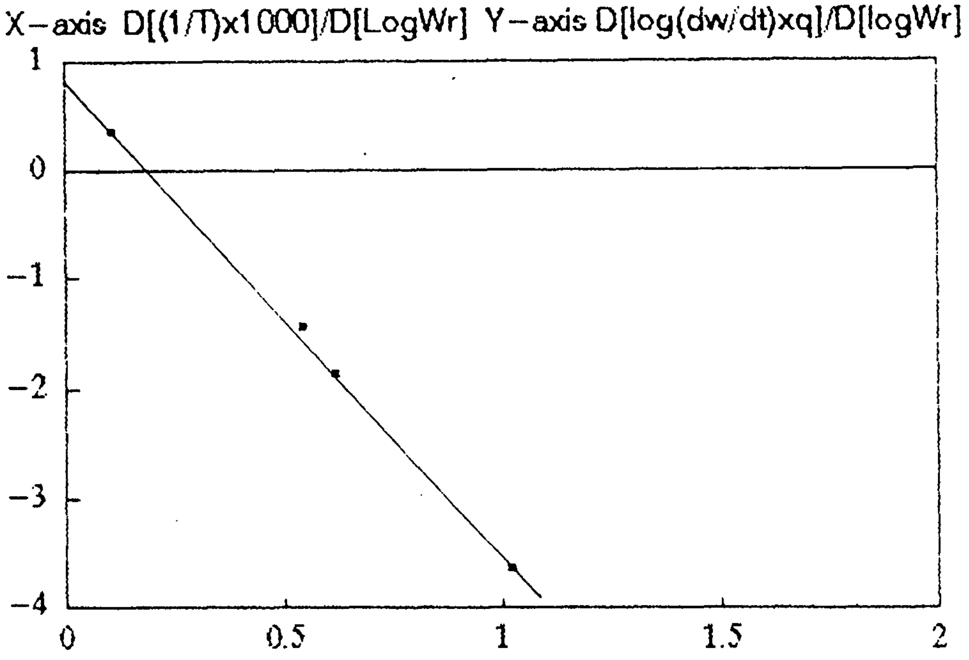

Fig. 5.2.1 FC Plot for the Step I in the TGA of sample MG-1

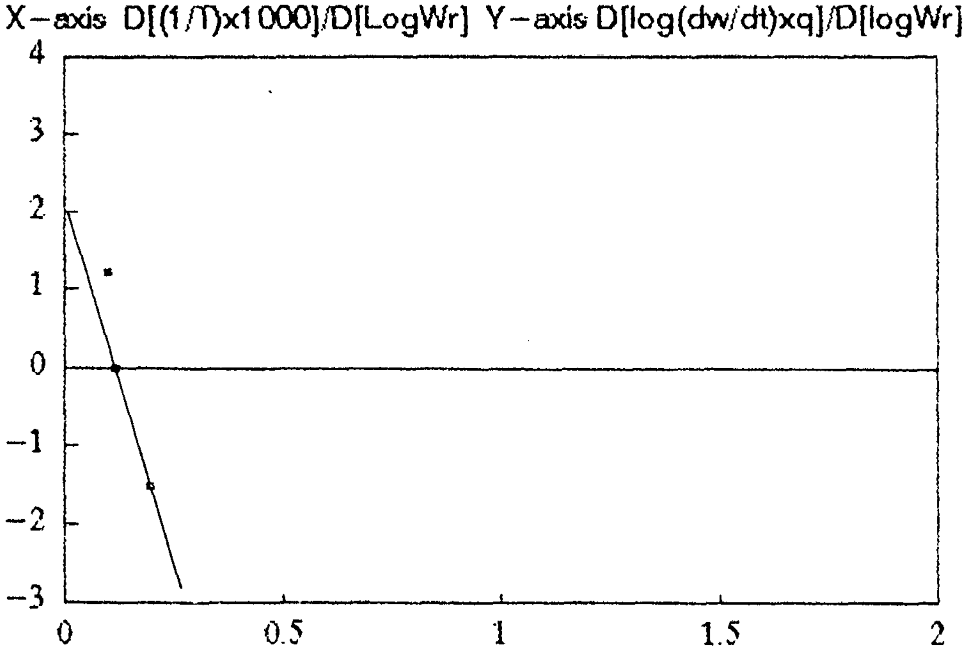

Fig. 5.2.2 FC Plot for the Step II in the TGA of sample MG-1

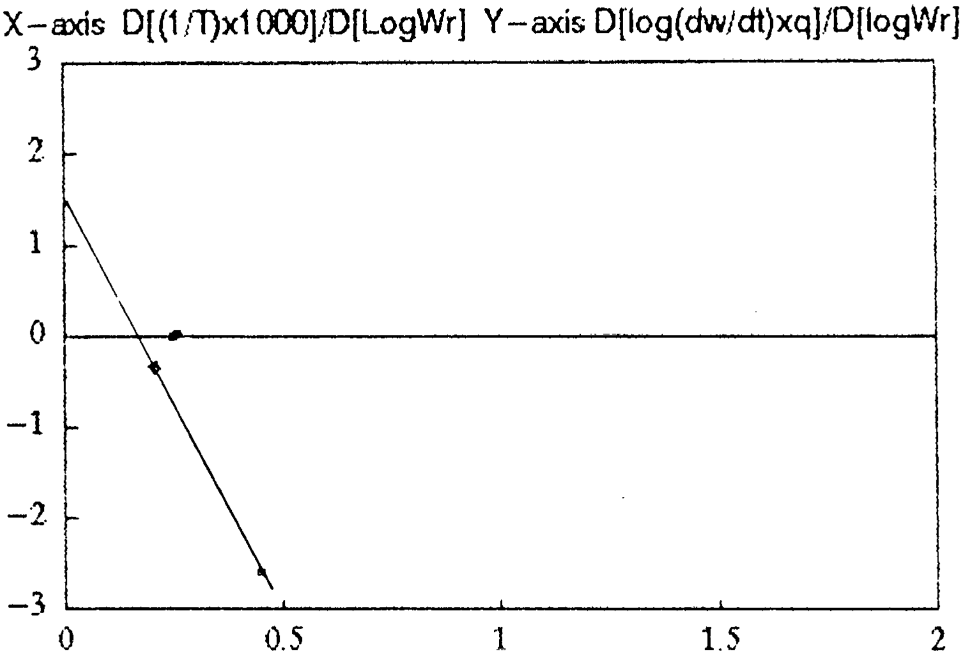

Fig. 5.2.3 FC Plot for the Step IV in the TGA of sample MG−1

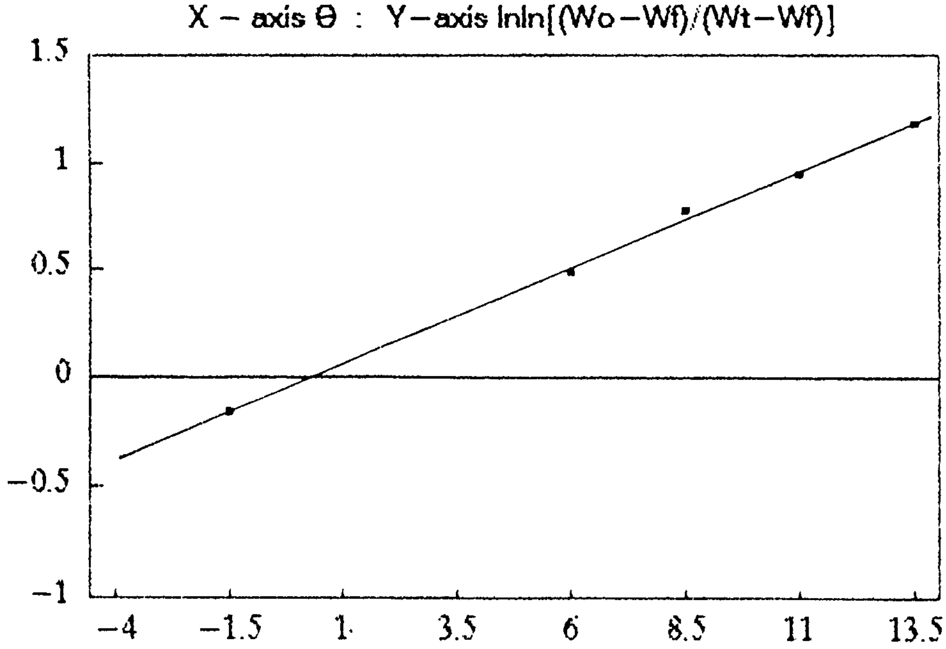

Fig. 5.3.1 HM Plot for Step I in the TGA of sample MG−3

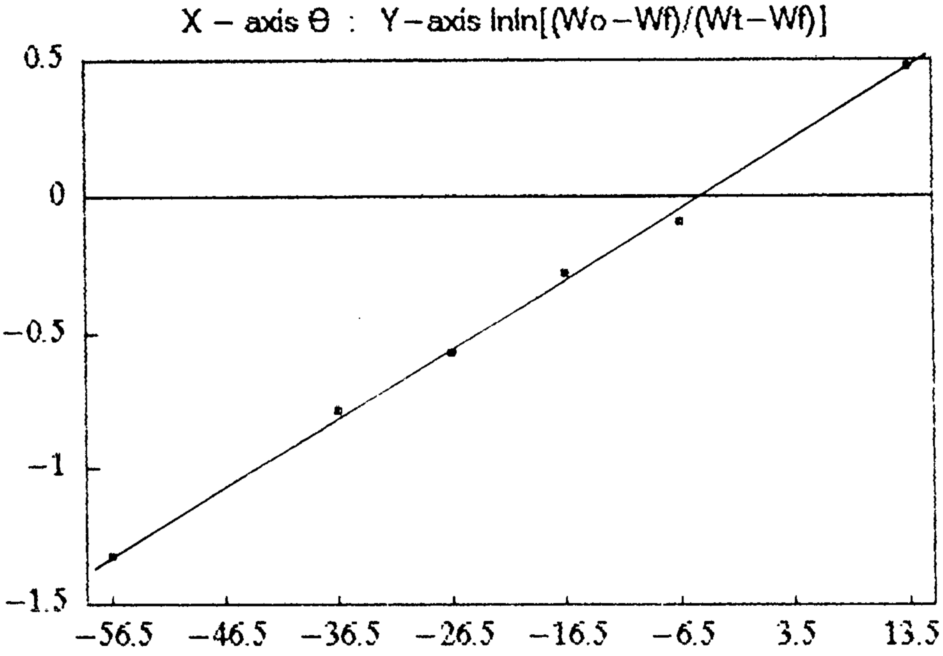

Fig. 5.3.2 HM Plot for Step II in the TGA of sample MG–3

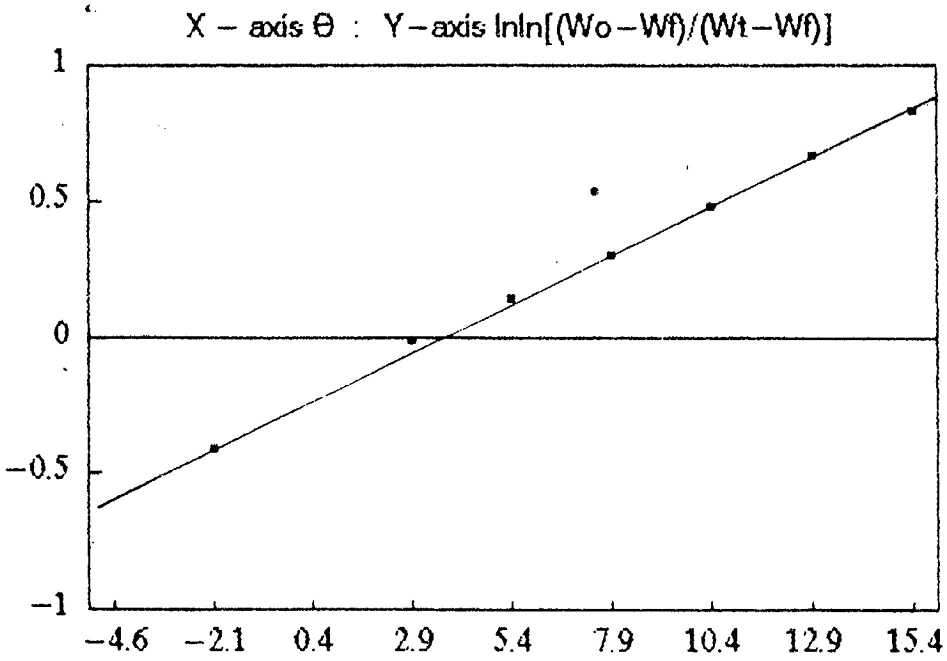

Fig. 5.3.3 HM Plot for Step III in the TGA of sample MG–3

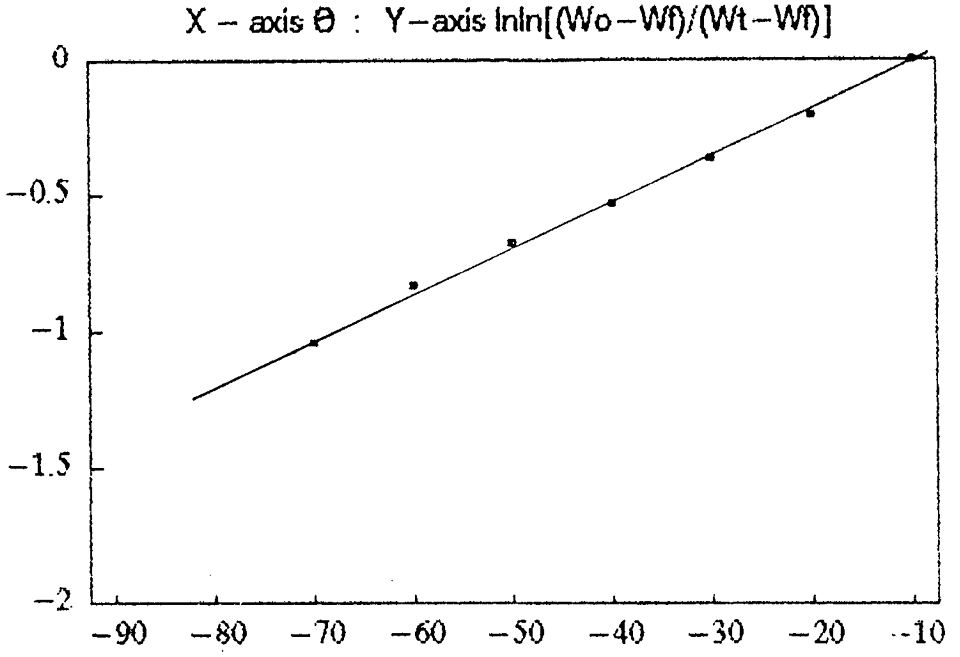

Fig. 5.3.4 HM Plot for Step IV in the TGA of sample MG–3

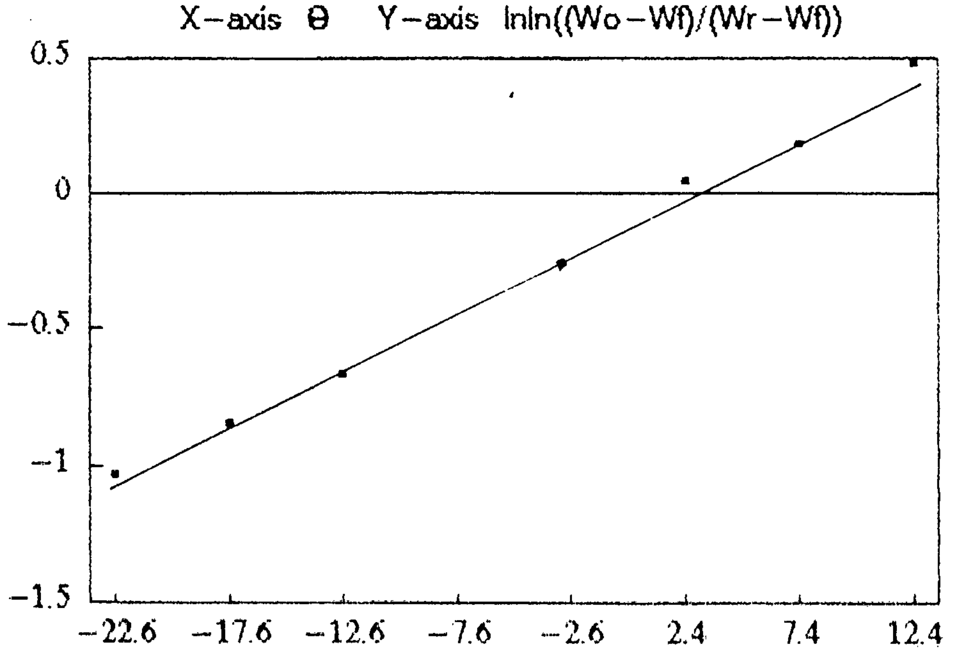

Fig. 5.4.1 HM Plot for Step I in the TGA of sample MG–4

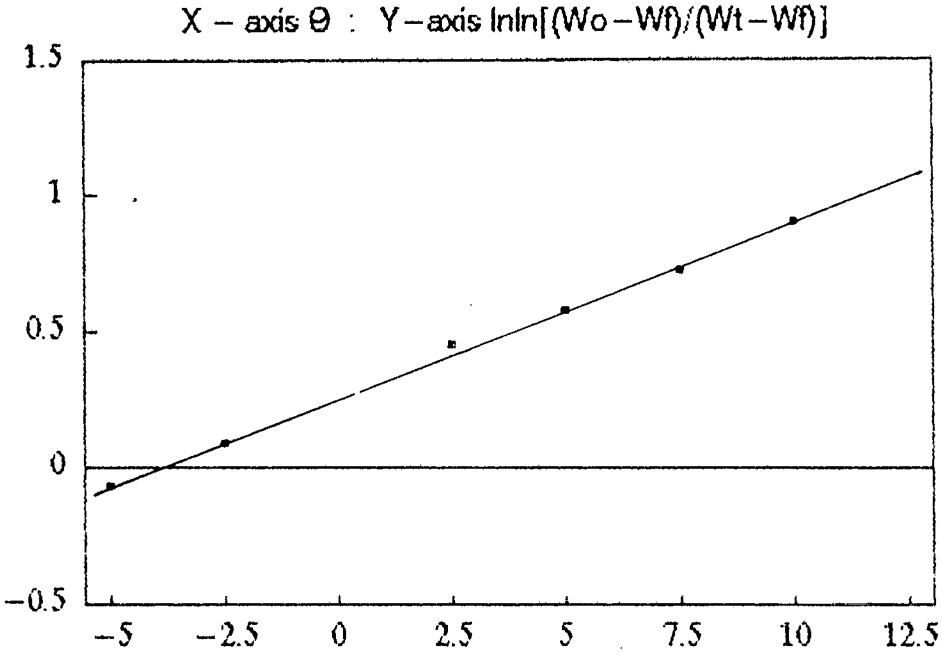

Fig. 5.5.1 HM Plot for Step I in the TGA of sample CA–1

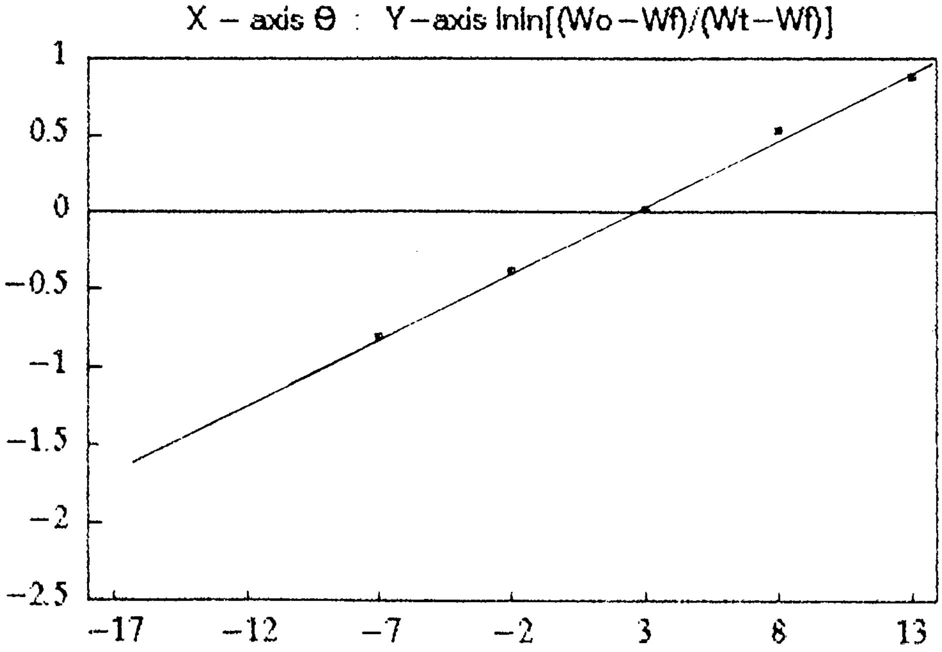

Fig. 5.5.2 HM Plot for Step II in the TGA of sample CA–1

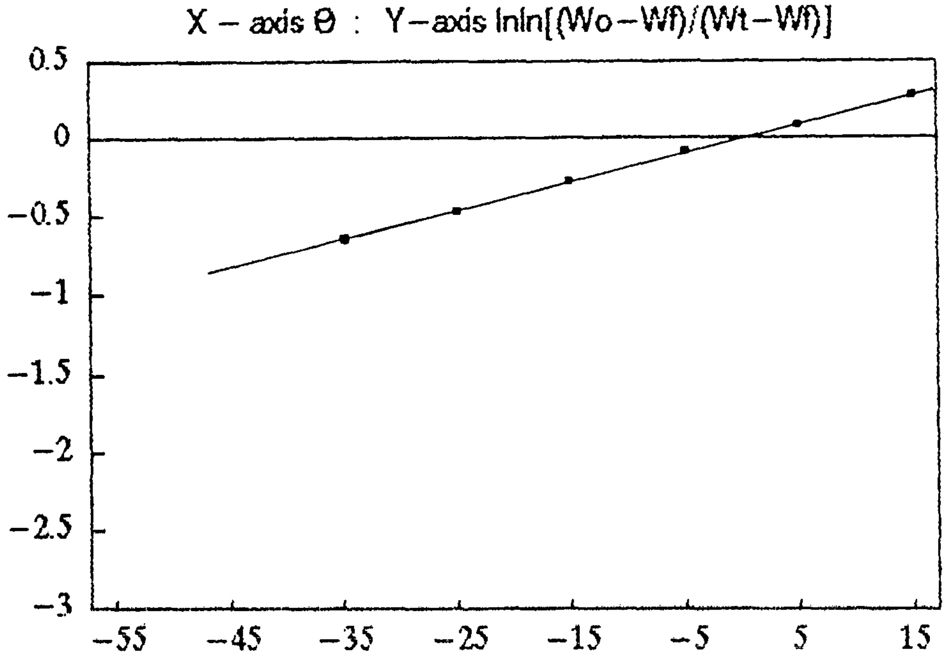

Fig. 5.5.3 HM Plot for Step III in the TGA of sample CA–1

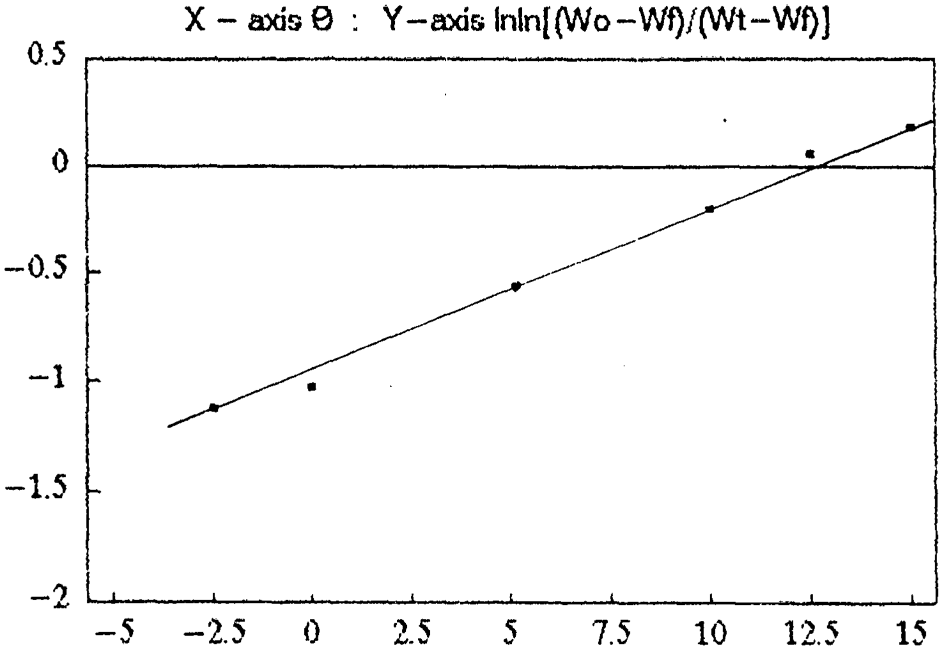

Fig. 5.5.4 HM Plot for Step IV in the TGA of sample CA–1

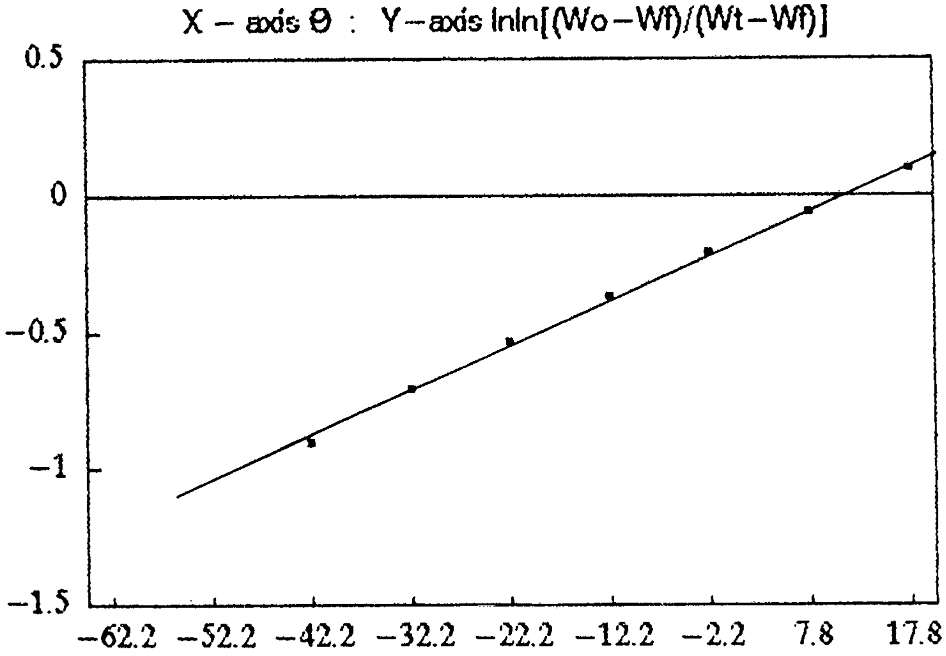

Fig. 5.5.5 HM Plot for Step V in the TGA of sample CA–1

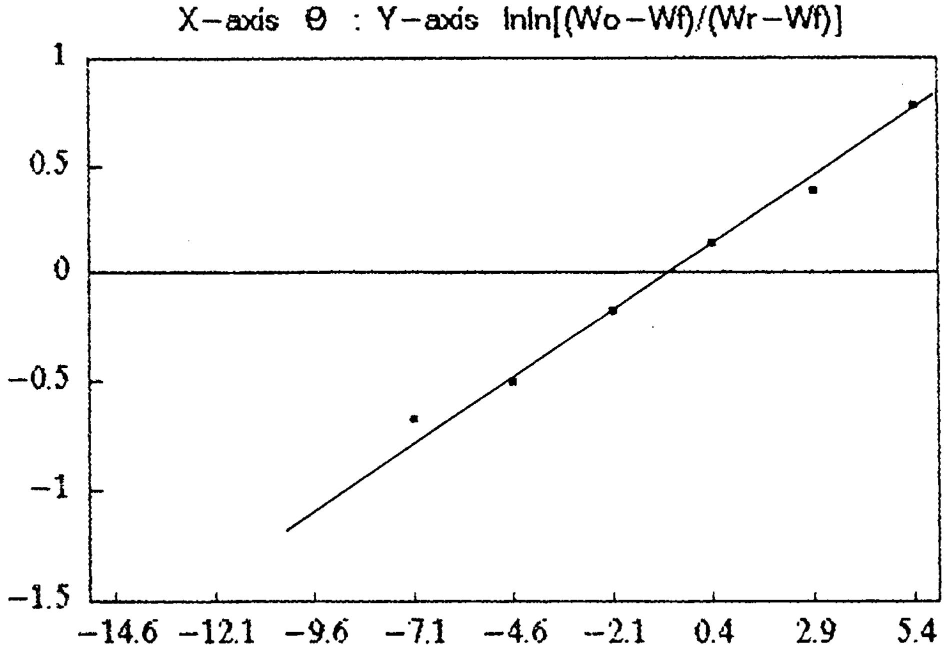

Fig. 5.6.1 HM Plot for Step I in the TGA of sample CA–3

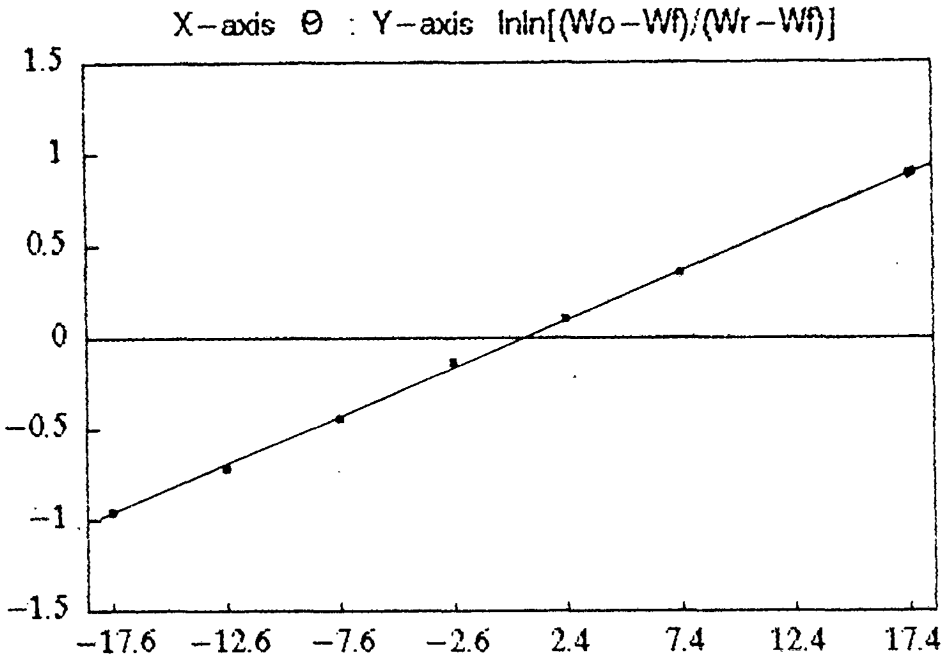

Fig. 5.6.2 HM Plot for Step II in the TGA of sample CA-3

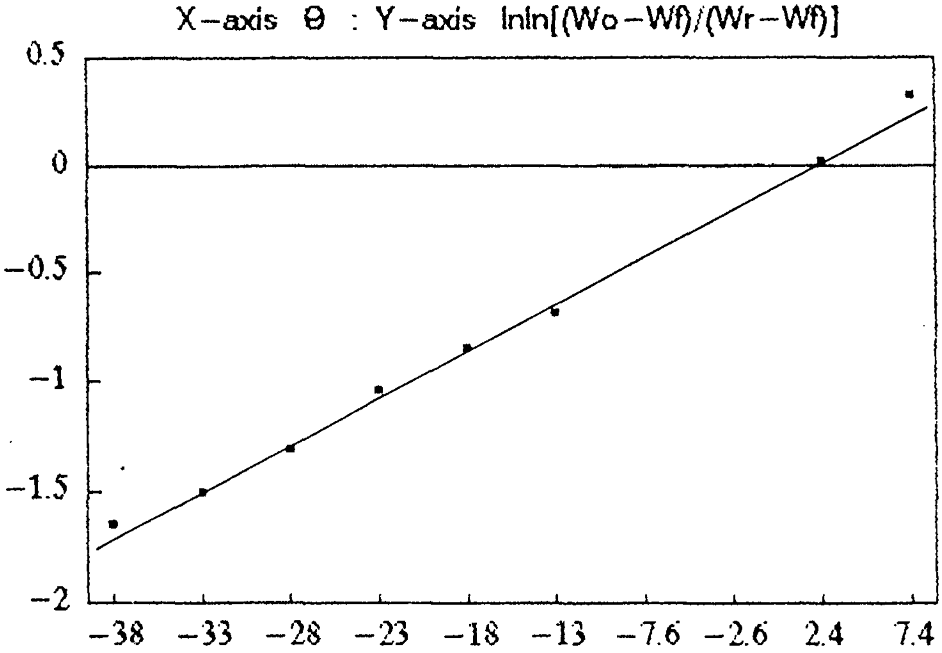

Fig. 5.6.3 HM Plot for Step III in the TGA of sample CA-3

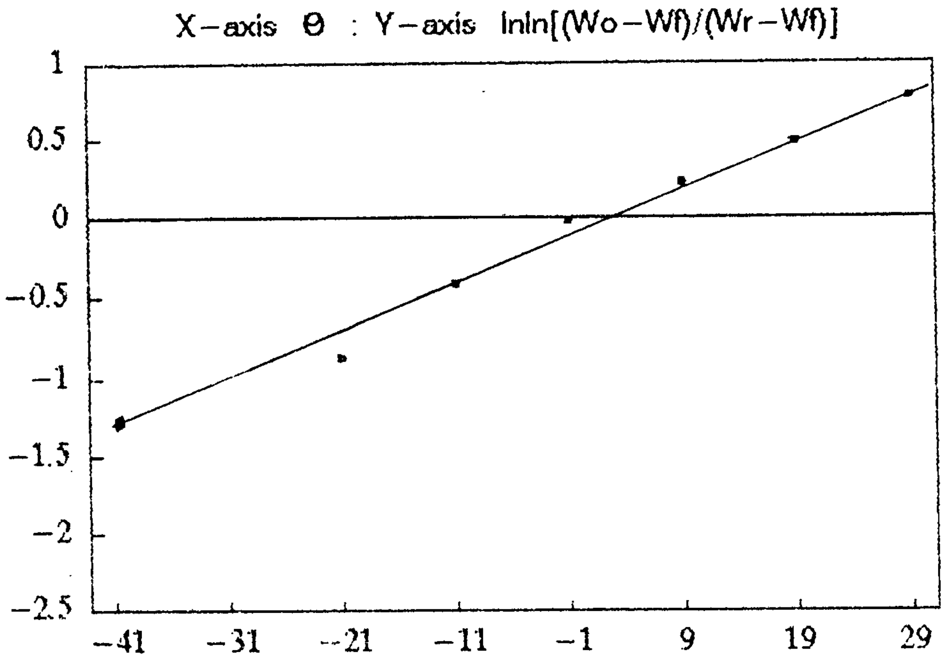

Fig. 5.6.4 HM Plot for Step IV in the TGA of sample CA-3

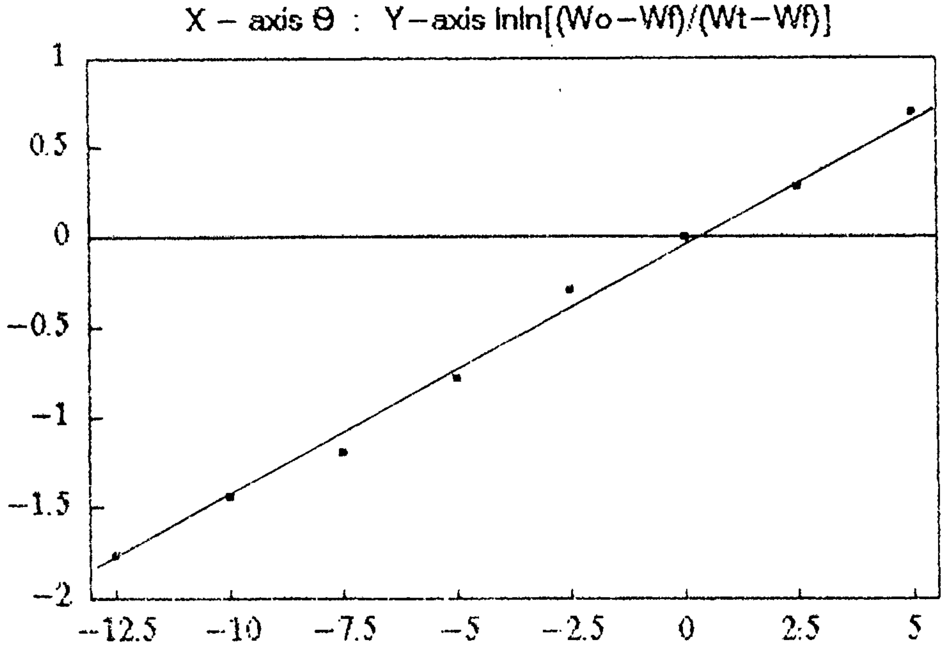

Fig. 5.7.1 HM Plot for Step I in the TGA of sample SR-1

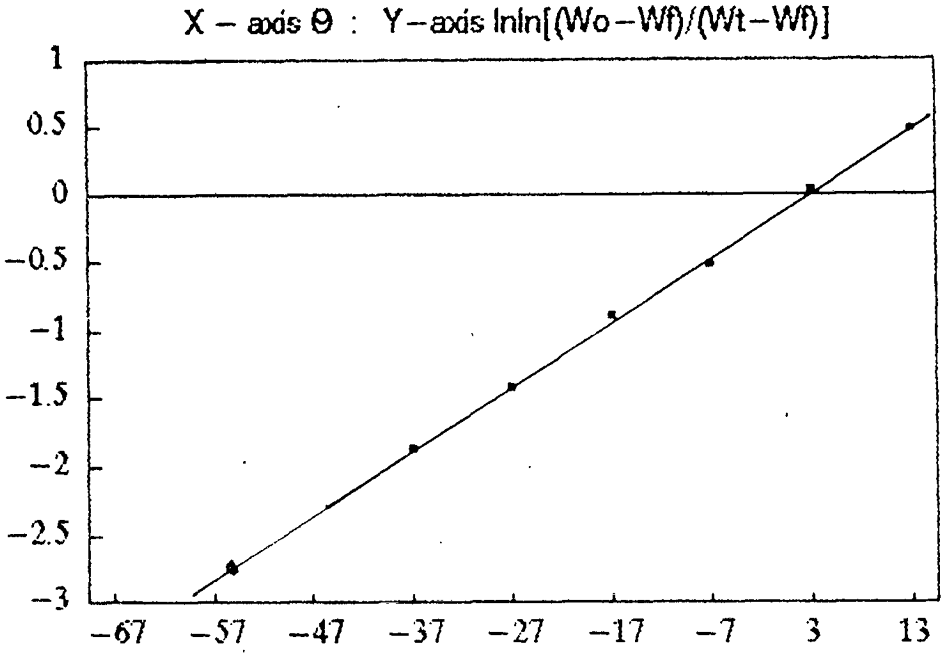

Fig. 5.7.2 HM Plot for Step II in the TGA of sample SR–1

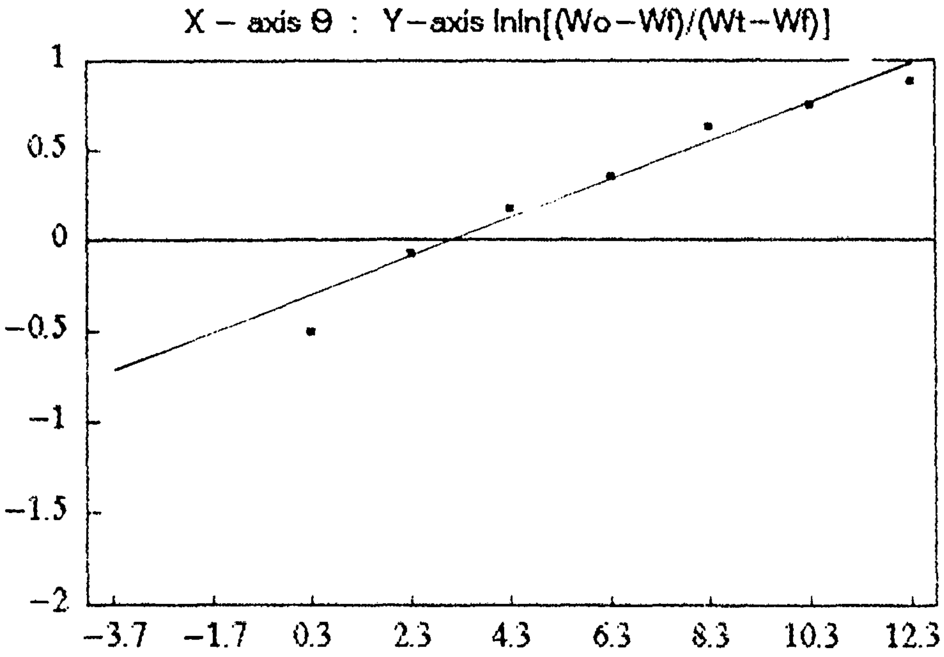

Fig. 5.7.3 HM Plot for Step III in the TGA of sample SR–1

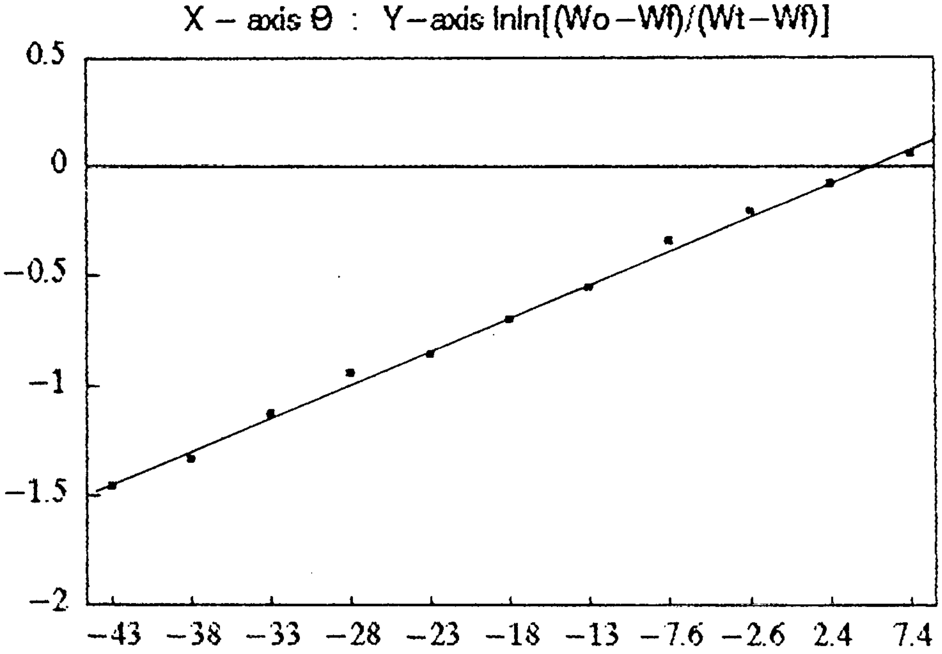

Fig. 5.7.4 HM Plot for Step IV in the TGA of sample SR–1

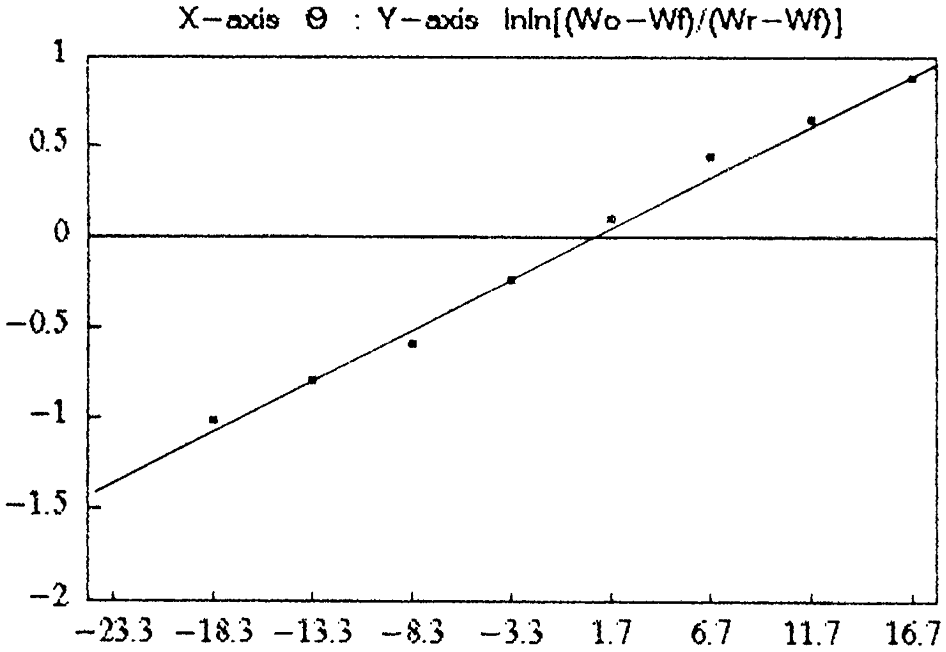

Fig. 5.8.1 HM Plot for Step I in the TGA of sample SR–3

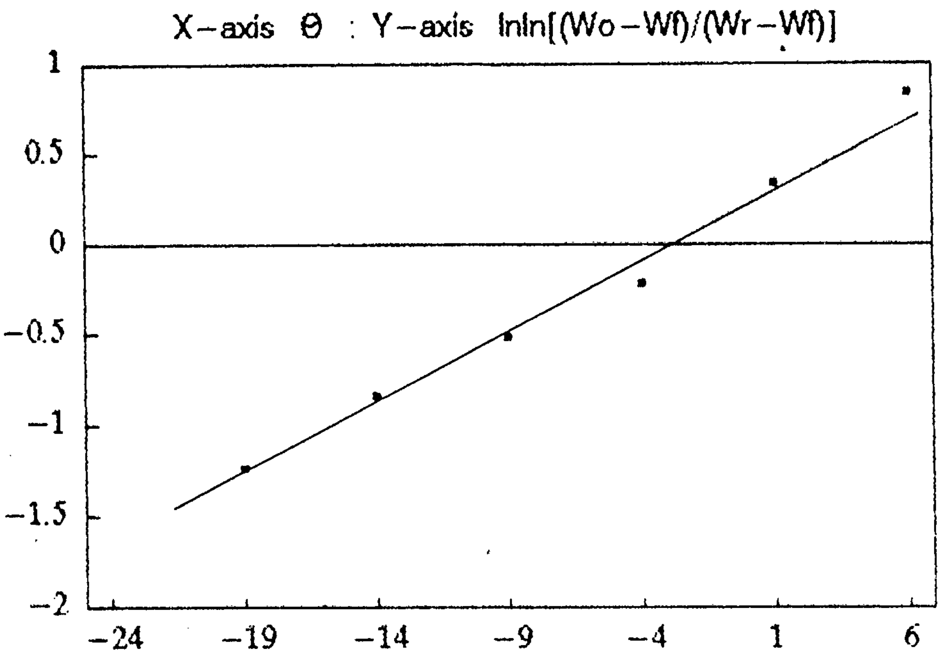

Fig. 5.8.2 HM Plot for Step II in the TGA of sample SR−3

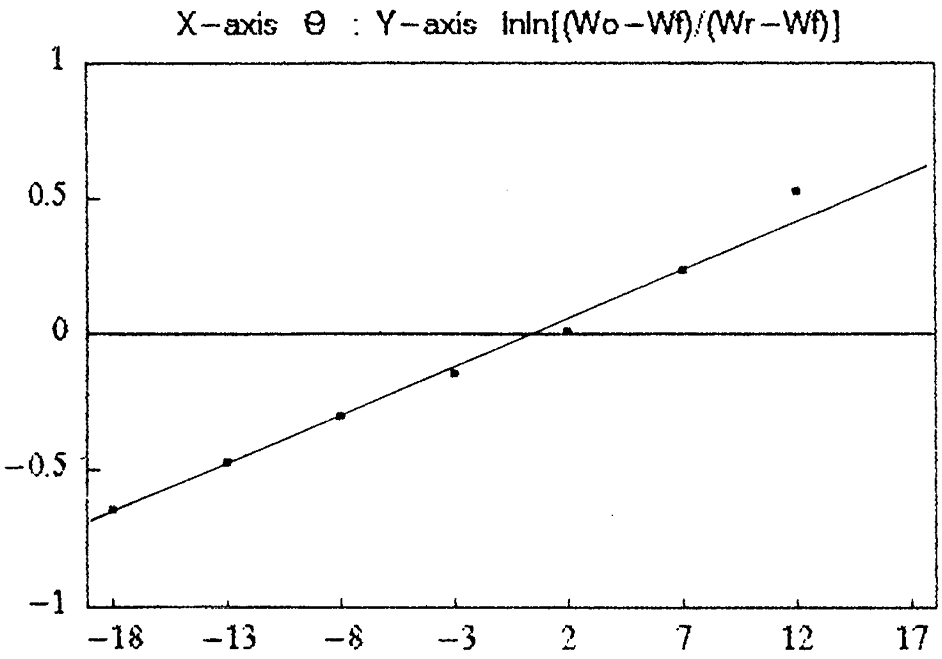

Fig. 5.8.3 HM Plot for Step III in the TGA of sample SR−3

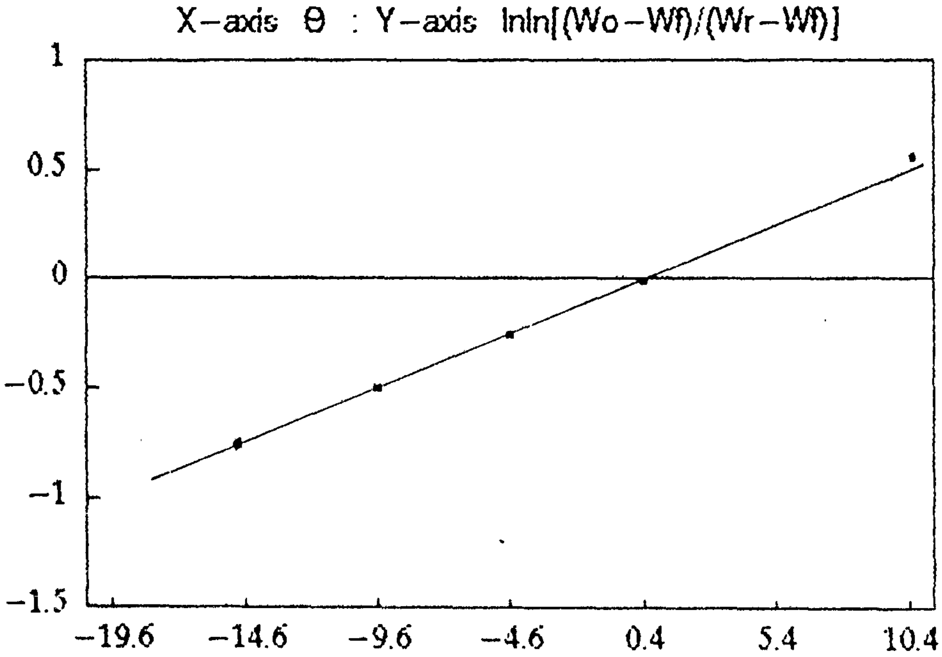

Fig. 5.8.4 HM Plot for Step IV in the TGA of sample SR-3

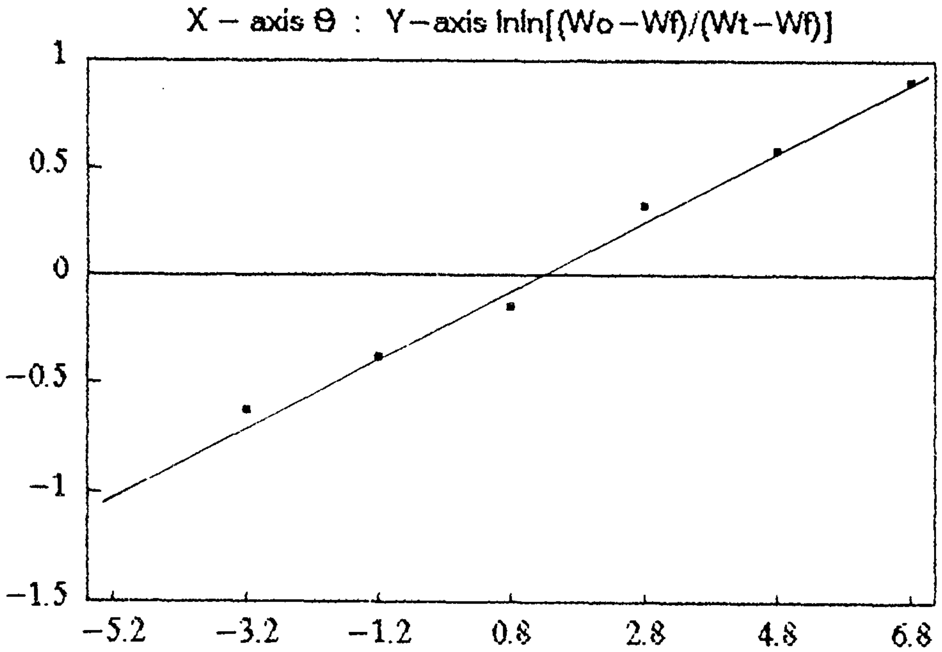

Fig. 5.9.1 HM Plot for Step I in the TGA of sample BA-1

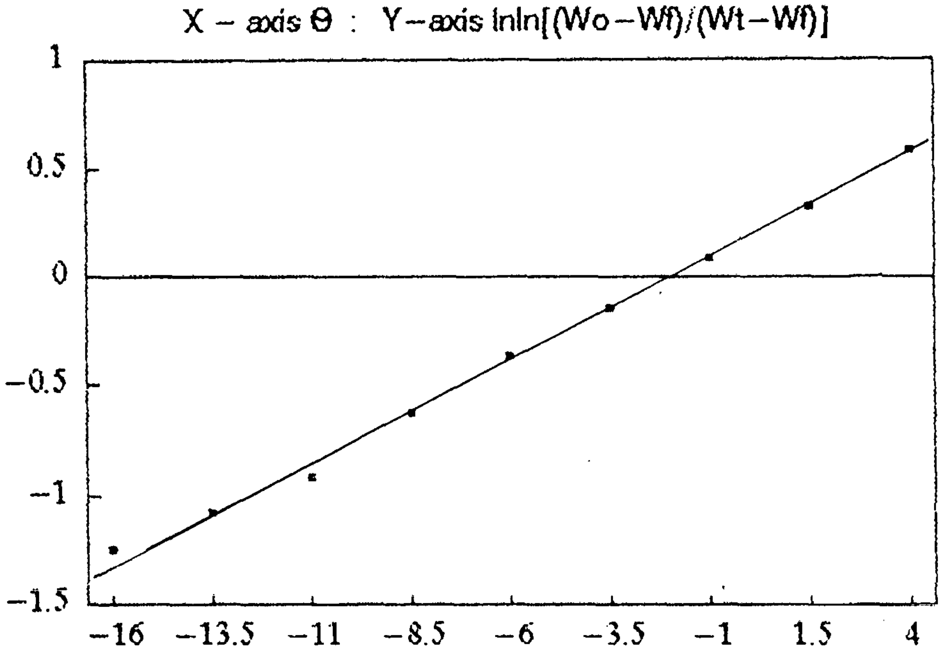

Fig. 5.10.1 HM Plot for Step I in the TGA of sample ZN–1

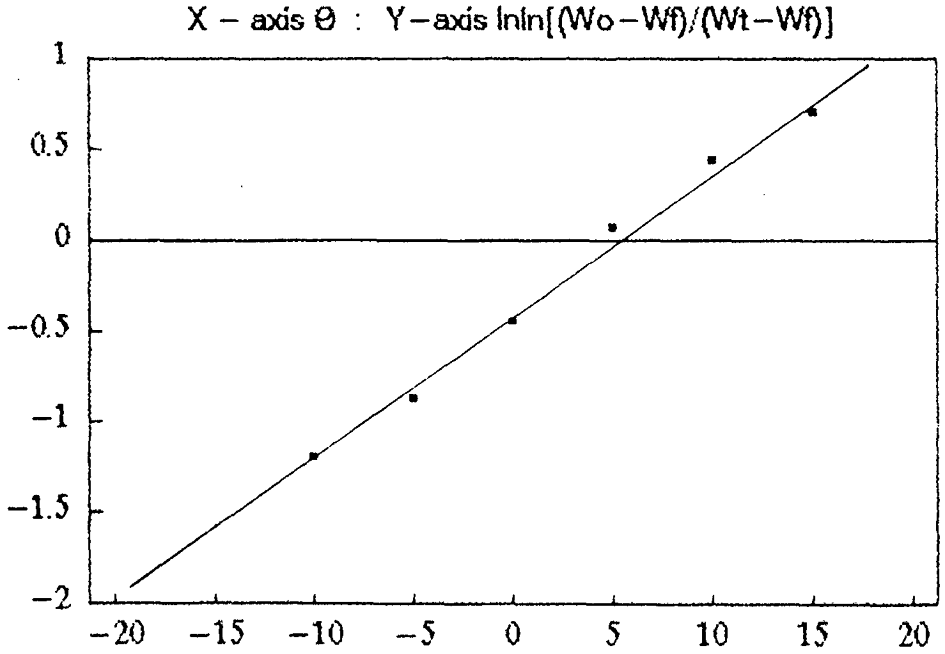

Fig. 5.10.2 HM Plot for Step II in the TGA of sample ZN–1

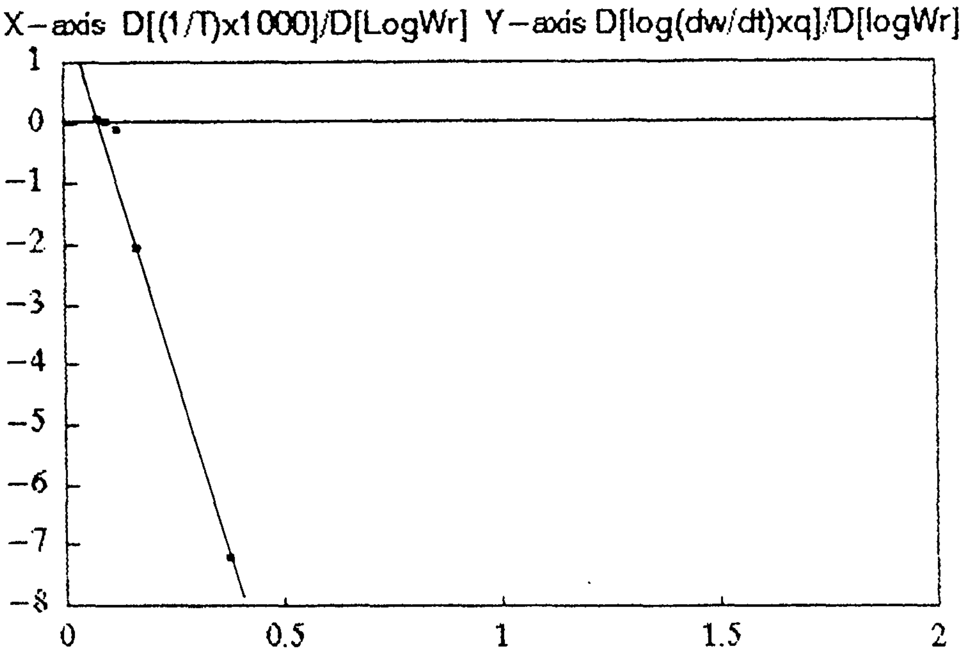

Fig. 5.11.1 FC Plot for the Step I in the TGA of sample ZN−1

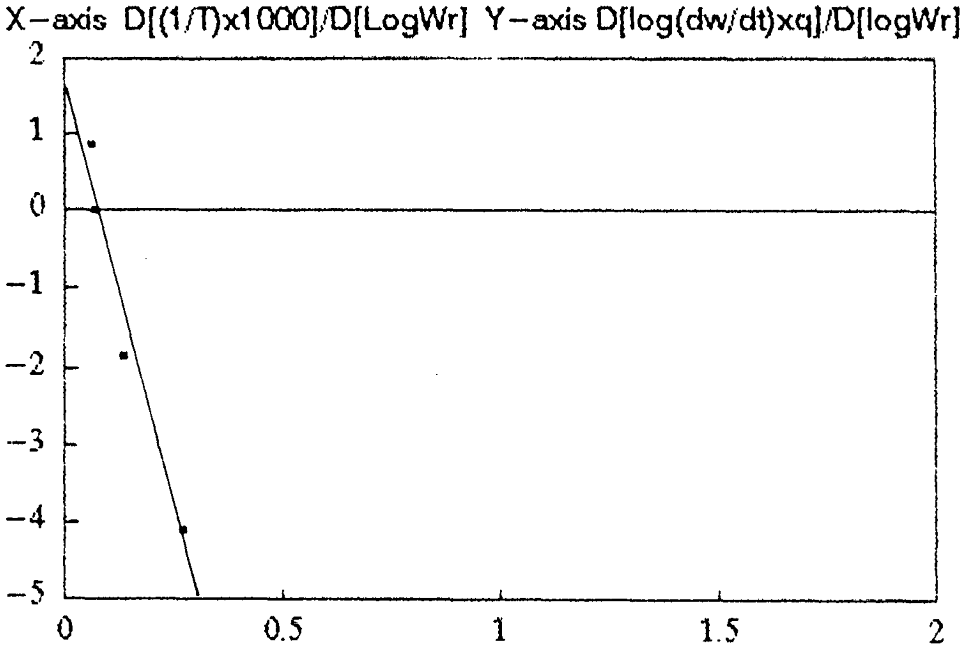

Fig. 5.11.2 FC Plot for the Step II in the TGA of sample ZN−1

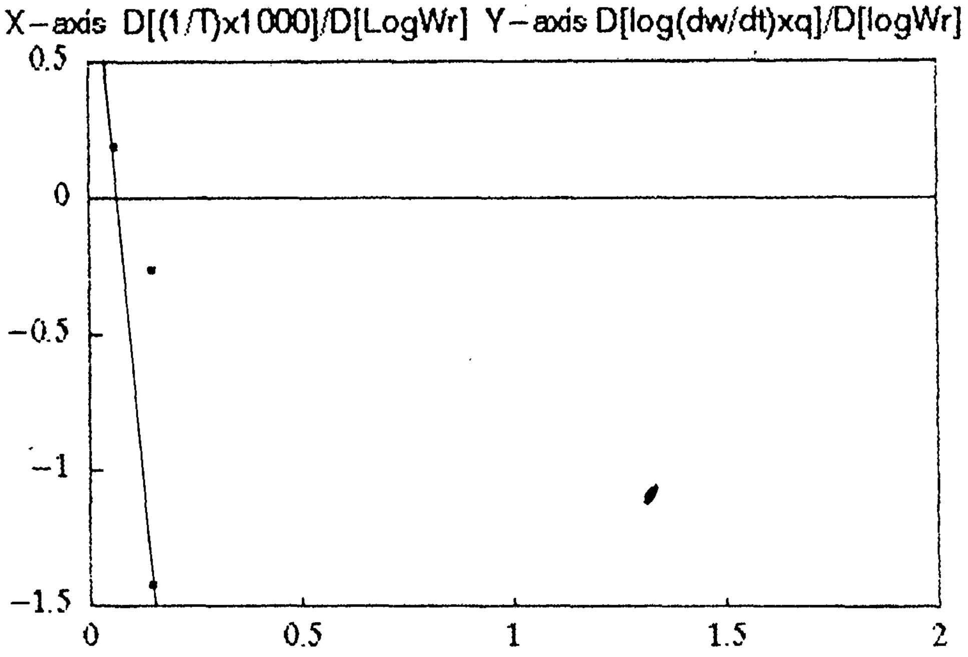

Fig. 5.11.3 FC Plot for the Step III in the TGA of sample ZN-1

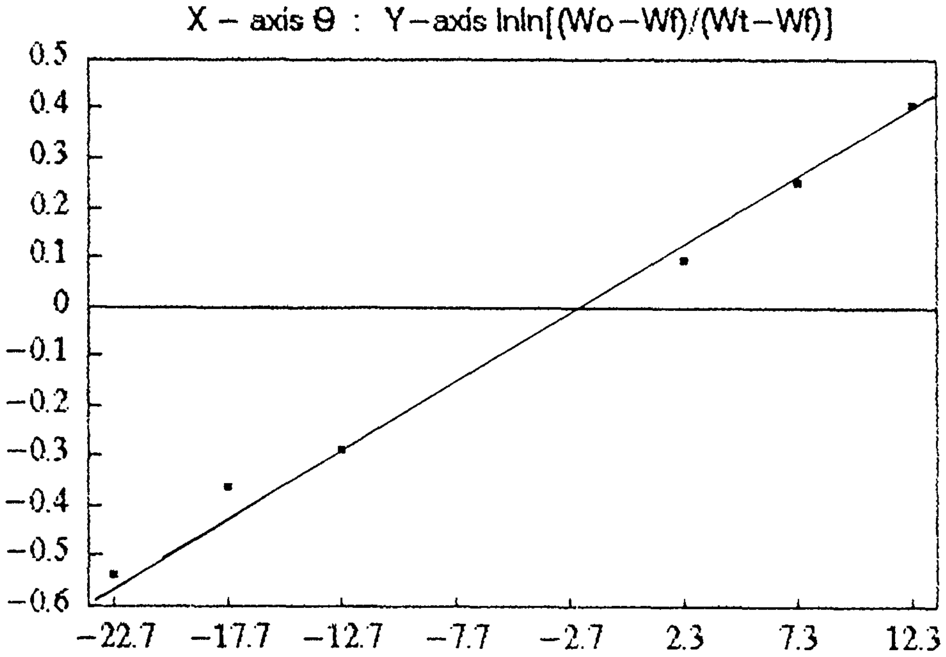

Fig. 5.12.1 HM Plot for Step I in the TGA of sample ZN-3

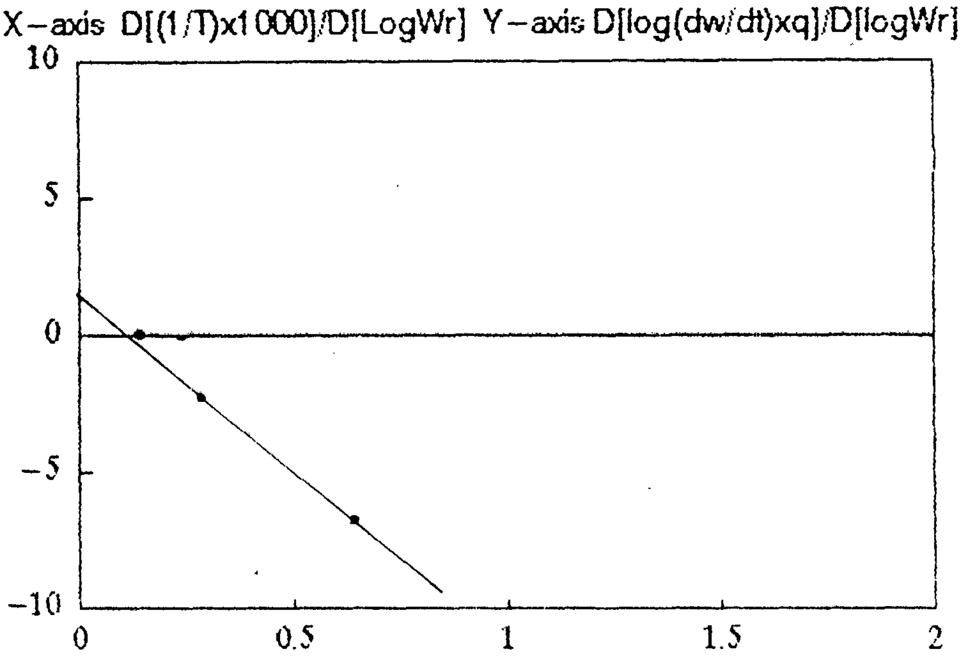

Fig. 5.13.1 FC Plot for the Step I in the TGA of sample ZN-3

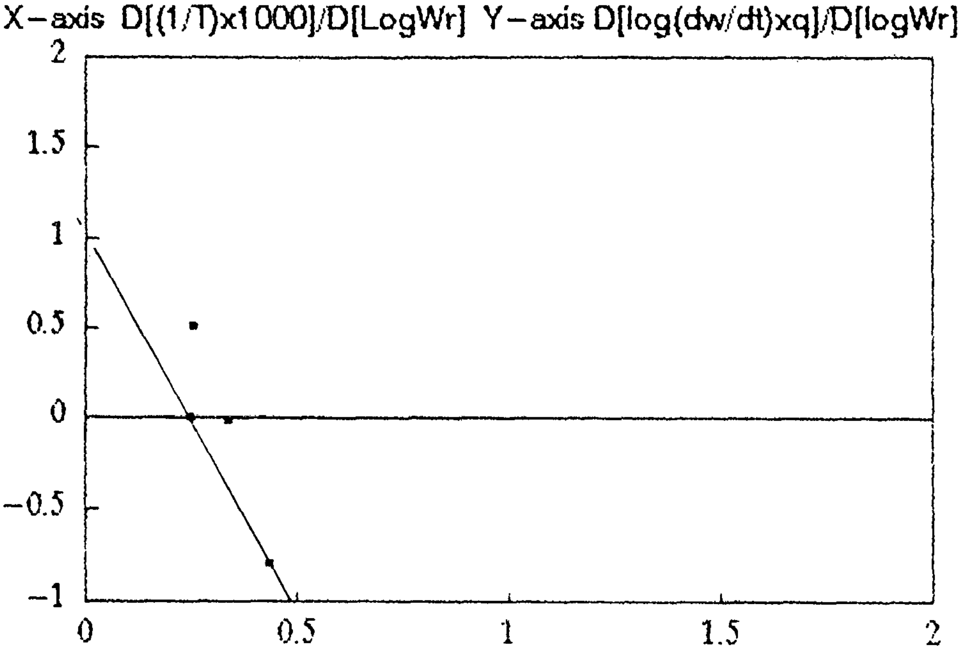

Fig. 5.13.2 FC Plot for the StepIII in the TGA of sample ZN-3

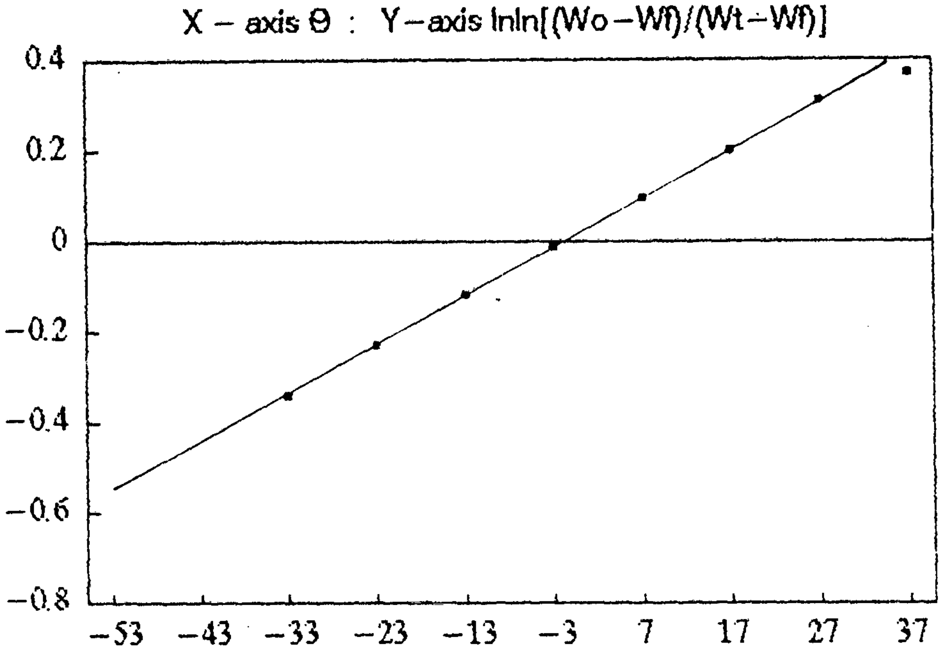

Fig. 5.14.1 HM Plot for Step I in the TGA of sample NI–1

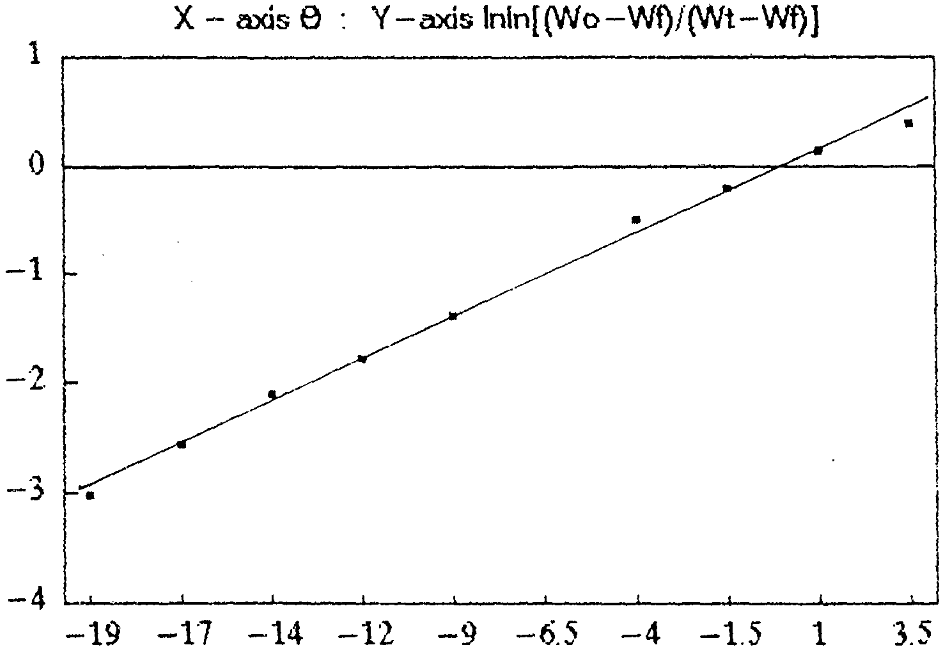

Fig. 5.14.2 HM Plot for Step II in the TGA of sample NI–1

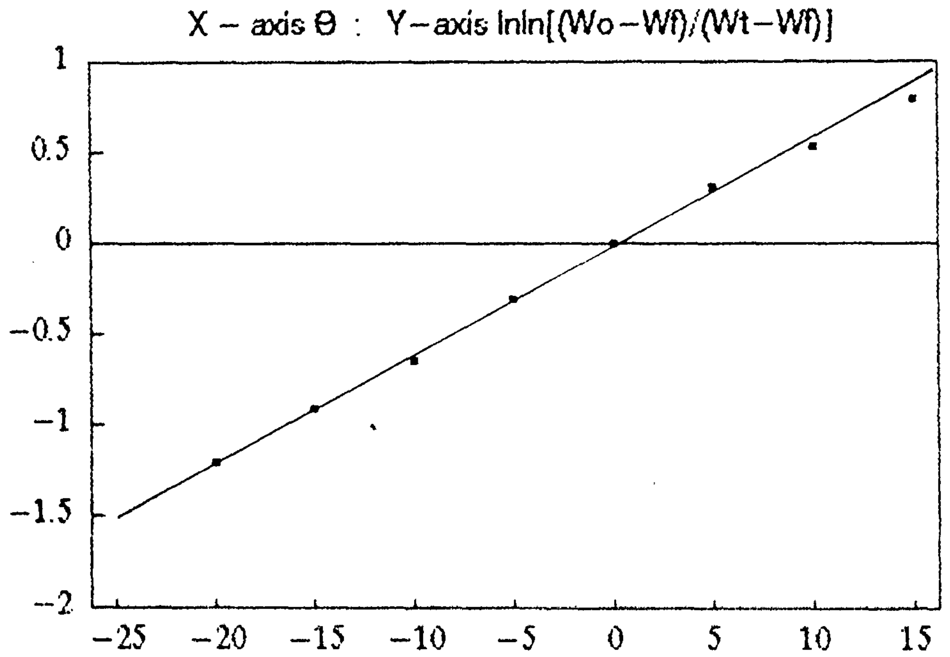

Fig. 5.14.3 HM Plot for Step III in the TGA of sample NI–1

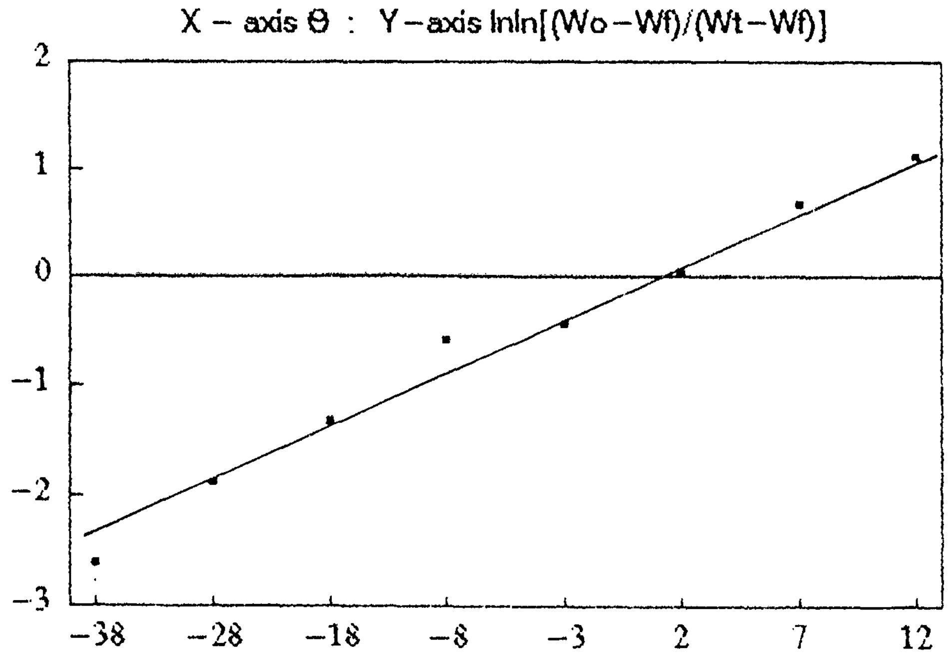

Fig. 5.15.1 HM Plot for Step I in the TGA of sample NI–3

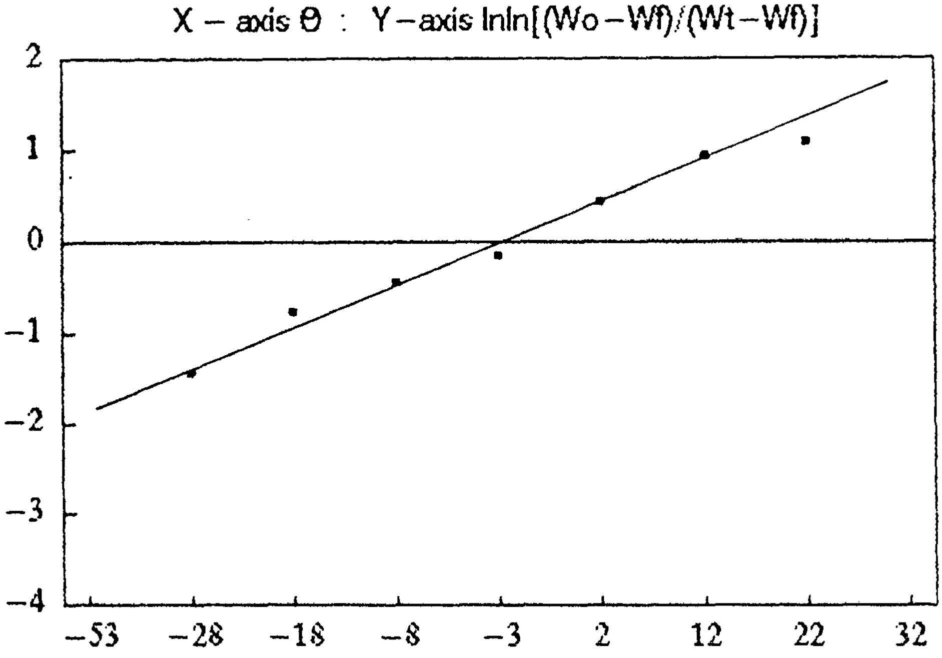

Fig. 5.15.2 HM Plot for Step II in the TGA of sample NI–3

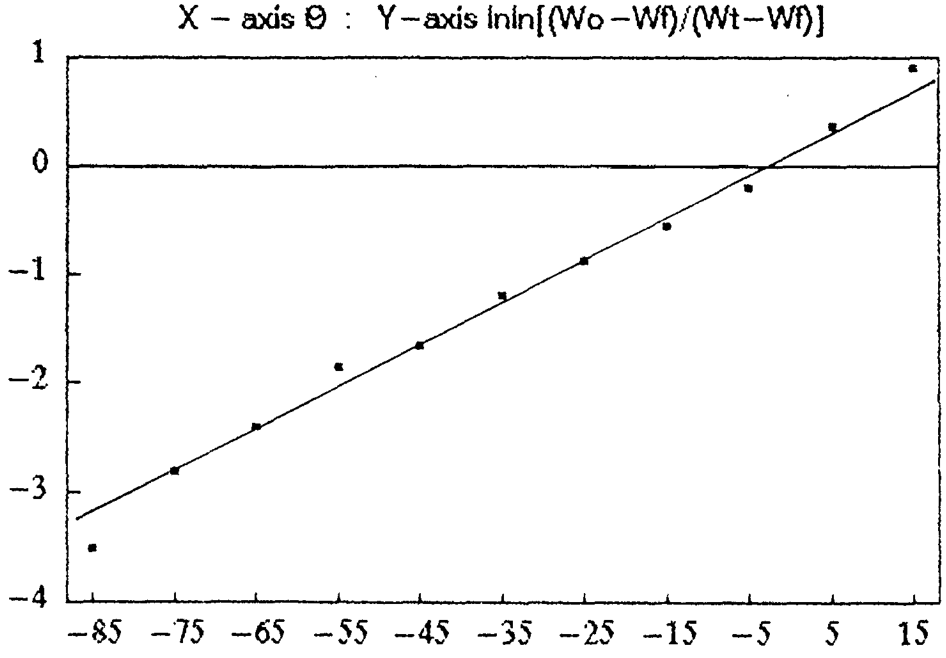

Fig. 5.15.3 HM Plot for Step III in the TGA of sample NI–3

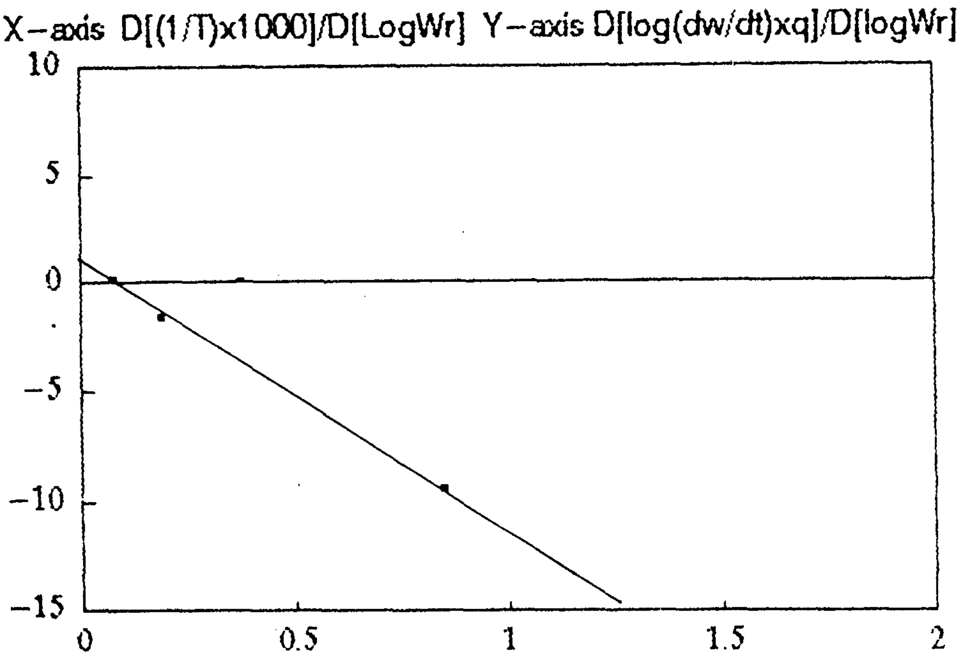

Fig. 5.16.1 FC Plot for the Step I in the TGA of sample NI-3

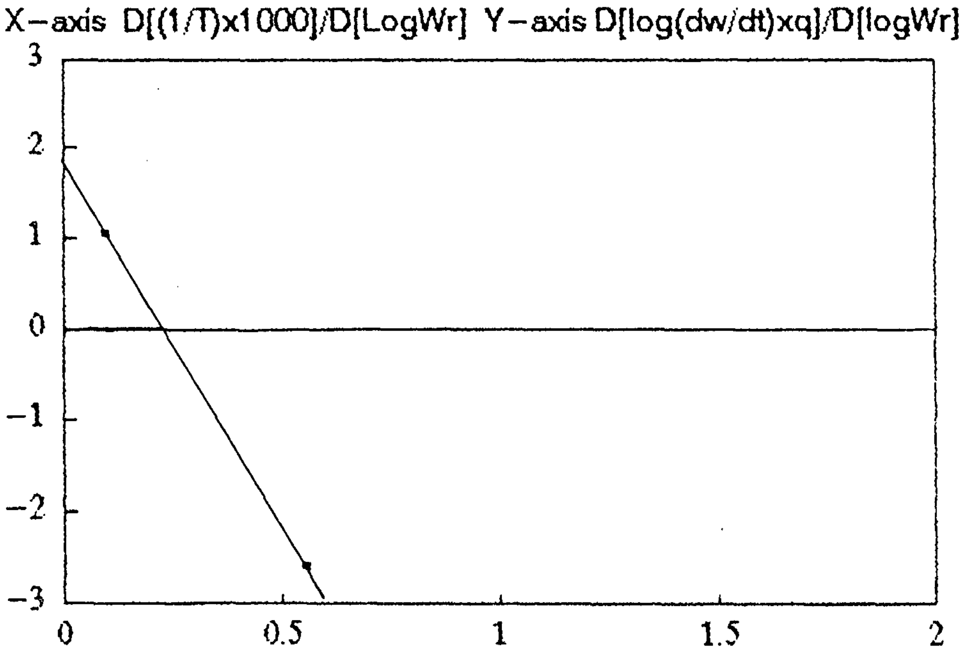

Fig. 5.16.2 FC Plot for the Step II in the TGA of sample NI-3

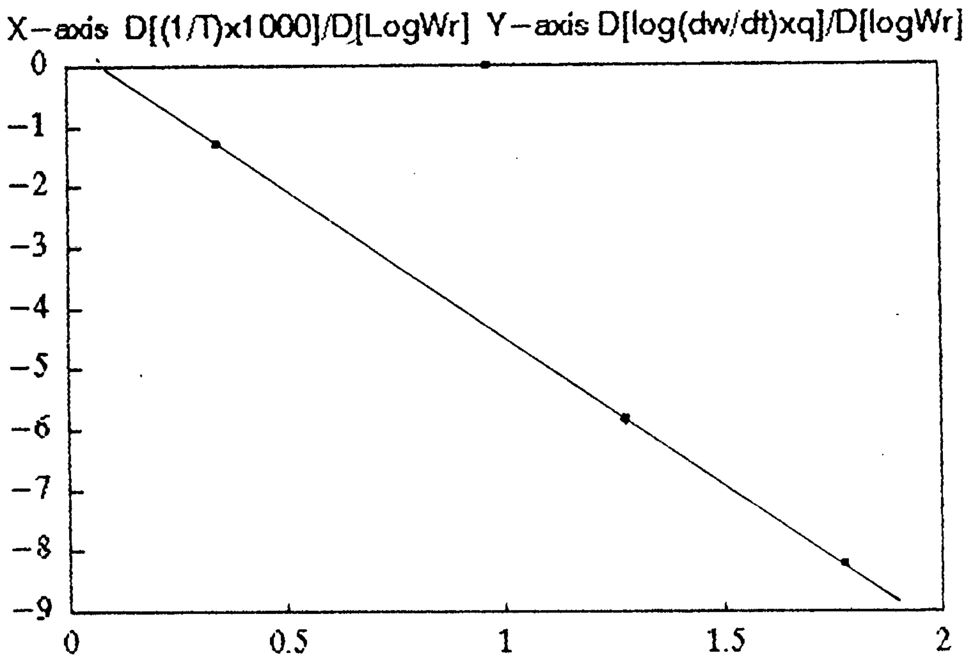

Fig. 5.16.3 FC Plot for the Step III in the TGA of sample NI-3

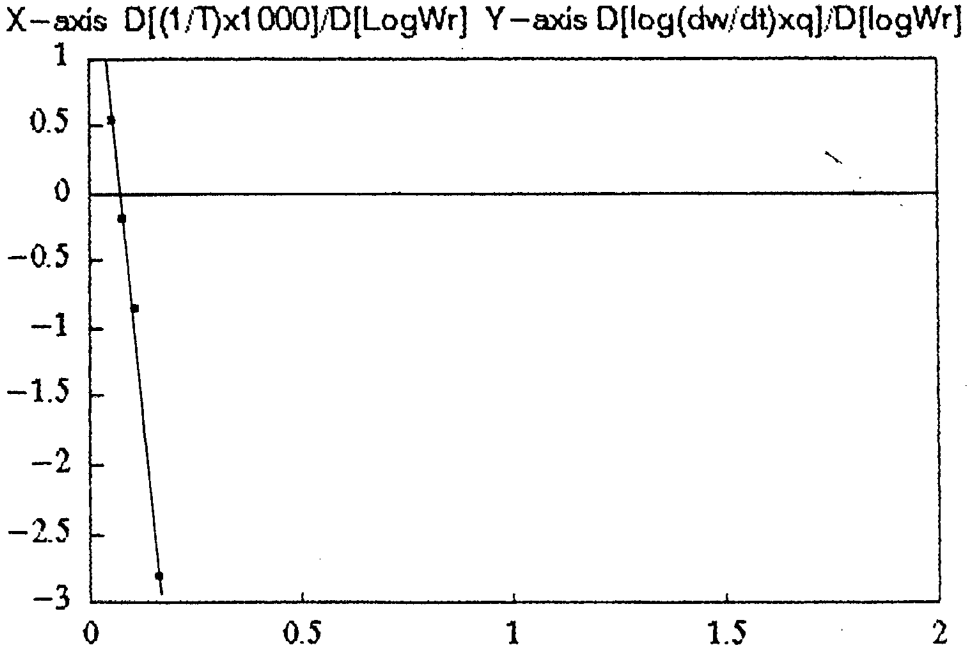

Fig. 5.16.4 FC Plot for the Step IV in the TGA of sample NI-3

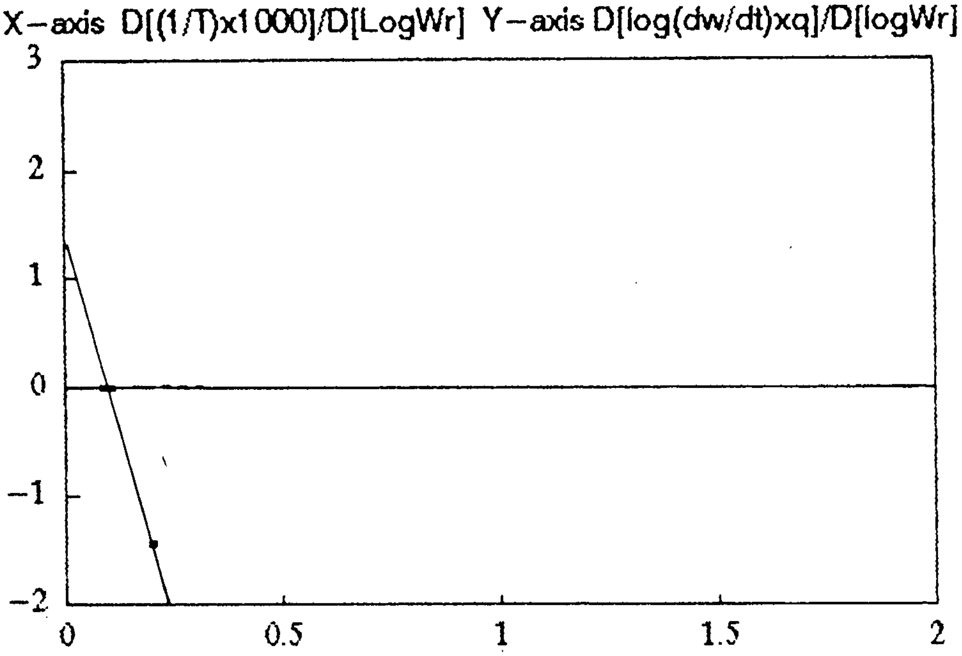

Fig. 5.16.5 FC Plot for the Step V in the TGA of sample NI–3

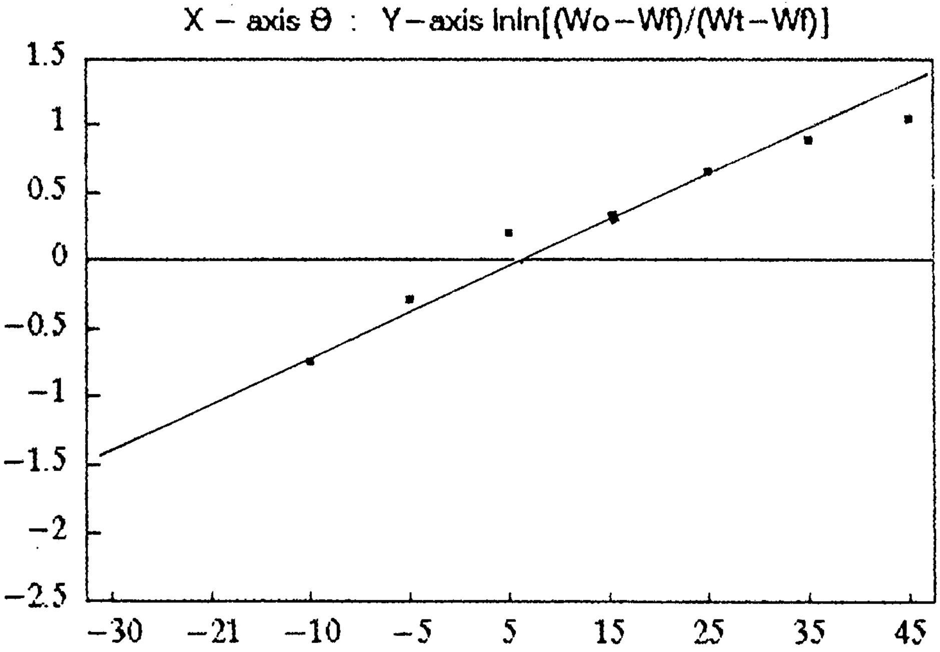

Fig. 5.17.1 HM Plot for Step I in the TGA of sample NI–4

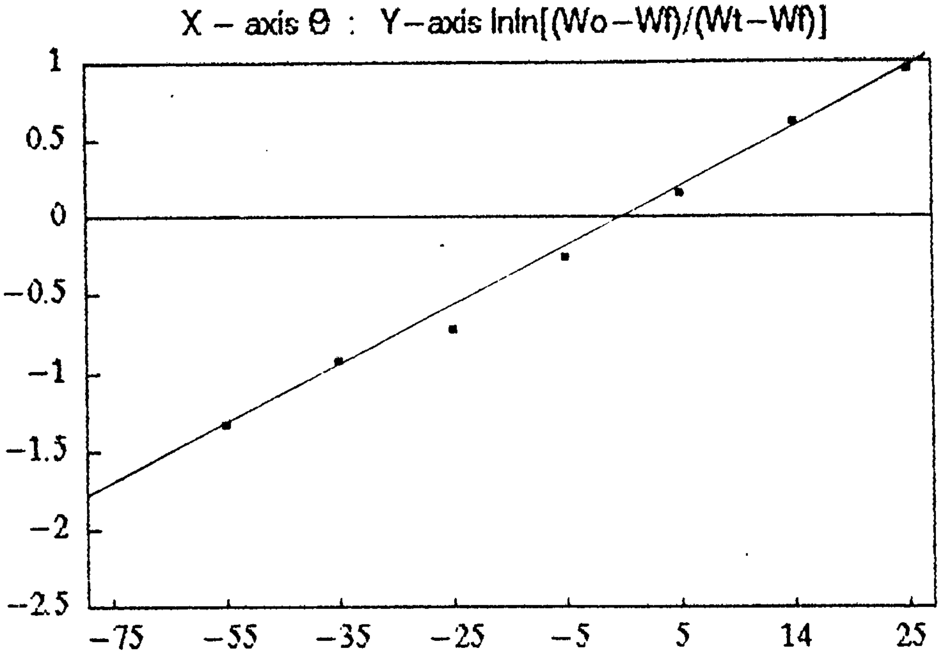

Fig. 5.17.2 HM Plot for Step II in the TGA of sample NI–4

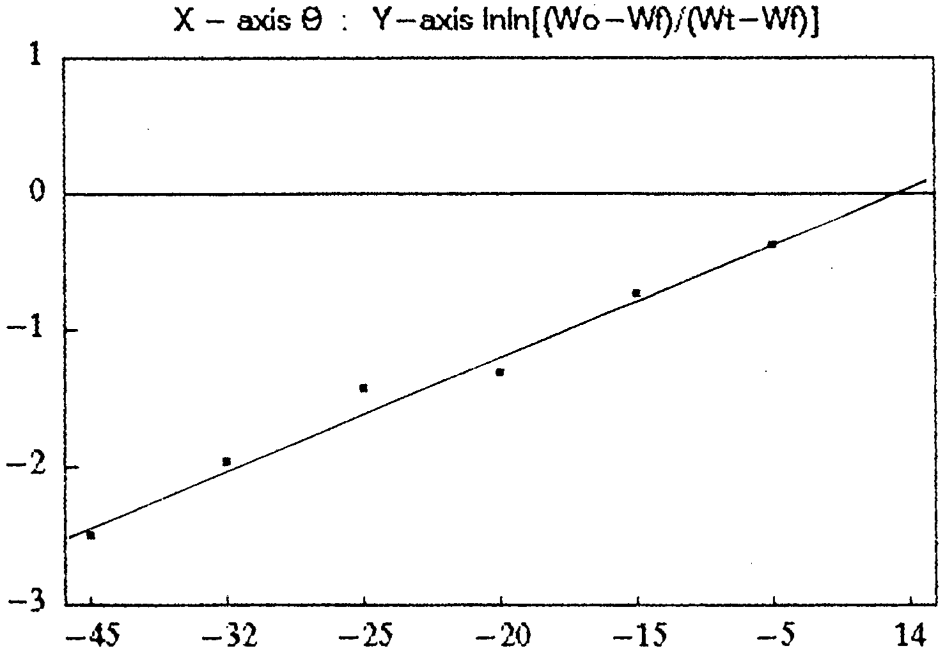

Fig. 5.17.3 HM Plot for Step III in the TGA of sample NI–4

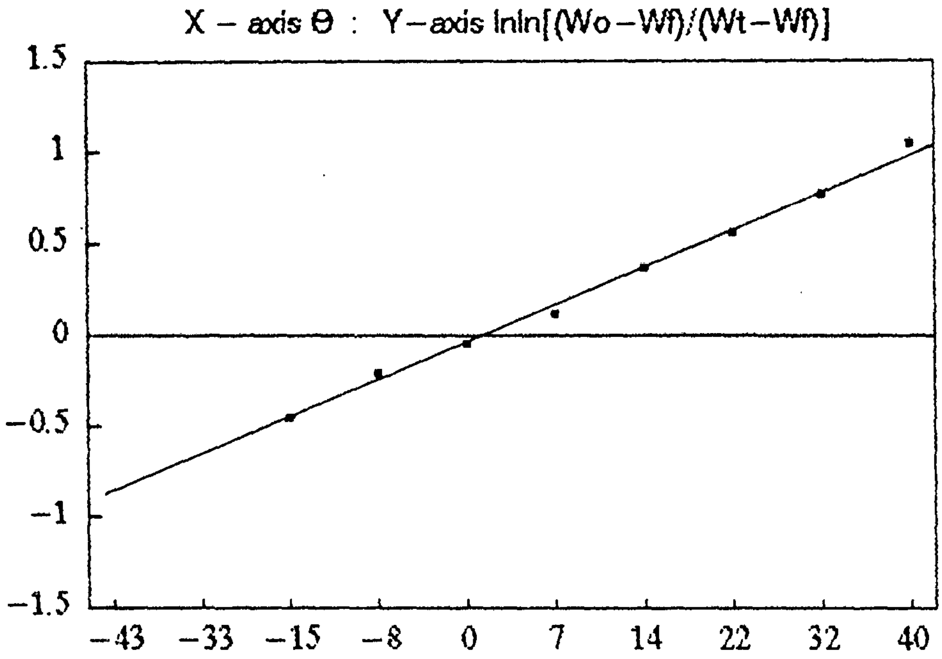

Fig. 5.17.4 HM Plot for Step IV in the TGA of sample NI–4

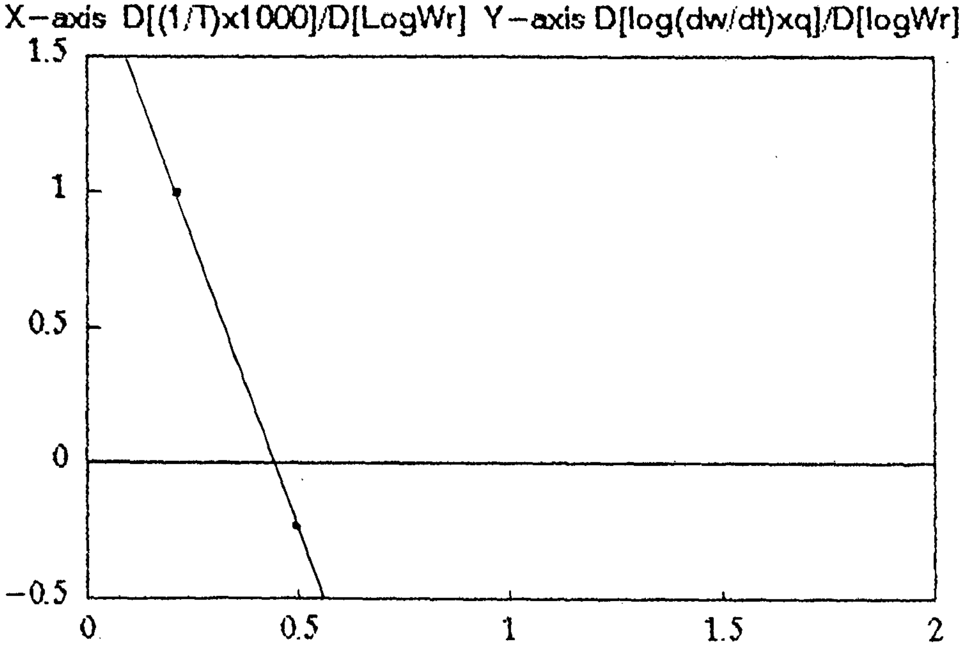

Fig. 5.18.1 FC Plot for the Step I in the TGA of sample NI–4

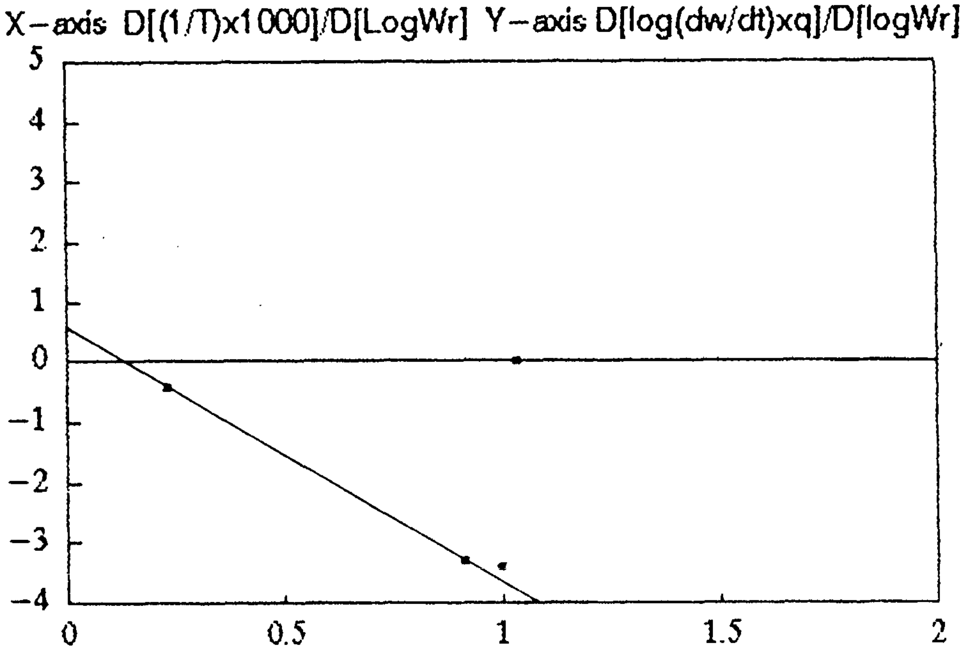

Fig. 5.18.2 FC Plot for the Step II in the TGA of sample NI−4

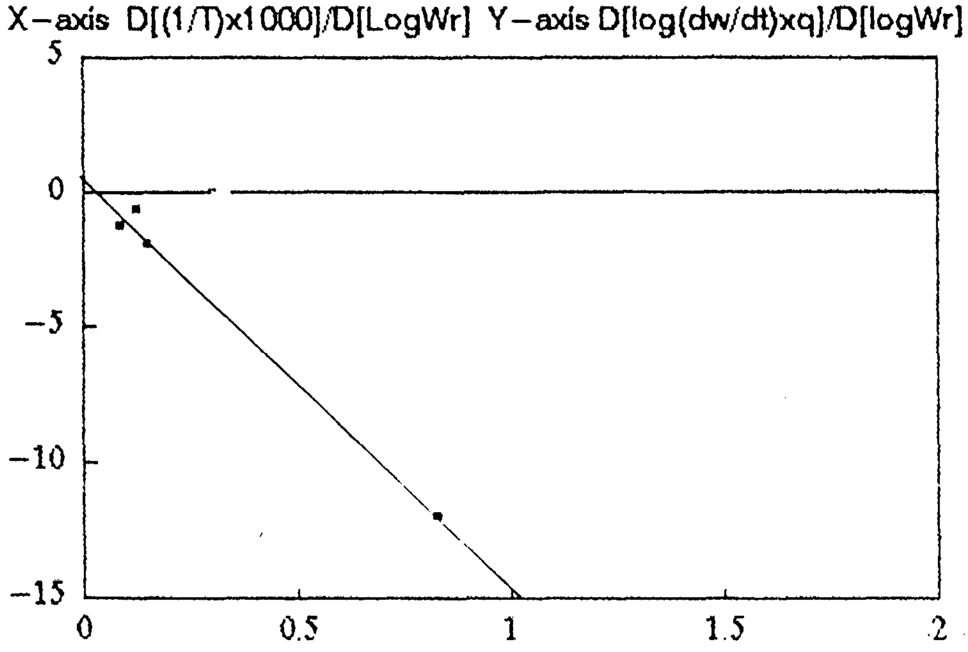

Fig. 5.18.3 FC Plot for the Step III in the TGA of sample NI−4

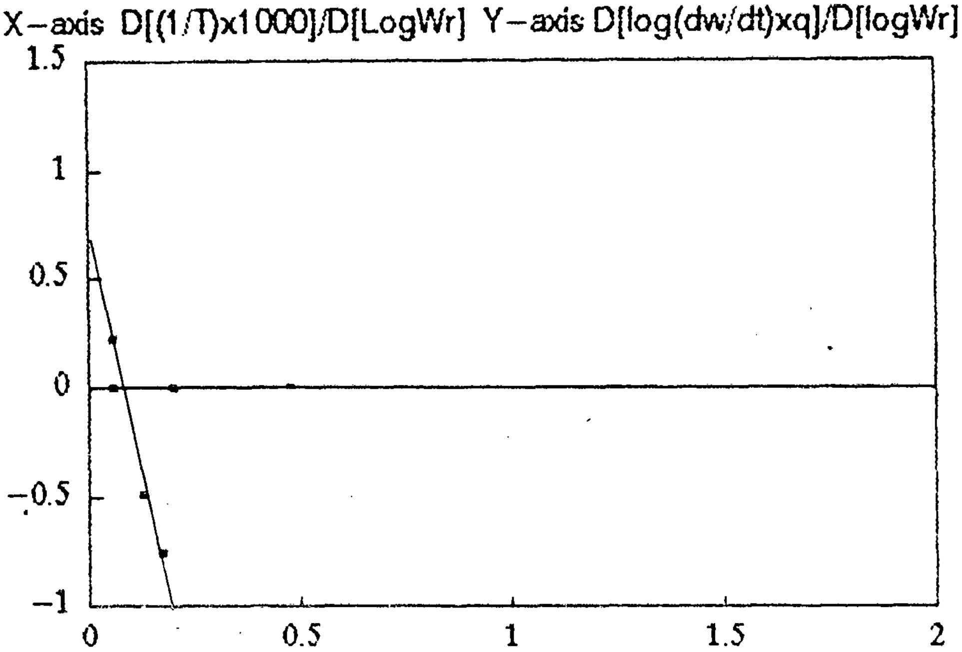

Fig. 5.18.4 FC Plot for the Step IV in the TGA of sample NI-4

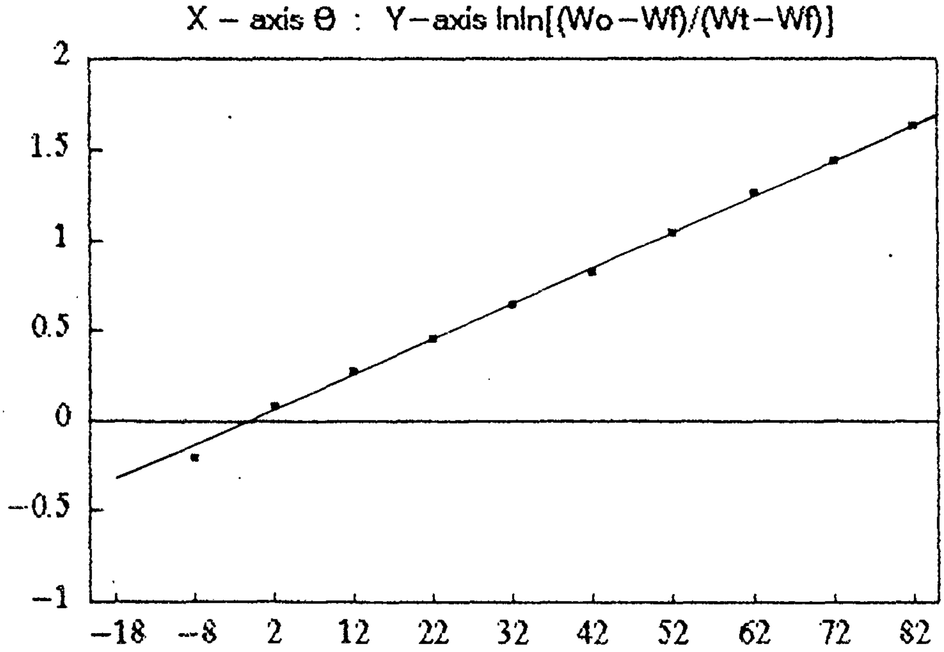

Fig. 5.19.1 HM Plot for Step I in the TGA of sample NI-5

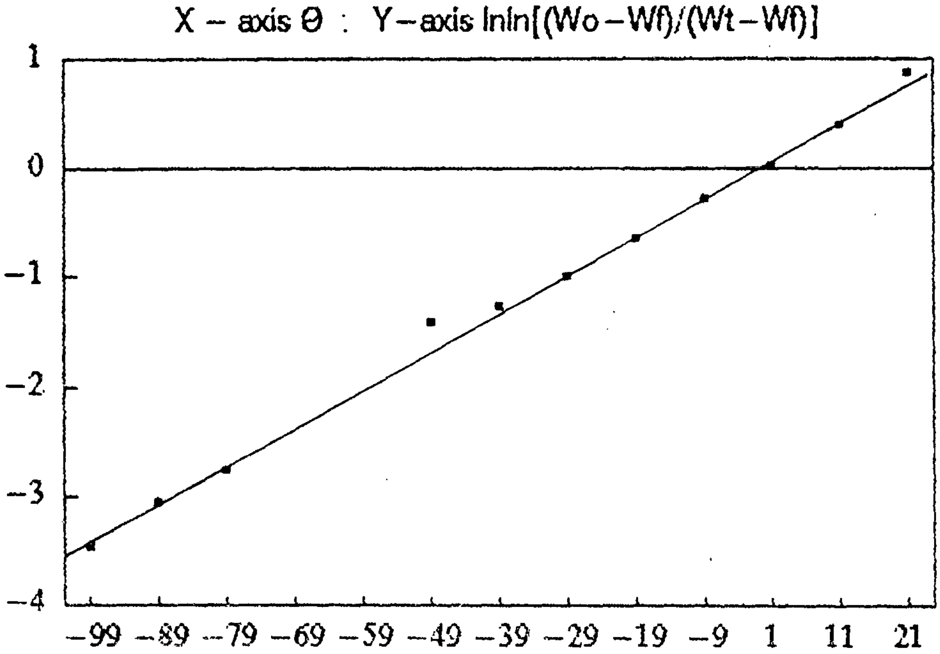

Fig. 5.19.2 HM Plot for Step II in the TGA of sample NI–5

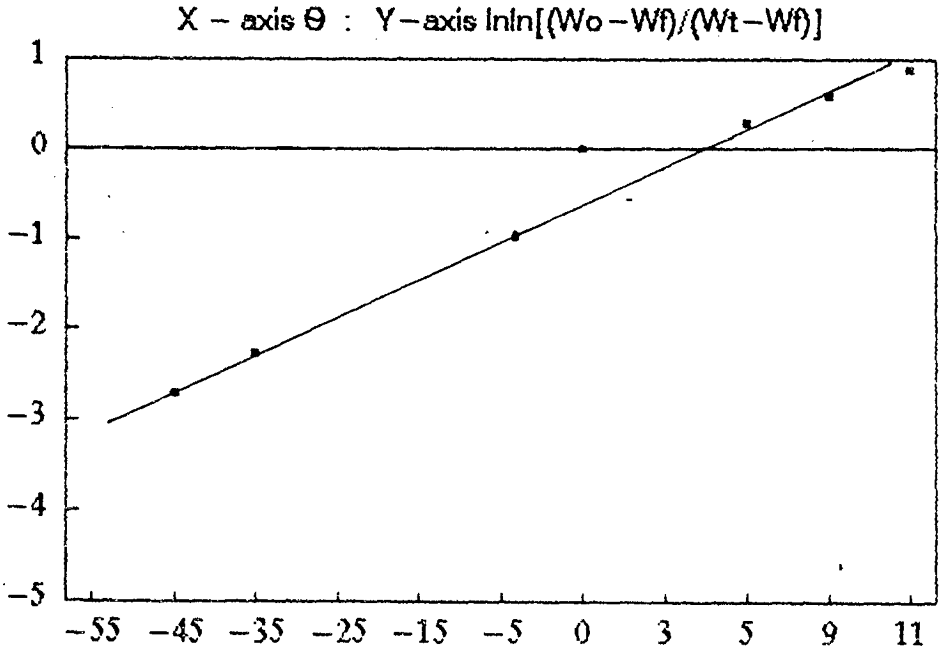

Fig. 5.19.3 HM Plot for Step III in the TGA of sample NI–5

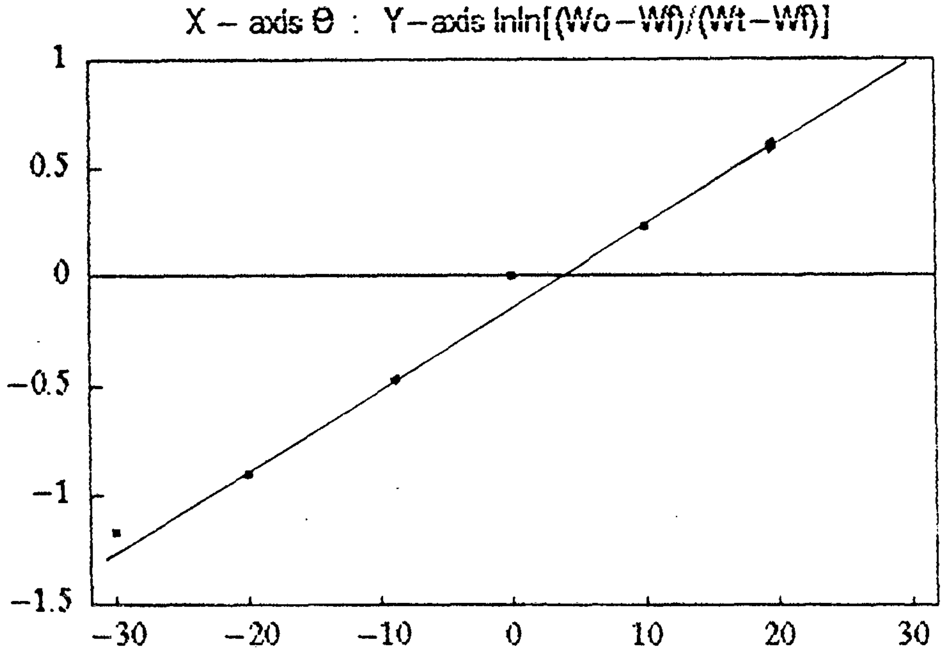

Fig. 5.19.4 HM Plot for Step IV in the TGA of sample NI–5

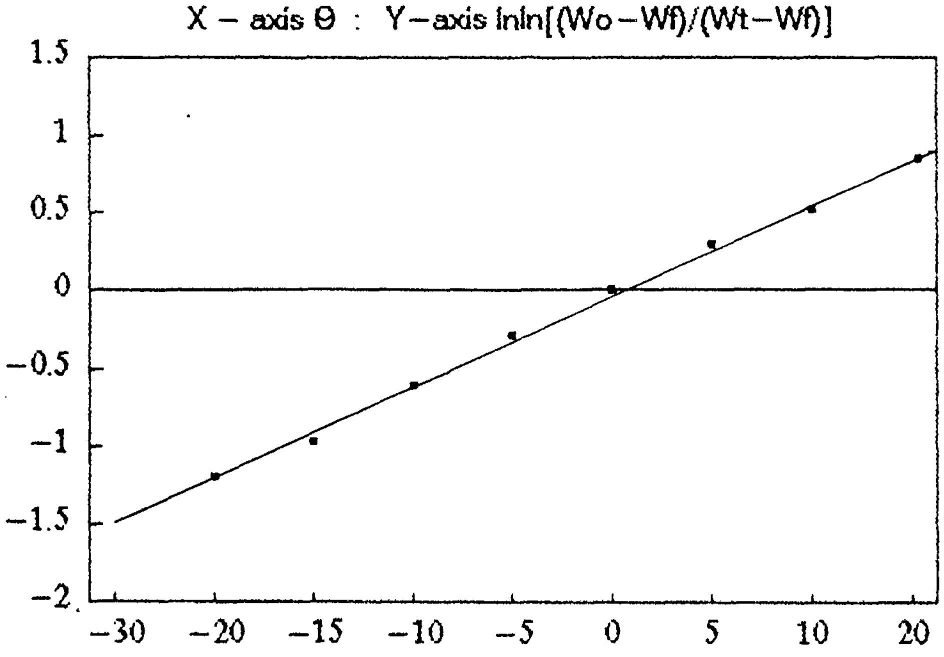

Fig. 5.20.1 HM Plot for Step I in the TGA of sample NI–6

TABLE 5.1

Calculated Kinetic Parameters of the compounds

Methods used : (i) Coats and Redfern (CR)
(ii) Freeman and Carroll (FC)
(iii) Horowitz and Metzger (HM)

Key : Ea = Activation Energy n = Order of Reaction

Compound	Step Nos.	CR		FC		HM
		Ea Kcal/mole	n	Ea Kcal/mole	n	Ea
MG-1	I	17.814	0.4	8.6100	0.82	22.397
	II	51.756	1.66	56.916	1.91	49.655
	III	30.138	1.05	11.321	0.32	30.074
	IV	16.734	0.3	15.146	1.53	27.892

Compound	Step Nos.	CR		FC		HM
		Ea Kcal/mole	n	Ea Kcal/mole	n	Ea
MG-3	I	–	–	52.6214	1.67	55.4472
	II	–	–	–	–	22.4742
	III	–	–	–	–	71.1835
	IV	–	–	–	–	20.8910

Compound	Step Nos.	CR		FC		HM
		Ea Kcal/mole	n	Ea Kcal/mole	n	Ea
MG-4	I	–	–	45.6347	2.62	24.4980
	II	–	–	54.2013	0.91	87.3978
	III	–	–	–	–	11.8213

TABLE 5.2

Compound	Step Nos.	CR		FC		HM
		Ea Kcal/mole	n	Ea Kcal/mole	n	Ea
CA-1	I	-	-	-	-	24.3932
	II	-	-	8.7403	1.07	37.5110
	III	-	-	17.0093	2.58	33.9633
	IV	-	-	41.2527	0.62	67.9511
	V	-	-	-	-	20.8910

Compound	Step Nos.	CR		FC		HM
		Ea Kcal/mole	n	Ea Kcal/mole	n	Ea
CA-3	I	-	-	19.3491	0.50	34.2595
	II	-	-	26.9495	0.14	37.4674
	III	-	-	38.1813	1.16	-
	IV	-	-	8.6533	0.05	34.8496

Compound	Step Nos.	CR		FC		HM
		Ea Kcal/mole	n	Ea Kcal/mole	n	Ea
SR-1	I	68.0913	1.38	35.9686	1.63	47.4861
	II	32.0429	0.70	26.8988	1.30	40.3517
	III	-	-	-	-	129.3200
	IV	30.7811	1.05	36.2355	1.34	35.2187

TABLE 5.3

Compound	Step Nos.	CR		FC		HM
		Ea Kcal/mole	n	Ea Kcal/mole	n	Ea
SR-3	I	-	-	15.8120	1.00	17.3270
	II	-	-	18.1147	0.16	31.7317
	III	-	-	43.0605	0.00	27.8690
	IV	-	-	50.7642	0.00	50.7162

Compound	Step Nos.	CR		FC		HM
		Ea Kcal/mole	n	Ea Kcal/mole	n	Ea
BA-1	I	81.2386	1.70	36.9256	1.00	48.7340
	II	48.1451	1.38	37.1338	1.42	54.370
	III	27.9480	0.94	-	-	32.2547

Compound	Step Nos.	CR		FC		HM
		Ea Kcal/mole	n	Ea Kcal/mole	n	Ea
ZN-1	I	41.2469	0.70	48.1827	1.55	49.4646
	II	39.8877	0.00	40.6884	1.25	67.5073
	III	51.9763	0.94	37.0620	1.09	52.8248
	IV	27.0593	0.94	-	-	30.7863

TABLE 5.4

Compound	Step Nos.	CR		FC		HM
		Ea Kcal/mole	n	Ea Kcal/mole	n	Ea
ZN-3	I	-	-	24.7804	1.42	18.7363
	II	-	-	-	-	75.8494
	III	-	-	8.3961	1.00	8.2436

Compound	Step Nos.	CR		FC		HM
		Ea Kcal/mole	n	Ea Kcal/mole	n	Ea
NI-1	I	1.483	0.5	4.2069	2.58	4.2178
	II	-	1.7	-	-	148.7420
	III	64.8781	1.66	62.1666	1.50	66.1465

Compound	Step Nos.	CR		FC		HM
		Ea Kcal/mole	n	Ea Kcal/mole	n	Ea
NI-3	I	16.2017	0.40	18.7550	0.78	29.726
	II	19.6464	0.50	11.1583	0.51	21.957
	III	23.5646	0.40	9.6109	0.45	35.656
	IV	49.6154	0.60	51.6198	2.06	62.617
	V	16.0328	0.50	30.4585	1.32	27.066

TABLE 5.5

Compound	Step Nos.	CR		FC		HM
		Ea Kcal/mole	n	Ea Kcal/mole	n	Ea
NI-4	I	–	–	8.6311	1.90	9.9613
	II	–	–	8.3339	0.47	16.3350
	III	40.3674	0.60	29.4915	0.43	75.2090
	IV	20.4322	0.70	16.7742	0.63	30.9250

Compound	Step Nos.	CR		FC		HM
		Ea Kcal/mole	n	Ea Kcal/mole	n	Ea
NI-5	I	2.9281	0.70	1.5878	0.72	5.3098
	II	16.3808	0.70	19.6530	0.58	22.7780
	III	46.0789	0.70	38.8102	0.30	55.0050
	IV	14.7261	0.30	22.8903	1.00	27.3890

Compound	Step Nos.	CR		FC		HM
		Ea Kcal/mole	n	Ea Kcal/mole	n	Ea
NI-6	I	13.6292	0.80	11.6636	1.36	16.9140
	II	22.9541	0.60	18.8577	0.31	30.0020
	III	–	–	15.2530	0.37	24.7060
	IV	54.9487	0.94	48.3625	1.17	64.0180
	V	29.0063	1.70	23.7135	2.28	27.8516

TABLE 5.6

Compound	Step Nos.	CR		FC		HM
		Ea Kcal/mole	n	Ea Kcal/mole	n	Ea
NI-8	I	19.1766	0.83	13.6493	1.00	21.2080
	II	34.9363	1.50	18.9704	1.82	27.3290
	III	21.1657	0.10	16.5514	1.88	33.8210
	IV	50.7331	0.20	59.0723	1.07	60.0424
	V	37.4425	1.90	42.1605	2.31	26.5485

Compound	Step Nos.	CR		FC		HM
		Ea Kcal/mole	n	Ea Kcal/mole	n	Ea
NI-9	I	15.8688	1.70	13.5826	2.13	9.2933
	II	13.3023	0.40	–	–	20.3610
	III	42.7566	0.60	44.1737	1.33	58.1630
	IV	19.9102	0.60	12.3798	0.47	27.4480

Compound	Step Nos.	CR		FC		HM
		Ea Kcal/mole	n	Ea Kcal/mole	n	Ea
NI-10	I	28.8666	1.50	28.5614	1.47	22.1297
	II	25.1307	0.50	28.0180	0.53	24.6741
	III	16.4473	1.10	11.5935	0.72	28.3346
	IV	69.4865	1.20	51.6901	2.30	60.9190
	V	28.8388		15.2061	1.16	28.4630

TABLE 5.7

Compound	Step Nos.	CR		FC		HM
		Ea Kcal/mole	n	Ea Kcal/mole	n	Ea
NI-11	I	22.3172	1.50	-	-	20.7340
	II	33.8947	1.20	11.3559	1.29	30.7840
	III	-	-	25.7922	1.42	38.3510
	IV	63.3035	1.20	63.1392	0.46	60.0370
	V	15.2370	0.50	9.9787	0.28	16.2920

Compound	Step Nos.	CR		FC		HM
		Ea Kcal/mole	n	Ea Kcal/mole	n	Ea
NI-12	I	13.8691	1.60	6.9592	1.66	8.7200
	II	12.7884	0.50	14.9350	1.42	19.5194
	III	61.8324	1.10	-	-	63.0360
	IV	19.1447	0.50	23.8327	0.50	24.8010

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RESUME'

The metal ions, reacting with nitrilotriacetic acid in an aqueous medium were found to yield metal nitrilotriacetate salts. When crystallized from this aqueous solution, metal NTA hydrates were obtained as reported by Tomita and Ueno. Generally, these salts decompose, when heated, around 100°C and above, depending on the metal ion present and the number of moles of water of hydration. Again dehydration occurs in single or multiple steps. The different metal ions studied are Mg, Ca, Sr, Ba, Zn, and Ni.

$$MCO_3 + H_3[N(CH_2COO)_3] \longrightarrow HM[N(CH_2COO)_3] + H_2O + CO_2\Uparrow$$

After the dehydration, the first intermediate step in the decomposition for all the salts was the formation of the anhydrous metal nitrilotriacetates. These anhydrous salts were stable at ~ 350°C, and on further heating decomposes to the corresponding metal acetates. This decomposition step is a combination of exo and endothermic reactions which includes the dehydration of the free radical, a product formed there in. It appears as a single endotherm immediately after the exotherm, and being a fast reaction could not be resolved. The products formed after the decomposition are identified as oxycarbonates, $xMO.yCO_2$ with a definite MO to CO_2 mole ratio. This ratio is evaluated, for the different salts, on the basis of the percentage weight loss. Along with this metal oxycarbonate some amount of metal is also formed.

$$HM[N(CH_2COO)_3].xH_2O \longrightarrow HM\ H_3[N(CH_2COO)_3] + xH_2O$$

$$HM[N(CH_2COO)_3] \longrightarrow M(CH_3COO)_2 + G.P.$$

$$G.P. = \text{Gaseous products} = aCO_2,\ bH_2O,\ cNH_3$$

$$2M(CH_3COO)_2 \longrightarrow xMO.yCO_2 + 2CH_3COCH_3 + (2-x)M + (2-y)CO_2 + (1-x/2)O_2$$

On further heating, the MO : CO_2 ratio increases due to the partial loss of CO_2. The final decomposition step observed in the TG is the gain in weight, which is due to the oxidation of corresponding metal formed in the previous steps. The salts are found to yield metal oxides when heated in air taken in a crucible.

Depending upon the amount of hydrazine hydrate added, the metal - NTA salts react with hydrazine hydrate in an aqueous medium to yield hydrazinium metal nitrilotriacetate hydrates (or hydrazinates). This reaction is confirmed by carrying out conductometric and infrared spectral studies. In the case of the alkaline earth metals and zinc, only hydrated salts are synthesised by using limited amount of $N_2H_4 . H_2O$. Where as in the case of nickel, as representative transition metal, both limited and excess of hydrazine hydrate is used in the preparation. The general formula assigned for these new complexes is $(N_2H_5)M[N(CH_2COO)_3] . xN_2H_4 . yH_2O$, Where M = Mg, Ca, Sr, Zn and Ni and

$x = 0$ for $M : N_2H_4.H_2O : NTA$ equal to one.

$$\begin{array}{l} HM[N(CH_2COO)_3] + N_2H_4 . H_2O \dashrightarrow (N_2H_5)M[N(CH_2COO)_3] + bH_2O \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \Downarrow N_2H_4 . H_2O \\ \qquad\qquad\qquad\qquad (N_2H_5)M[N(CH_2COO)_3] . xN_2H_4 . yH_2O \end{array}$$

The decomposition patterns of these complexes is similar to those observed in the case of the simple metal nitrilotriacetate salts. The sequence of decomposition, in general, can be written as :

$$\begin{tikzcd} \text{Metal hydrazinium nitrilotriacetate hydrate} \arrow[r, Rightarrow] & \text{Unhydrous salt} \arrow[r, Rightarrow] & \text{metal nitrilotriacetate} \arrow[d, Rightarrow] \\ \text{metal oxide} & \text{metal oxycarbonate (with increased ratio)} \arrow[l, Rightarrow] & \text{metal oxycarbonate} \arrow[l, Rightarrow] & \text{metal acetate} \arrow[l, Rightarrow] \end{tikzcd}$$

Similarly, mixed metals hydrazinium nitrilotriacetate complexes with Na / K and Nickel are synthesized. The thermal reactivity of these complexes is also investigated. The final residue in the decomposition of these complexes are found to be the mixture of oxides.

$$HM\,[\,N(CH_2COO)_3\,]$$

$$\Downarrow\ Na_2CO_3$$

$$Na\,M\,[\,N(CH_2COO)_3\,]$$

$$\Downarrow\ N_2H_4 .\ H_2O$$

$$Na(\,N_2H_5\,)\,M_2\,[\,N(CH_2COO)_3\,]_2\ .\ xN_2H_4 .\ yH_2O$$

The Kinetic parameters for the different steps in the decomposition are proposed after evaluating them by known methods. The values obtained by coats and Redfern method are more reliable and consistant.

It can therefore be concluded that the (alkaline earth, or Nickel) metal nitrilotriacetates or their hydrazinium derivative, in their aqueous solution,are stable upto a moderately high temperature. At very high temperatures, whether in detergents or in electrodeposition process, the solution or bath could be unstable thus resulting in the decrease of its efficiency.

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