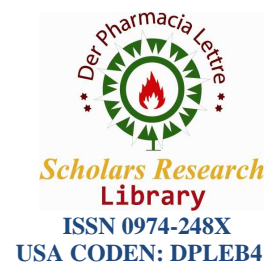




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### Study of electrical property, adsorption chromatography and thermal stability of p-cresol and oxamide with formaldehyde terpolymer resin-IV

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#### ABSTRACT

Terpolymer resin p-COF-IV was synthesized by the condensation polymerization of reacting monomers. The electrical property of p-COF-IV terpolymer was measured over a wide range of temperature (313-423K), activation energy of electrical conduction has been evaluated and plot of  $\log \sigma$  vs  $10^3/T$  is found to be linear over a wide range of temperature, therefore can be ranked as semiconductor. The adsorption chromatography chelating ion-exchange properties of this terpolymer was studied for Fe (III), Cu (II), Ni (II), Co (II), Zn (II), Cd (II) and Pb (II) ions. A batch equilibrium method was employed in the study of the selectivity of metal ion uptake. The study was carried out over a wide pH range, shaking time and in media of various ionic strengths. The terpolymer showed a higher selectivity for Fe (III), Cu (II), and Ni (II) ions than for Co (II), Zn (II), Cd (II) and Pb (II) ions. Thermal study of the resin was carried out to determine its mode of decomposition and thermal stability. The Freeman-Carroll and Sharp-Wentworth methods have been used in the present investigation to calculate thermal activation energy. And different kinetic parameter like frequency factor (Z), entropy change ( $\Delta S$ ), free energy change ( $\Delta F$ ) and apparent entropy ( $S^*$ ) have been determined using Freeman-Carroll method.

**Keywords:** Semiconductor, ion-exchanger, adsorption, thermogravimetric analysis, synthesis.

#### INTRODUCTION

The synthesized terpolymer resins, showing versatile applications and properties, attracted the attention of scientist and introduce the recent innovations in the polymer chemistry. These terpolymers can be used as high energy material [1], ion-exchanger [2], semiconductors [3], antioxidants, fire proofing agent, optical storage data, binders, molding materials etc.

The semiconducting properties of terpolymer resins have gained sufficient ground in recent years. Work on organic conducting polymers is carried out extensively due to their wide applications, [4, 5] in areas such as chemically modified electrodes, sensors etc. An industrially useful semiconducting material has been reported by Dewar, et al. [6]. The conductivity of an 8-

hydroxyquinoline–oxamide-formaldehyde terpolymer resins have been reported over a wide range of temperature [7]. Pal et al. [8] have reported electrical conductivity of salicylic acid-biuret / dithioxamide / dithibiuret-trioxane terpolymer resins.

Ion-exchange technique can remove traces of ionic impurities from water/process liquors and gives out a product of ultra pure quality in a simple efficient and techno-economically viable manner. Ion exchangers are widely used in water treatment and pollution control [9, 10]. Various hydroxybenzoic acid-formaldehyde and 4-hydroxyacetophenone- biuret - formaldehyde copolymers have been reported and found use as ion-exchangers [11, 12].

The study of the thermal degradation of terpolymer resins have recently become a subject of interest. Zhao Hong et al. studied the thermal decomposition behaviour of phosphorous containing copolystar [13]. The present paper explored the newly synthesized terpolymer resin p-cresol and Oxamide with Formaldehyde (p-COF-IV) in the light of its semiconducting, chelating adsorption chromatography and thermogravimetric study and its applications.

## MATERIALS AND METHODS

### Starting Materials:

The chemicals (starting materials) were of Analar or Chemically pure grade, and wherever necessary the purity was tested and confirmed by TLC.

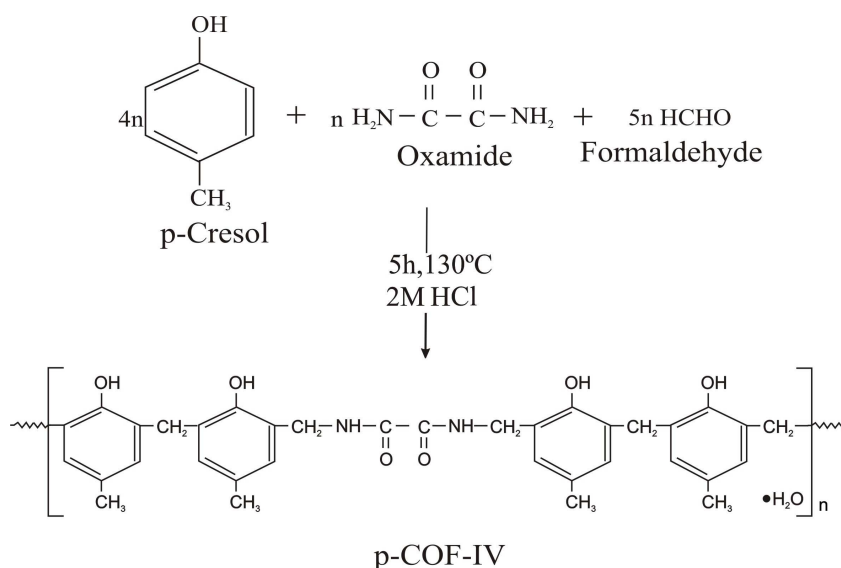


Fig.1: Reaction and expected structure of p-COF-IV terpolymer resin

### Synthesis of p-COF-IV terpolymer resin

The new terpolymer resin p-COF-IV was synthesized by condensing p-cresol (0.4 mol) and oxamide (0.1 mol) with 37 % formaldehyde (0.5 mol) in a mol ratio of 4:1:5 in the presence of 2M 200 ml HCl as a catalyst at  $130^{\circ}\text{C} \pm 2^{\circ}\text{C}$  for 5h in an oil bath with occasional shaking to ensure thorough mixing. The separated terpolymer was washed with hot water and methanol to remove unreacted starting materials and acid monomers. The properly washed resin was dried, powdered and then extracted with diethyl ether and then with petroleum ether to remove p-cresol-formaldehyde copolymer which might be present along with p-COF-IV terpolymer. The terpolymer was purified further by dissolving in 8% aqueous sodium hydroxide solution, filtered and reprecipitated by gradual drop wise addition of ice cold 1:1 (v/v) concentrated hydrochloric acid / distilled water with constant and rapid stirring to avoid lump formation. The process of reprecipitation was repeated twice. The copolymer sample p-COF-IV thus obtained was filtered,

washed several times with hot water, dried in air, powdered and kept in vacuum desiccator over silica gel. The yield of the copolymer resin was found to be 80%. The reaction and suggested structure has been given in Fig. 1.

### Conductivity Measurement

The DC electrical conductivity measurements in solid state were carried out in a suitable sample holder designed for the purpose, for finding out the resistance of the sample, in the temperature range of 313K to 423K at constant voltage of 50 volts across the pellet prepared from terpolymer resin. The measurements were made by Auto Compact LCR-Q tester model 4910.

To prepare the pellets, the purified terpolymer resin was thoroughly ground with an agate pestle and mortar. The well powdered terpolymer was palatalized in a steel die at  $5 \text{ t/cm}^2$  pressure with the help of a hydraulic press. Pellet of 1.2 cm in diameter and nearly 0.2 to 0.3 cm thickness was prepared. The pellet of the test sample was put in a typical sample holder fabricated in this laboratory and resistance was measured using conductivity bridge over wide range of temperature.

For this purpose, the sample pellet was heated in a tubular furnace in which the temperature of the furnace being increased by steps from room temperature to about 423 K

### Ion-exchange properties:

The terpolymer sample (25mg) was suspended in an electrolyte solution (25ml) of known concentration. The pH of the suspension was adjusted to the required value by using either 0.1M  $\text{HNO}_3$  or 0.1M  $\text{NaOH}$ . The suspension was stirred for 24hrs at  $30^\circ\text{C}$ . To this suspension 2 ml of 0.1M solution of the metal ion was added and the pH was adjusted to the required value. The mixture was again stirred at  $30^\circ\text{C}$  for 24 hrs. The polymer was then filtered off and washed with distilled water. The filtrate and the washing were collected and then the amount of metal ion was estimated by titrating against standard EDTA (ethylene diamine tetra-acetic acid) at the same pH (experimental reading). The same titration has been carried out without polymer (blank reading). The amount of metal ion uptake of the polymer was calculated from the difference between a blank experiment without polymer and the reading in the actual experiments. The experiment was repeated in the presence of several electrolytes at various pH and different time intervals [14].

### Thermogravimetric analysis

From the data of thermogravimetric analysis, we can determine order of the reaction, energy of activation and different thermodynamic parameters by using following steps.

1. Initially find out  $dw/dt$  with the help of weight loss in gm (w) and time (t) from thermoanalytical data.
2. Find out  $W_r$  from equation  $W_r = W_c - W_t$ , where,  $W_c$  is the weight loss at the completion of reaction and  $W_t$  is the total weight loss up to time t.
3. Plot a graph between  $\log dw/dt / \log W_r$  on Y axis versus  $1/T / \log W_r$  on X axis where T is the absolute temperature at weight loss, from this graph the value of n (order of reaction) is obtained. It is the value of intercept on Y axis.
4. Find out the value of  $\alpha$  by equation  $W_t / W_c$ , the value of  $g(\alpha)$  by equation  $g(\alpha) = 1 - (1 - \alpha)^{1-n} / (1 - n)$  and the value of  $\log(\alpha) / T^3$
5. Plot a graph between  $\log(\alpha) / T^3$  on Y axis versus  $1/T \times 10^{-3}$  on X axis we get energy of activation from the value of slope. The energy of activation can be determined by equation  $E_a = \text{slope} \times 2.303 \times R$ , where R is the gas constant.

6. From the value of activation energy, the different thermodynamic parameters can be derived.

### **Ion-Exchange Capacity**

The term ion exchange capacity is intended to describe the total available exchanged capacity of an exchange resin, as described by the number of functional group on it. Ion exchange capacity was determined by following experimental procedure.

25 mg of resin sample was suspended in 50 ml of double distilled water; to this add 25 ml of 0.5 M sodium acetate solution. The mixture has been stirred for 2 to 5 min. when  $H^+$  from resin liberated in the solution to form acetic acid and adsorbed sodium ion ( $Na^+$ ). Then the solution was filtered and the filtered is titrated with 0.5 M NaOH solution.

The ion-exchange capacity for  $Na^+$  can be calculated by using following equation, in millimols per gram ( $mmol.g^{-1}$ )

$$\text{Ion-exchange capacity of terpolymer resin} = XY / Z$$

Where,

X = molarity of NaOH

Y = volume of NaOH required during titration

Z = Weight of the exchanger

The ion-exchange capacity of terpolymer resin has been determined and compared it with commercial ion-exchangers.

## **RESULTS AND DISCUSSION**

### **Electrical conductivity**

The thermal activation energy and the values of electrical conductivity at different temperatures are given in Table 1. The resistance values of the pellets of the terpolymers ranging from 313 K to 423 K were converted into conductivity values ( $\sigma$ ) by taking into account the thickness of the pellet and its diameter and evaluating thickness area parameters of the pellet of a particular terpolymer. The temperature dependence of the electrical conductivity of the terpolymers are shown in Fig. 5. In the electrical conduction domain, the temperature dependence of the electrical conductivity obeys the well known equation [4].

$$\sigma = \sigma_0 \exp^{(\Delta E/kT)}$$

Where,

k = Boltzmann constant

$\sigma_0$  = electrical conductivity at temperature  $T \rightarrow \infty$

$\sigma$  = electrical conductivity at temperature T

$\Delta E$  = electrical conductivity energy of electrical conduction.

This relation has been modified as

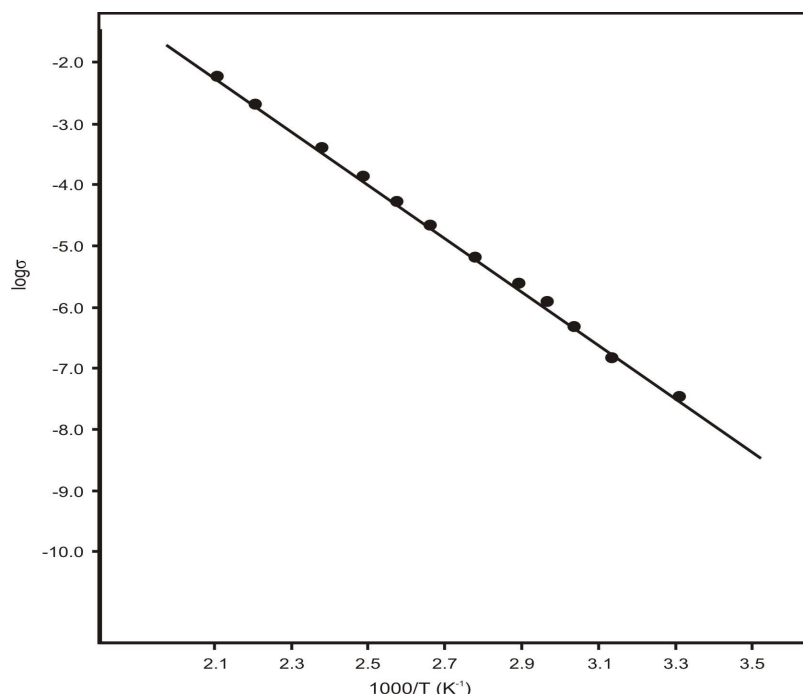
$$\log \sigma = \log \sigma_0 + \frac{-\Delta E}{2.303kT}$$

According to this relation, a plot of  $\log \sigma$  Vs.  $1000/T$  would be linear with a negative slope. The result of the D.C. conductivities are presented here in the form of plots of  $\log \sigma$  Vs.  $1000/T$ , as the range of conductivities was found to be  $1.54 \times 10^{-8}$  to  $5.01 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$ .

It will be seen from the plots (Fig. 5) of terpolymer that there is a consistent increase in electrical conductivity as the temperature rises roughly from 313 K to 423 K. This trend is a characteristic of semiconduction [5]. The activation energy was determined from the curves  $\log \sigma$  Vs.  $(10^3/T)$ . The plot of  $\log \sigma$  Vs.  $10^3/T$  is found to be linear (Fig. 5) over wide range of temperature which indicates the semiconducting nature of terpolymer [5, 6].

**Table 1 Electrical conductivity data of p-COF-IV terpolymer resin**

Terpolymer	Electrical Conductivity $\text{ohm}^{-1} \text{ cm}^{-1}$		$\Delta T$ (K)	$\Delta E$ (ev)
	313 K	423 K		
p-COF-IV	$1.54 \times 10^{-8}$	$5.01 \times 10^{-4}$	313 – 423	$0.73 \times 10^{-4}$



**Fig. 5 Electrical conductivity plot of p-COF-IV terpolymer resin**

### Ion-exchange properties

Batch equilibrium technique developed by Gregor et al and De Geiso et al was used to study ion exchange properties of p-COF-IV terpolymer resin. The results of the batch equilibrium study carried out are presented in Table 2, 3 and 4. Seven metal ions  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  in the form of aqueous metal nitrate solution were used. The ion exchange study was carried out using three experimental variables : a) Electrolyte and its ionic strength b) uptake time and c) pH of the aqueous medium. Among these three variables, two were kept constant and only one was varied at a time to evaluate its effect on metal uptake capacity of the polymer similar to the earlier co-workers [18,19]. The details of experimental procedure are given below.

### Effect of electrolyte and its ionic strengths on metal uptake

We examined the influence of  $\text{ClO}_4^-$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  at various concentrations on the equilibrium of metal-resin interaction. Table 2 shows that the amount of metal ions taken up by a given amount of terpolymer depends on the nature and concentration of the electrolyte present in the solution. Generally as concentration increases of the electrolyte, the ionization decreases, the number of ligands decreases in the solution which form the complex with less metal ions and more ions are available for adsorption. Hence on increasing concentration there should be increase in uptake of metal ion. But trend disturbed due to formation of more stable complex with more number of ligands which decrease the number of metal ions available for adsorption, hence uptake decreases. In the presence of perchlorate, chloride and nitrate ions, the uptake of Fe(III), Cu(II) and Ni(II) ions increase with increasing concentration of the electrolytes, whereas in the presence of sulphate ions the amount of the above mentioned ions taken up by the terpolymer decreases with increasing concentration of the electrolyte [19]. Moreover, the uptake of Co (II), Zn (II), Cd (II) and Pb (II) ions increase with decreasing concentration of the chloride, nitrate, perchlorate and sulphate ions. This may be explained on the basis of the stability constants of the complexes with those metal ions [20]. The ratio of physical core structure of the resin is significant in the uptake of different metal ions by the resin polymer. The amount of metal ion uptake by the p-COF-IV terpolymer resin is found to be higher when comparing to the other polymeric resins [20].

### Estimation of the rate of metal ion uptake as a function of time

The rate of metal adsorption was determined to find out the shortest period of time for which equilibrium could be carried to while operating as close to equilibrium conditions as possible. As shaking time increases the polymer gets more time for adsorption, hence uptake increases. Table 3 shows the dependence of the rate of metal ion uptake on the nature of the metal. The rate refers to the change in the concentration of the metal ions in the aqueous solution which is in contact with the given polymer. The result shows that the time taken for the uptake of the different metal ions at a given stage depends on the nature of the metal ion under given conditions. It is found that Fe (III) ions require about 3hrs for the establishment of the equilibrium, whereas Cu (II), Ni (II), Co (II) and Zn (II) ions required about 5 or 6 hrs [21]. Thus the rate of metal ions uptake follows the order  $\text{Cu (II)} > \text{Ni (II)} > \text{Co (II)} \approx \text{Zn (II)} > \text{Cd (II)} > \text{Pb (II)}$  for the terpolymer [21]. The rate of metal uptake may depend upon hydrated radii of metal ions. The rate of uptake for the post transition metal ions exhibit other trend for Cd(II), the rate of uptake is in the comparable that of Pb(II) because of difference in 'd' orbital.

### Distribution ratios of metal ions at different pH

The distributions of metal ion depend upon pH of the solution. As pH, increases the  $\text{H}^+$  ion concentration in the solution decrease and only metal ion in the solution available for adsorption which increase uptake.

The effect of pH on the amount of metal ions distributed between two phases can be explained by the data given in Table 4. The data on the distribution ratio as a function of pH indicate that the relative amount of metal ion taken up by the p-COF-IV terpolymer increases with increasing pH of the medium [18]. The magnitude of increase, however, is different for different metal cations. The study was carried from 2.5 upto pH 6.5 to prevent hydrolysis of metal ions at higher pH. For  $\text{Fe}^{3+}$  ion the highest working pH is 3, has lower distribution ratio since  $\text{Fe}^{3+}$  forms octahedral complex with ligand of electrolyte, which shows crowding effect. This steric hindrance may be lower the distribution ratio of  $\text{Fe}^{3+}$  ion.  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  have higher distribution ratio over pH range of 2.5 to 6.5 which may be due to the less steric hindrance. Thus the value

of distribution ratio for given pH depends upon the nature and stability of chelates formation for particular metal ion.

The data of distribution ratio shows a random trend in certain cases [19]. This may be due to the amphoteric nature of the p-COF-IV resin. Table 4 shows that reported resin provides better selectivity for one metal ion in presence of other metal ions. From the result it reveals that with decrease in atomic number the ion uptake capacity is increasing at that particular pH. In case of Cd (II) and Pb (II) purely electrostatic factors are responsible. The ion uptake capacity of Cd (II) is lower owing to the large size of its hydrated ion than that of Cu (II). The steric influence of the methyl group and hydroxyl group in p-COF-IV resin is probably responsible for their observed low binding capacities for various metal ions. Thus the interaction of this resin material with various metal ions in an aqueous environment may largely limit the binding sites, which are suitably, disposed in a conformational favorable manner on the surface layer.

**Table 2 Evaluation of the effect of different electrolytes on the uptake of several metal ions<sup>a</sup> by p-COF-IV terpolymer resin**

Metal ion	Electrolyte (mol/l)	pH	Weight of the metal uptake (mmol.g <sup>-1</sup> ) in the presence of			
			NaNO <sub>3</sub>	NaCl	NaClO <sub>4</sub>	Na <sub>2</sub> SO <sub>4</sub>
Fe(III)	0.01	2.5	1.29	0.73	1.20	3.22
	0.05		1.41	0.95	1.72	2.45
	0.10		1.63	1.29	1.85	1.89
	0.50		1.84	1.56	2.52	1.13
	1.00		2.45	2.29	3.22	0.72
Cu(II)	0.01	4.5	1.86	1.21	1.81	3.45
	0.05		2.20	1.96	2.32	2.81
	0.10		2.52	2.54	3.01	2.18
	0.50		2.82	3.10	3.69	1.35
	1.00		2.89	3.71	4.27	0.65
Ni(II)	0.01	4.5	0.87	0.74	1.33	2.92
	0.05		1.46	1.22	1.92	2.33
	0.10		2.02	1.69	2.51	1.74
	0.50		2.50	2.21	3.09	1.16
	1.00		3.22	2.98	3.68	0.57
Co(II)	0.01	5.00	1.40	1.33	1.16	1.87
	0.05		1.16	1.14	1.04	1.23
	0.10		0.92	0.97	0.86	0.92
	0.50		0.69	0.79	0.69	0.75
	1.00		0.45	0.57	0.41	0.51
Zn(II)	0.01	5.00	2.41	1.74	1.79	2.08
	0.05		2.02	1.47	1.66	1.42
	0.10		1.56	1.10	1.40	1.28
	0.50		1.17	0.84	1.16	0.89
	1.00		0.64	0.51	0.71	0.57
Cd(II)	0.01	5.00	2.43	2.30	1.95	1.66
	0.05		1.98	1.82	1.55	1.28
	0.10		1.49	1.42	1.11	1.02
	0.50		0.98	0.97	0.92	0.79
	1.00		0.77	0.66	0.68	0.57
Pb(II)	0.01	6.00	2.41	2.24	1.87	3.47
	0.05		1.77	1.67	1.52	2.84
	0.10		1.12	1.40	1.21	2.18
	0.50		0.45	1.21	0.93	1.56
	1.00		0.17	0.92	0.59	0.91

<sup>a</sup> [M(NO<sub>3</sub>)<sub>2</sub>] = 0.1 mol/l; Volume = 2 ml; Volume of electrolyte solution : 25 ml  
Weight of resin = 25 mg; time : 24 h : Room temperature.

The higher value of distribution ratio for Cu (II) and Ni (II) at pH 2.6 to 6.0 may be due to the formation of most stable complex with chelating ligands. Therefore the polymer under study has more selectivity of Cu<sup>2+</sup> and Ni<sup>2+</sup> ions at pH 4.0 to 6.0 than other ions which form rather weak complex. While at pH 3 the terpolymer has more selectivity of Fe<sup>3+</sup> ions. The p-COF-IV terpolymer resin takes up Fe (III) ion more selectively than any other metal ions under study. The order of distribution ratio of metal ions measured in pH range 2.5 to 6.5 is found to be Fe (III) > Cu (II) > Ni (II) > Zn (II) > Co (II) > Pb (II) > Cd (II). Thus the results of such type of study are helpful in selecting the optimum pH for a selective uptake of a particular metal cation from a mixture of different metal ions [18- 22].

**Table 3 Comparison of the rates of metal (M) ion uptake<sup>a</sup> by p-COF-IV terpolymer resin**

Metal ion	pH	Percentage of metal ion uptake <sup>b</sup> at different times (h)						
		1	2	3	4	5	6	7
Fe(III)	2.5	53.3	78.6	96.4	-	-	-	-
Cu(II)	4.5	49.5	61.3	68.6	79.9	93.7	-	-
Ni(II)	4.5	50.7	60.6	70.1	86.1	94.6	-	-
Co(II)	5	45.2	59.7	69.1	84.2	94.1	-	-
Zn(II)	5	49.1	59.6	69.5	84.5	96.1	-	-
Cd(II)	5	30.1	50.6	60.2	70.1	85.2	94.1	-
Pb(II)	6	28.5	49.3	57.2	69.2	84.1	95.7	-

<sup>a</sup>  $[M(NO_3)_2] = 0.1 \text{ mol/l}$ ; volume : 2ml;  $NaNO_3 = 1.0 \text{ mol/L}$ ; volume: 25ml, Room temperature.

<sup>b</sup> Metal ion uptake = (Amount of metal ion absorbed x 100) / amount of metal ion absorbed at equilibrium.

**Table 4 Distribution ratio D<sup>a</sup> of various metal ions<sup>b</sup> as function of the pH by p-COF-IV terpolymer resin**

Metal ion	Distribution ratio of the metal ion at different pH							
	1.5	2	2.5	3	3.5	4	5	6
Fe(III)	20.2	125.6	237.1	368.2	-	-	-	-
Cu(II)	-	-	-	68.3	93.4	212.1	681.4	1209.4
Ni(II)	-	-	-	52.1	74.8	230.4	462.1	914.1
Co(II)	-	-	-	41.5	65.4	155.8	248.2	445.4
Zn(II)	-	-	-	43.7	73.1	99.3	133.0	225.8
Cd(II)	-	-	-	31.2	65.7	107.1	174.2	234.3
Pb(II)	-	-	-	39.6	63.5	126.2	197.2	273.6

<sup>a</sup>  $D = \text{weight (in mg) of metal ions taken up by 1g of copolymer} / \text{weight (in mg) of metal ions present in 1ml of solution}$ .

<sup>b</sup>  $[M(NO_3)_2] = 0.1 \text{ mol/l}$ ; volume : 2ml;  $NaNO_3 = 1.0 \text{ mol/l}$ ; volume: 25ml, time 24h (equilibrium state) at Room temperature.

Ion exchange properties of various resins can be studied by comparing their ion exchange capacity. The ion exchange capacity (IEC) is a fundamental and important quantity for the characterization of any ion exchange material. It is defined as the amount of ion that undergoes ion exchange in a definite amount of material, under specified experimental conditions. However, there may be complication in the determination of the capacity. The ion exchange capacity of p-COF-IV terpolymer has been calculated, which was found to be 4.12 mmol.g<sup>-1</sup> which indicates that p-COF-II terpolymer resin is better ion exchanger than phenolic and some polystyrene commercial ion exchangers.

For the strongly acidic cation exchange resin such as cross linked polystyrene sulphonic acid resins, the ion exchange capacity is virtually independent of the pH of the solutions. For weak acid cation exchangers, such as those containing carboxylate group, ionizations, occurs only in alkaline solution. Similarly weakly basic cation exchanger does not work above pH-9.



### Thermogravimetry of p-COF-IV terpolymer resin

Thermogram of p-COF-IV terpolymer resin is shown in Fig. 6, in the temperature range of 40°C to 800°C, showing three stages in the decomposition reaction with initial loss of water molecule corresponding the mass loss of 2.75% found and 3.00% calculated. The first stage of decomposition starts from 160°C to 410°C, which is corresponding to the mass loss (26.26% found and 26.71% calculated) of four hydroxyl and four CH<sub>3</sub> groups attached to four aromatic benzene nucleus, may be due to increasing cross linking, strain and unstability in the molecule by increasing thermal vibration due to increasing temperature in the molecule. The second step of decomposition starts from 410°C to 600°C, when strain increases high, leading to the mass loss equal to 86.35% found and 86.91% calculated, which may be due to the degradation of four aromatic benzene rings. The third and last step decomposition may be due to the loss of side chain of oxamide moiety, when the strained molecule suffer unzipping of cross linking, leading to the mass loss equal to 90.12% found and 90.31% calculated and consequently the residue left behind is oxamide moiety (9.83% found and 9.69% calculated) [23].

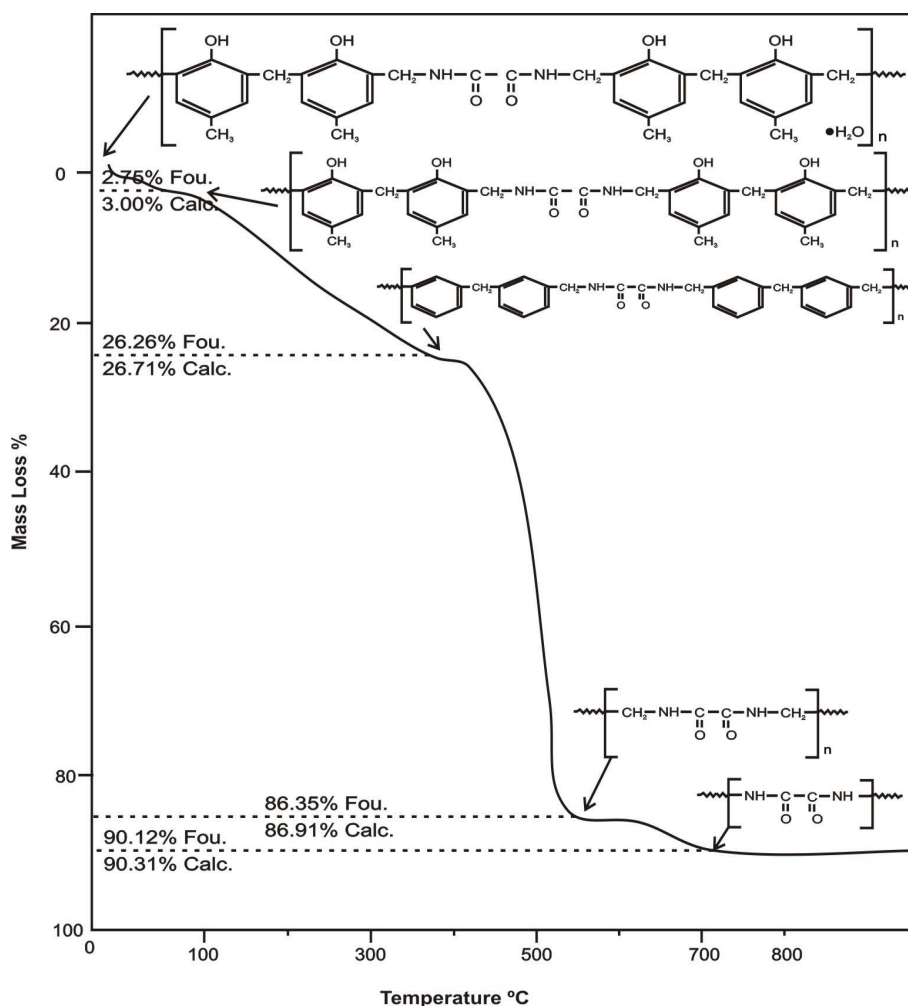


Fig. 6 Decomposition pattern of p-COF-IV terpolymer resin

In the present investigation Sharp-Wentworth and Freeman-Carroll methods have been used to determine the kinetic parameters of p-COF-IV terpolymer sample.

**Sharp-Wentworth method:** In this method following expression is used.

$$\log \left[ \frac{dc/dt}{\Delta(1-c)} \right] = \log(A/\beta) - E_a/2.303R - 1/T$$

where  $\beta$  is the linear heating rate. The graph of  $\log \left[ \frac{dc/dt}{\Delta(1-c)} \right]$  versus  $1/T$  has been plotted. The graph is a straight line with  $E_a$  as slope and  $A$  as intercept. The linear relationship confirms that the assumed order ( $n$ ) = 1 is correct.

**Freeman-Carroll method:** In this method following expression is used.

$$\frac{\Delta \log(dw/dt)}{\Delta \log W_r} = (-E_a/2.303R) - \frac{\Delta(1/T)}{\Delta \log W_r} + n$$

where  $dw/dt$  = rate of change of weight of terpolymer sample with respect to time  $W_r = W_c - W$ , where  $W_c$  is the weight loss at the completion of the terpolymer reaction or at definite time and  $W$  is the total weight loss upto time  $t$ .  $T$  is the temperature,  $R$  is the gas constant and  $n$  is the order of reaction. Hence the graph of

$$\frac{\Delta \log(dw/dt)}{\Delta \log W_r} \text{ versus } \frac{\Delta(1/T)}{\Delta \log W_r}$$

Should give on Y axis ( $x=0$ ) an intercept for the value of  $n$ , the order of reaction and the slope  $m = -E_a/2.303R$ .

Using thermal decomposition data and then applying the Sharp-Wentworth method (Fig. 7) activation energy is calculated which is in agreement with the activation energy calculated by Freeman-Carroll method [23] (Fig. 8). Thermodynamic parameters such as entropy change ( $\Delta S$ ), free energy change ( $\Delta F$ ), frequency factor ( $Z$ ) and Apparent entropy ( $S^*$ ) calculated on the basis of thermal activation energy are given in Table 5. The thermogravimetric data and various decomposition temperatures of p-COF-II terpolymer resin are given in Table 9.

**Table 5 Results of thermogravimetric analysis of p-COF-IV terpolymer rein**

Terpolymer resins	Half decomposition Temp. (°C)	Activation energy $E_a$ (KJ)		Entropy change $\Delta S$ (J)	Free energy $\Delta F$ (KJ)	Frequency factor (Z) (Sec. <sup>-1</sup> )	Apparent entropy ( $S^*$ ) (KJ)	Order reaction (n)
		FC	SW					
p-COF-IV	810	30.252	29.256	-165.662	104.721	812	-19.02	0.96

*SW – Sharp-Wentworth Method, FC – Freeman–Carroll Method*

The degradation with increasing temperature may be due to increasing strain in the molecule due to the thermal vibrations, which in increased the cross linking among the chain and increase unstability. To maintain stability and to decrease strain, the molecule undergoes degradation slowly.

By using the data of the Freeman-Carroll method, various thermodynamics parameters have been calculated (Table 5). From the abnormally low values of frequency factor, it may be concluded

that the decomposition reaction of p-COF-IV terpolymers can be classed as a 'slow' reaction. There is no other obvious reason [24].

Fairly good straight line plots are obtained using the two methods. This is expected since the decomposition of terpolymer is known not to obey first order kinetics perfectly [25, 26].

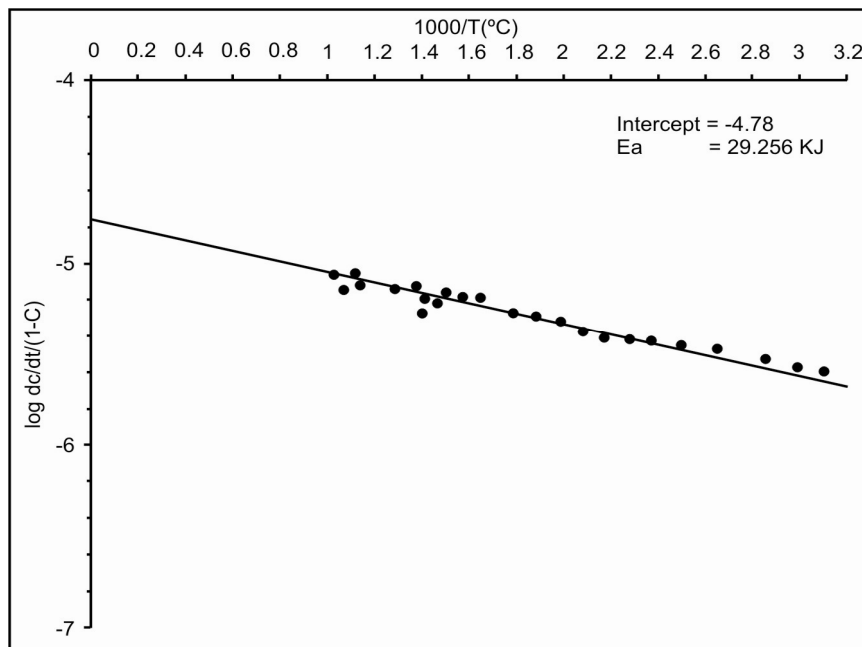


Fig. 7 Sharp – Wentworth plot of p-COF-IV terpolymer resin

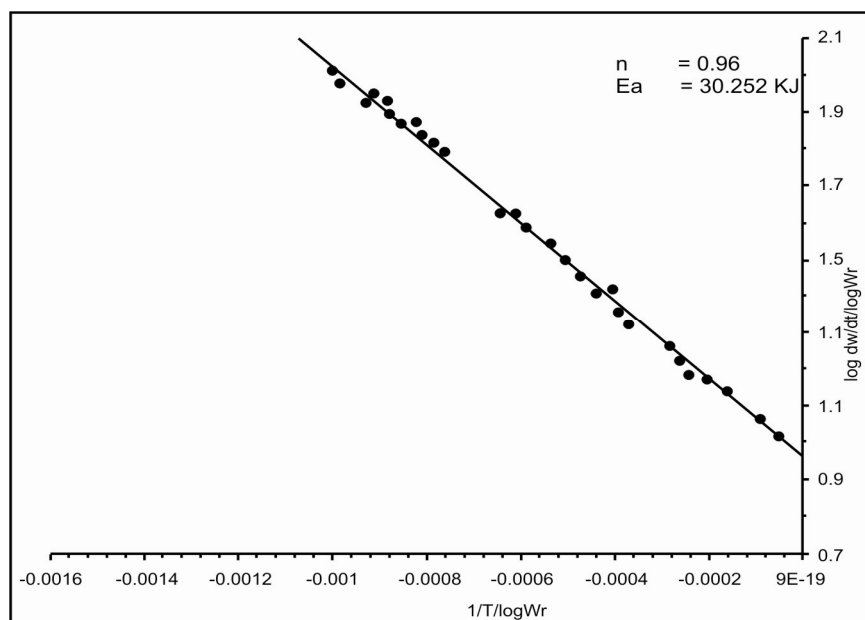


Fig. 8 Freeman – Carroll and Thermal energy plot of p-COF-IV terpolymer resin

## CONCLUSION

1. Electrical conductivity of this terpolymer resin increases with increase in temperature. Hence, this terpolymer may be ranked as semiconductor.
2. The uptake of some metal ions by the resin was carried out by the batch equilibrium technique. The uptake capacities of metal ions by the terpolymer resin were pH dependent. From the results of distribution coefficients, it can be observed that Cu (II) has higher value of distribution ratio. Due to considerable difference in the uptake capacities at different pH and media of electrolyte, the rate of metal ion uptake and distribution ratios at equilibrium, it is possible to use for separation of particular metal ions from their admixture.
3. Low values of frequency factor may be concluded that the decomposition reaction of p-COF-IV terpolymer resin can be classified as 'slow reaction'.

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