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## Synthesis & thermal studies on some polyvanadate and polymolybdate complexes containing $Zn^{++}$ and $Ni^{++}$ cations

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### ABSTRACT

Two new polyvanadate and polymolybdate containing  $Zn^{++}$  and  $Ni^{++}$  cations have been prepared in dilute acetic acid medium PH 4.4- 4.6 at reflux temperature. The Polyvanadate product obtained is dull yellow in appearance which gradually losses associated water molecules at room temperature yielding the final product containing only two water molecules as water of hydration. The Polymolybdate residue obtained posses light brown colour. The polyvanadate and polymolybdate both are paramagnetic at room temperature having magnetic moment value 3.02 BM & 3.78 BM. These magnetic moment values of triheteropoly complexes suggest the six co-ordinated octahedral around Ni (II) environment in weak field. The I.R. Spectrum of the products suggest the presence of  $NH_4^+$ ,  $M=O$ ,  $M-O-M'$  and hydrogen bonded  $H_2O$  group in the Complexes where  $M=V$  or  $Mo$  and  $M'=Zn$  or / and  $Ni$ . The TG and DTA curve of Polyvanadate show it decomposition in two major steps while the decomposition of polymolybdate in multi steps process. The Polymolybdate starts losing weight at 30°C and it losses 4.079% water with endothermic steps with DTA peak Maxima at 51.22°C, which correspond to  $3H_2O$  weight loss. After that the other TG and DTA steps of Polymolybdate exhibit multistep elimination and decomposition of the residue which was entirely different from the polyvanadate product. On the basis of analytical results thermogravimetric studies, i.r. spectral, bond position, thermal stability and thermodynamic, parameter results of the isolated products the composition of the Polyvanadate and polymolybdate are assigned as:-  $(NH_4)_2[Zn.NiV_6O_{18}].2H_2O$  and  $(NH_4)_4[Zn.NiMo_6O_{22}].10H_2O$  respectively.  
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### KEYWORDS

Polyvanadate and polymolybdate preparation;  
Thermal studies;  
I.R. spectral studies.

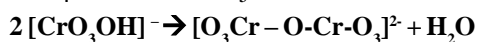
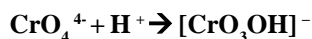
### INTRODUCTION

Isopoly and heteropoly complexes of transition Metals especially those of vanadium (V), Molybdenum (VI) and Tungsten (VI) have developed into important

and exceedingly diverse classes of compounds. Now a days isopoly and heteropoly complexes should best be categorized as "Isopoly and heteropoly oxometalates" as suggested by Michael T.Pope<sup>[1,2]</sup> and latter by Bernt Krabs<sup>[3]</sup>. The Synthesis is based on the condensation

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process<sup>[4,5,6]</sup> which lead to the formation of oxobridges by elimination of water molecules from the molecules of weak acids. Such condensation reactions generally take place freely and reversibly in acidic medium. simplest example of such reaction is the condensation of chromate ion to form isopoly dichromate ion. An equilibrium reaction of which is dependent upon the pH of the system.



In acidic medium dichromate ion while in basic medium the chromate ion is stable. The condensation behaviour of molybdates & vanadates are basically almost similar. The heteropoly complexes are named according to I.U.P.A.C. System<sup>[7]</sup>. In general the Heteropoly Complexes have been Prepared<sup>[8-14]</sup> by mixing the theoretical quantities of the required reactants in proper acidic medium followed by heating and crystallization. Maintenance of acid medium is must for the preparation of heteropoly molybdates, tungstates and vanadates. All these anions are decomposed in alkaline medium. The thermal studies of synthesized triheteropoly complexes are important regarding their stability since they contain large number of water molecules as water of hydration, which fixed their position between the interstices or at peripheral region of the crystal. Hence the thermal stability of heteropoly complexes were determined by direct heat treatment<sup>[8-18]</sup> or by dehydration experiments which involve by thermogravimetric and differential thermal analysis<sup>[19-20]</sup> of the complexes. Isothermal Measurement<sup>[21]</sup> have also been found successful for determination of thermal nature of the complexes in this research paper the emphasis regarding characterization of the newly synthesized polyvanadate and polymolybdate triheteropoly complexes having two hetero atom Zinc and Nickel based on the i.r. spectral studies and the thermal analysis which include TGA and DTA studies.

## RESULTS AND DISCUSSION

### I.R. spectral results of polymolybdate products

The i.r spectrum of product showed very broad and strong i.r band around 3000 to 3396 cm<sup>-1</sup>. The broadband at 2769 to 3180 cm<sup>-1</sup> can be attributed to

strong hydrogen bonded H<sub>2</sub>O and NH<sub>4</sub><sup>+</sup> cations. The Prominent  $\delta$  (NH<sub>2</sub>) and  $\beta$  (NH<sub>2</sub>) of NH<sub>4</sub><sup>+</sup> cations are isolated at 1627 and 1406 cm<sup>-1</sup>. The broad and weak band of 1680 cm<sup>-1</sup> can be assigned to  $\delta$  (H<sub>2</sub>O) in polymolybdate anions. The prominent and strong band observed at 875.68 cm<sup>-1</sup>. In i.r. spectrum assigned to (Mo=O) stretching band and sharp band at 927.76 cm<sup>-1</sup> to NH<sub>4</sub><sup>+</sup> rocking band. The strong band at 638.42 cm<sup>-1</sup> can be assigned to  $\nu$  (Mo-O-Mo) stretching vibration. The medium i.r band observed at 578.6 and 478.3 cm<sup>-1</sup> are attributed to  $\nu$  (Ni-O) and  $\nu$  (Zn-O) vibration.

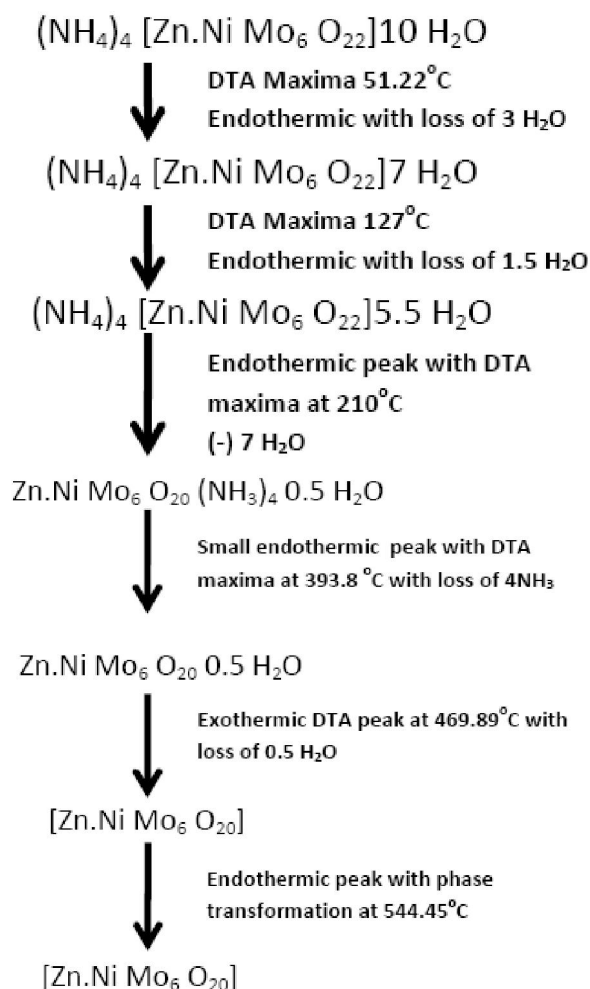
### I.R. spectral result of polyvanadate residue

The infrared spectral analysis of polyvanadate show characteristics vibrations of NH<sub>4</sub><sup>+</sup> VO<sub>3</sub><sup>3+</sup> and Coordinated H<sub>2</sub>O molecule. The sharp i.r. band at 3230 wave number is attributed to  $\nu$ (NH) vibration and broad weak band at 2821 cm<sup>-1</sup> to  $\nu$ (H<sub>2</sub>O). The medium band at 1565 cm<sup>-1</sup> and strong band near 1409.9 cm<sup>-1</sup> observed are due to  $\delta$  (NH<sub>4</sub><sup>+</sup>) and  $\beta$  (NH<sub>4</sub><sup>+</sup>) vibrations. Weak band at 1643 cm<sup>-1</sup> can be assigned to  $\delta$ (H<sub>2</sub>O) of bonded water molecule which is substantiated by  $\rho\omega$ (H<sub>2</sub>O) at 590 cm<sup>-1</sup>. The V=O stretch of vanadyl group is assigned to strong band at 966 cm<sup>-1</sup> and medium band at 734 cm<sup>-1</sup> is attributed to (V-O-V) stretching band @ the V=O force constant was calculated and found to have K=14.3 x 10<sup>5</sup> dyne cm<sup>-1</sup>. The V=O force constant. The larger value of V=O force constant indicated strong V=O band having large double bond character. The i.r. band located at 526, 457 and 405 cm<sup>-1</sup> are attributed to  $\nu$ (V-O),  $\nu$ (Zn-O), and  $\nu$ (Ni-O) vibration in polyvanadate cluster.

### Thermal studies of polymolybdate

The TG and DTA curve of polymolybdate show multistep elimination and decomposition of product. The TG analysis was performed with heating rate 10°C per minutes in static air. Unlike polyvanadate it started losing weight 30°C at and it losses 4.079 % water with endothermic step with DTA peak maxima at 51.22°C. The weight loss approximately corresponds to 3H<sub>2</sub>O. The second stage of loss of H<sub>2</sub>O starts around 109°C with DTA Peak maxima at 127.85°C. The DTA curve show endothermic nature of weight loss and the weight loss correspond to 1.5H<sub>2</sub>O. The third step of thermal loss is also endothermic in nature with strong DTA

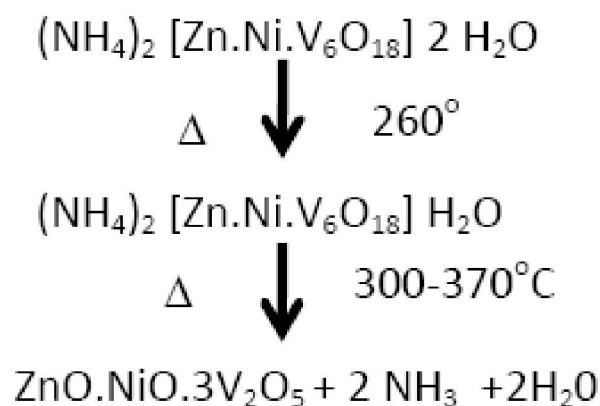
maxima at 210.58°C. The weight loss corresponds to elimination of 7H<sub>2</sub>O from polymolybdate species. The fourth DTA peak is accompanied by loss in weight correspond to elimination of 4NH<sub>3</sub> molecules from the polymolybdate species. The last phase of elimination corresponds to ½ H<sub>2</sub>O. It is lost from lattice space which shows exothermic DTA maxima at 469.89°C. The last DTA maxima is observed at 544°C without negligible loss in weight of the sample. The DTA curve is also endothermic in nature which can be attributed to phase transformation in the residual polymolybdate. The sequence of thermal decomposition reaction taking place can be summarized in following step:-



### Thermal studies of polyvanadate

The thermogravimetric analysis (TG and DTA) in temperature range 30-500°C with heating rate 10°C per minute was performed in static air. The TG curve of polyvanadate showed slight decrease in weight approximately 0.8 H<sub>2</sub>O till 360°C. The complex started losing

weight around 300°C with endothermic maxima at 341.44°C and loss in weight of complex continuous up to 370°C giving thermal stable product. The loss in weight observed about 9.365%. Which correspond to composition of residue ZnO.NiO.3V<sub>2</sub>O<sub>5</sub>. The loss in weight is due to release of 2H<sub>2</sub>O and 2NH<sub>3</sub> (expected loss 9.25%) The loss in weight can be expressed by equation:-



The DTA peak over 1808.959 μV x sec having peak height -10.524 V indicate strong endothermic character in weight loss of polyvanadate. The thermodynamic parameters and thermal reaction rate constant value of TG analysis was calculated by conventional method. The second DTA maxima was observed at 541°C with peak height -2.451 μV and having peak area 220.753 μV x second without any change in weight of the sample. The range in endothermic DTA maxima can be attributed to phase change of solid product of interaction of metal oxide with each other having change in internal arrangement of environment of Ni (II) and Zn (II) cations.

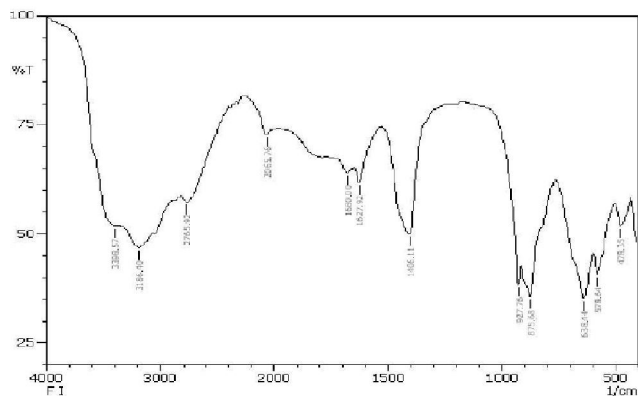
### DISCUSSION

The transformation of mono and hetero polymolybdate, polyvanadate and similar poly complexes are typical characteristics of Vth and VIth group of transition metal oxy cations and have widely been studied with their structural and catalytic view point. It has been found that in presence of Zn<sup>+2</sup>, Ni<sup>+2</sup> and (NH<sub>4</sub>)<sub>6</sub> Mo<sub>7</sub>O<sub>24</sub> in acetic acid medium a definite Polymolybdate of composition (NH<sub>4</sub>)<sub>4</sub> [Zn.Ni.Mo<sub>6</sub>O<sub>22</sub>] 10 H<sub>2</sub>O was isolated between pH range 4.4 – 4.6 at reflux temperature and standing its solution for 5-7 days at room temperature.

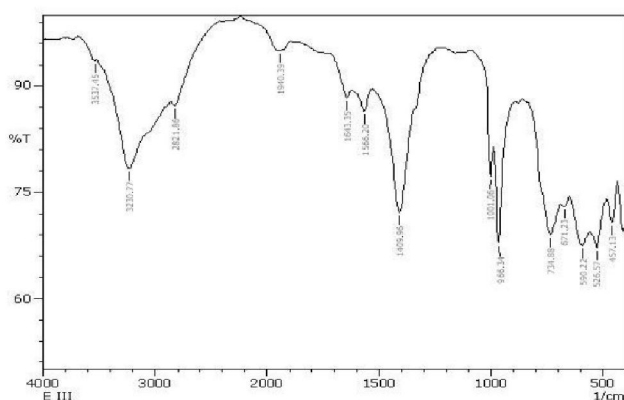
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The Interaction of ammonium vanadate  $\text{NH}_4\text{VO}_3$  with  $\text{Zn}^{2+}$  and  $\text{Ni}^{2+}$  in acetic acid medium between pH 4.5 – 4.6 in Zn : Ni : V ratio 1:1:6 gave a light brown product of composition  $(\text{NH}_4)_2[\text{Zn.Ni.V}_6\text{O}_{18}]2\text{H}_2\text{O}$ . The same Product was obtained in more than 3 consecutive repetition of process in appropriate ratio of constituent components. The Product of both Mo(VI) and V(V)

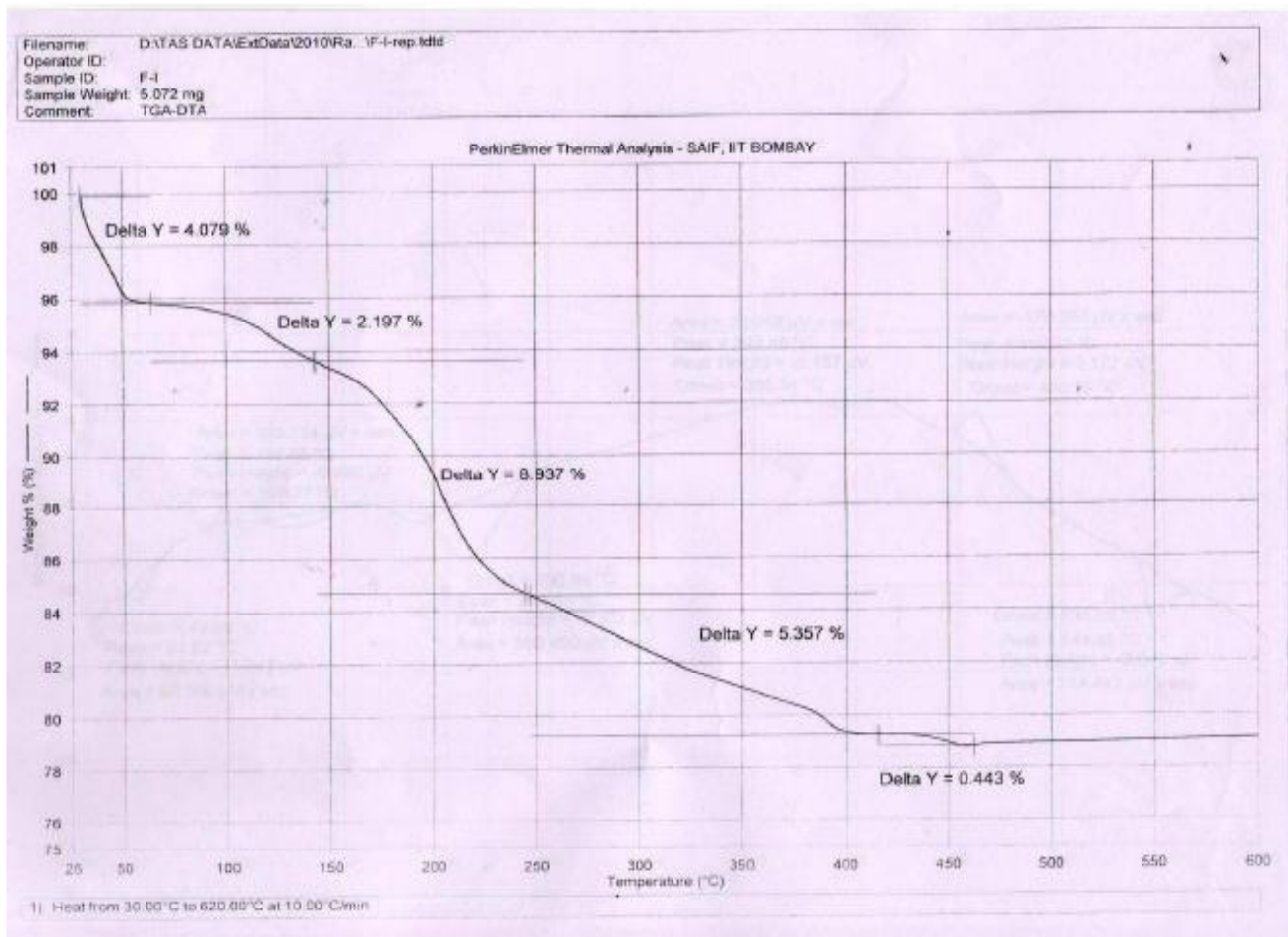
are quite stable in air and has poor solubility in water cold condition. The Products on boiling water partially dissolves yield light colored solution. The aqueous solution of polycomplexes are indicating ionic nature of ammonium ion  $[\text{NH}_4^+]$ . The complexes readily evolve  $\text{NH}_3$  on heating it with aqueous NaOH, Supporting ionic nature of  $\text{NH}_4^+$  radical.



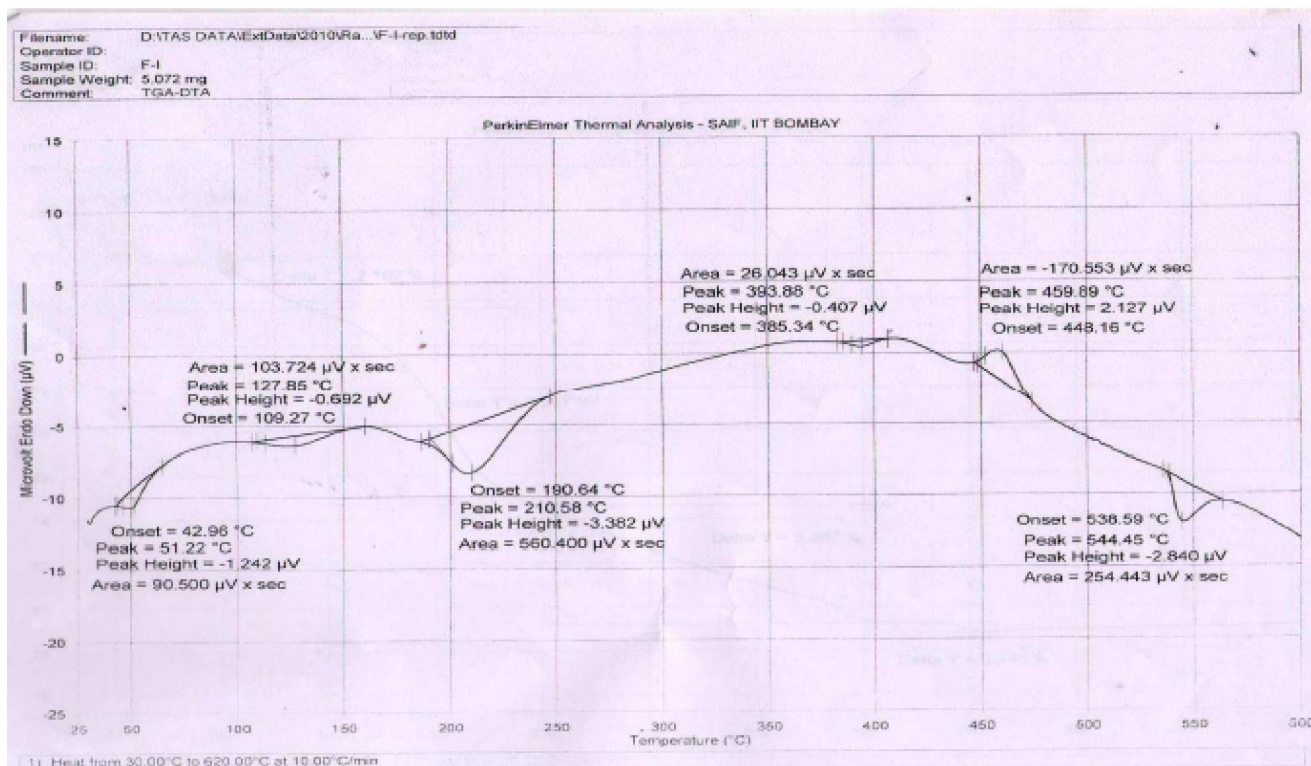
Graph 1 : FTIR graph for polymolybdate



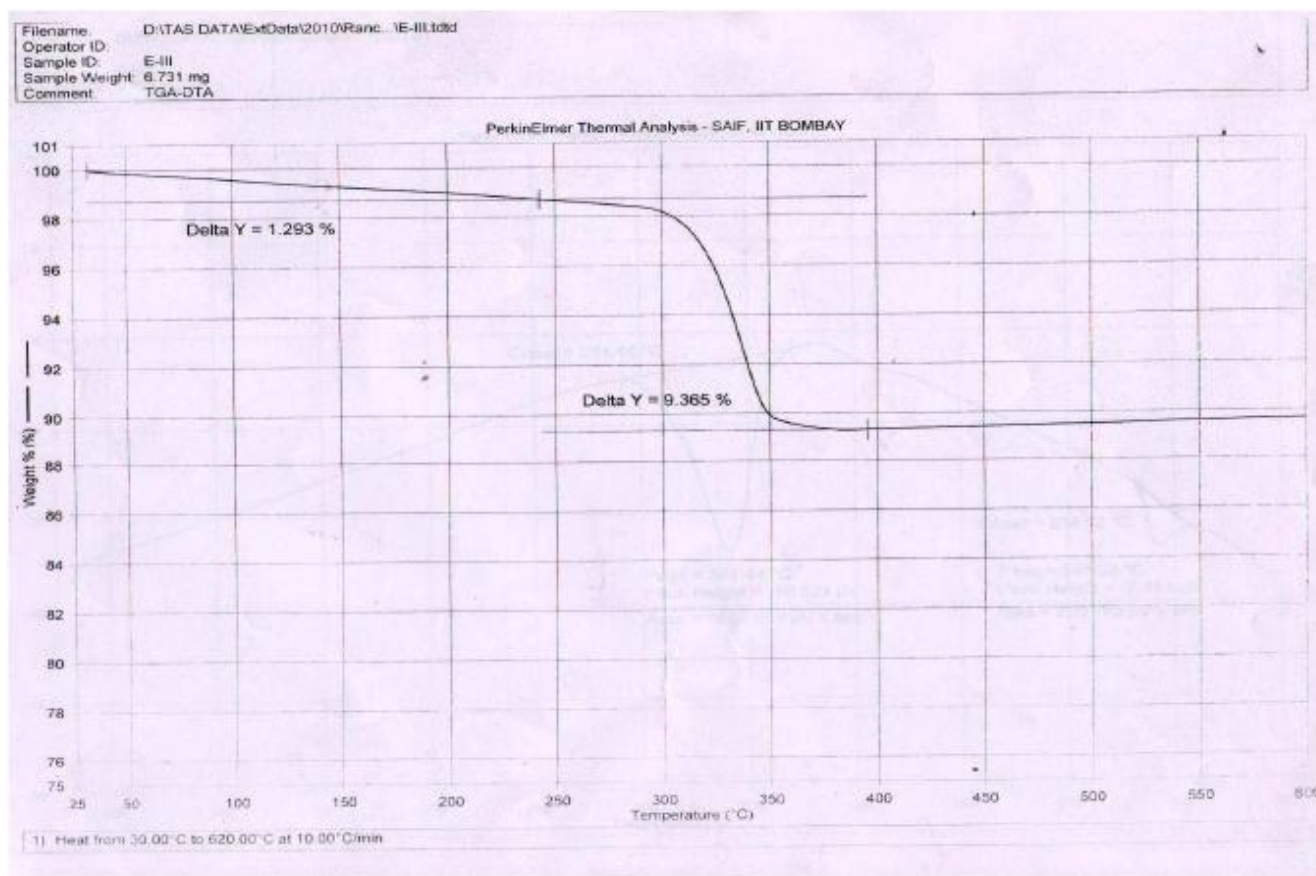
Graph 2 : FTIR graph of polyvanadate



Graph 3 : T.G. of polymolybdate

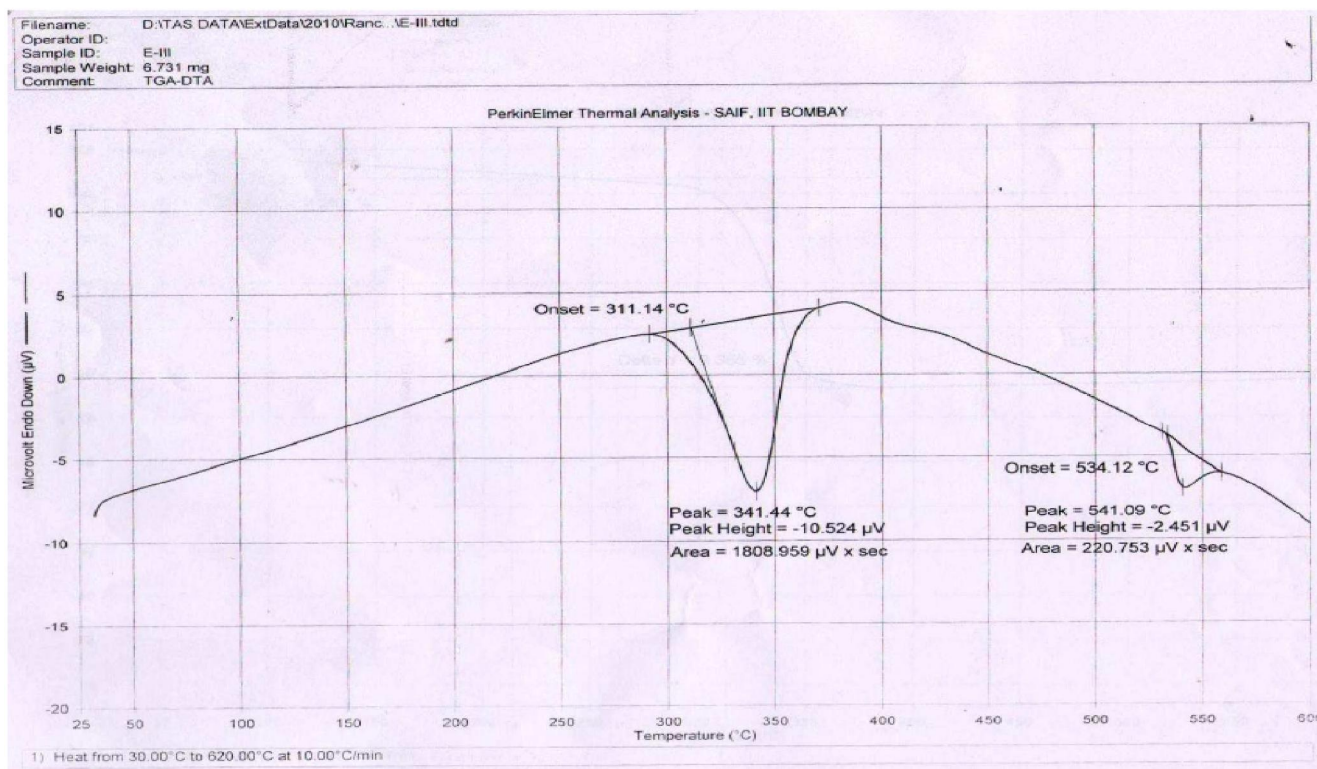


Graph 4 : D.T.A. of polymolybdate



Graph 5 : T.G. of polyvanadate

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Graph 6 : D.T.A. of polyvanadate

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