Terpolymer Resin II: Synthesis, Characterization, and Ion-Exchange Properties of 2,4-Dihydroxyacetophenone–Dithiooxamide–Formaldehyde Terpolymers

S. S. Rahangdale,[1] A. B. Zade,[1] W. B. Gurnule[2]

[1]Department of Chemistry, Laxminarayan Institute of Technology, RTM, Nagpur University, Nagpur 440 010, India
[2]Department of Chemistry, Kamla Nehru College, Nagpur 440 009, India

ABSTRACT: Terpolymers have been prepared by the condensation of 2,4-dihydroxyacetophenone (2,4-HA) and dithiooxamide (D) with formaldehyde (F) in the presence of hydrochloric acid as catalyst with varying the molar proportions of the reactant. Compositions of the terpolymer have been determined by elemental analysis. The number average molecular weight $\overline{M}_n$ has been determined by conductometric titration in nonaqueous medium. Intrinsic viscosities of the solution of the terpolymer have been determined in *N,N*-dimethyl formamide (DMF). The terpolymers have been characterized by UV–visible, IR, and proton NMR spectra. Chelation ion-exchange properties have also been studied employing the batch equilibrium method. It was employed to study selectivity of metal ion uptake over a wide pH range and in media of various ionic strength. The overall rate of metal uptake follows the order: $Fe^{3+} > Cu^{2+} > Ni^{2+} > Co^{2+} = Zn^{2+}$. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 747–756, 2008

Key words: synthesis; polycondensation; ion-exchanger; resins

INTRODUCTION

In recent years, there has been considerable interest shown in sulfur containing compounds.[1] Dithiooxamide have attracted the attention on account of their wide ranging ion-exchange properties.[2] The terpolymers of hydroxy benzoic acid, urea/thiourea, and formaldehyde/trioxane have been widely investigated because of their numerous applications.[3,4] Copolymers have also been synthesized by condensation of a mixture of phenol or hydroxybenzoic acid, various amine, and formaldehyde.[5–8] Their ion-exchange properties and semiconducting properties have been studied. However, a literature survey revealed that no terpolymers have been synthesized from 2,4-dihydroxyacetophenone, dithiooxamide and formaldehyde. Therefore, we have carried out synthesis and characterization of these terpolymer and results of our studies are reported in the present article.

The basic requirements that are essential for any polymeric material to be useful as ion-exchange resins are as follows:

(a) It must be sufficiently hydrophilic to permit diffusion of ions through the structure at a finite and usable rate.

(b) It must contain sufficient number of accessible ion-exchangeable groups which do not undergo degradation during use, and

(c) the swollen material must be denser than water.

The commercially available ion-exchange resins are given below.

Trade name	Functional group	Polymer matrix	Capacity (mequiv g^{-1})
Dowex-1	$-N^+(CH_3)_3 \, Cl^-$	PS	3.5
Amberlite IRA-45	$-NR_2, -NHR, -NH_2$	PS	5.6
Dowex-3	$-NR_3, -NHR, -NH_2$	PS	5.8
Allassian AWB-3	$-NR_2, -N^+R_3$	Epoxy-Amine	8.2
Amberlite IR-120	$-C_6H_4SO_3H$	PS	5.0–5.2
Duolite C-3	$-CH_2SO_3H$	Phenolic	2.8–3.0
Amberlite IRC-50	$-COOH$	Methacrylic	9.5
Duolite ES-63	$-OP(O)(OH)_2$	PS	6.6
Zeocarb-226	$-COOH$	Acrylic	10.0

EXPERIMENTAL

Materials

Solvents like *N,N*-dimethyl formamide and dimethyl sulfoxide were used after distillation. 2, 4-Dihydroxy-acetophenone, dithiooxamide, and formaldehyde (37%)

*Correspondence to:* W. B. Gurnule (wbgurnule@yahoo.co.in).

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TABLE I
Elemental Analysis

Terpolymer resin ratio (%)	C found (calculated) (%)	H found (calculated) (%)	N found (calculated)	S found (calculated) (%)	Average molecular weight of repeating unit
2,4-HADF-I	45.85 (49.32)	4.45 (4.16)	8.91 (8.10)	20.38 (19.89)	296
2,4-HADF-II	52.71 (55.16)	4.60 (4.32)	5.85 (5.00)	13.38 (12.72)	460
2,4-HADF-III	56.25 (58.37)	4.68 (4.17)	4.37 (4.23)	10.00 (10.03)	622
2,4-HADF-IV	58.06 (54.12)	4.71 (4.29)	3.47 (3.22)	7.94 (7.09)	788

were purchased from Merck. All other chemicals used were of chemically pure grade.

Preparation of 2,4-HADF terpolymer resin

The 2,4-HADF terpolymer resins were prepared by condensing 2,4-dihydroxyacetophenone (2,4-HA) and dithiooxamide (D) with formaldehyde (F) with the mole ratios of 1 : 1 : 2, 2 : 1 : 3, 3 : 1 : 4, and 4 : 1 : 5, respectively, in the presence of 2M HCl. The mixture was heated at (120 ± 2)°C in an oil bath for 5 h.[8–11] The solid product obtained was immediately removed from the flask as soon as the reaction period was over. It was washed with cold water to remove unreacted monomers. The air dried terpolymer resin was extracted with ether to remove excess of 2,4-dihydroxyacetophenone - formaldehyde copolymer which might be present along with 2,4-HADF terpolymer resin. It was then precipitated by dropwise addition of 1 : 1 (v/v) conc. HCl/water with constant stirring and filtered. The process was repeated twice. The resulting polymer sample was washed with boiling water and dried in vacuum at room temperature.The purified terpolymer resins were finally ground well to pass through a 300 mesh size sieve and kept in vacuum over silica gel. The yields of these terpolymer resins were found to be 70%.
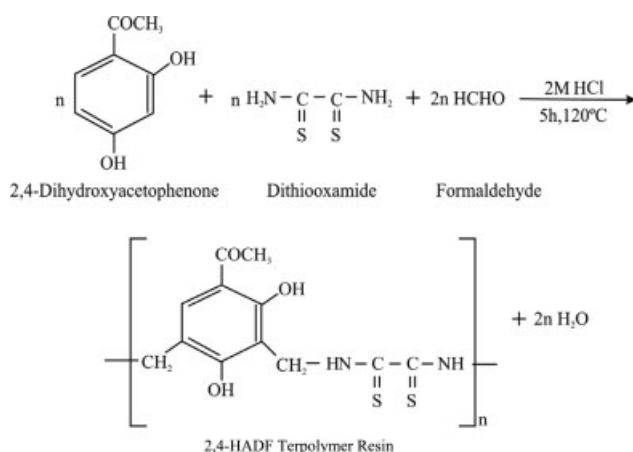
The terpolymer resins were subjected to microanalysis C, H, N, and S on Elemental Vario EL III Carlo Erba 1108 Elemental Analyzers. The number average molecular weights ($\overline{M}_n$) were determined by nonaqueous conductometric titrations in DMF using ethanolic KOH as the titrant. From the plots of specific conductance against milliequivalents of titrant base added, the first break and the last break were noted. The degrees of polymerization $\overline{DP}$ of the terpolymer resin samples were obtained from the ratio of total milliequivalents of base used for neutralization of all phenolic —OH groups to the milliequivalents of base used for neutralization of first phenolic —OH group (first break). The value of $\overline{DP}$ was multiplied by the average molecular weight of the repeating unit to get the number average molecular weight.[8–12]

The viscosities were determined using a Tuan - Fuoss[13] viscometer at six different concentrations ranging from 3.0 to 0.5 wt % of resin in DMF at 30°C. Intrinsic viscosity η was calculated by the Huggin's equation [eq. (1)] and Kraemer's equation [eq. (2)]
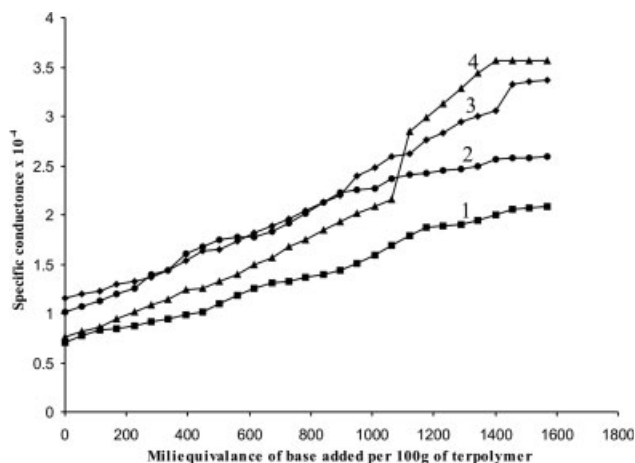
$$\eta_{sp}/C = [\eta] + K_1[\eta]^2 C \qquad (1)$$

Figure 1 Conductometric titration curve of terpolymers. (1) 2,4-HADF-I, (2) 2,4-HADF-II, (3) 2,4-HADF-III, (4) 2,4-HADF-IV.

Terpolymer resin	First stage of neutralization (meq/100 g of terpolymer resin)	Final stage of neutralization (meq/100 g of terpolymer resin)	Degree of Polymerization $\overline{DP}$	Molecular weight $\overline{M}_n$	Huggin's constant K_1	Krammer's constant K_2	$K_1 + K_2$	Intrinsic viscosity $[\eta] \times 10^2$ (dL/g)
2,4-HADF-I	224	1400	8.66	2563	3.88	−3.33	0.55	0.031
2,4-HADF-II	168	1344	8.00	3680	4.37	−3.75	0.62	0.041
2,4-HADF-III	110	1512	13.7	8549	3.15	−2.63	0.52	0.054
2,4-HADF-IV	100	1550	15.5	12214	1.90	−1.42	0.48	0.065

$$\ln \eta_r/C = [\eta] - K_2[\eta]^2 C \qquad (2)$$

Infrared spectra of 2,4-HADF terpolymer resins were recorded on Shimadzu 8201 PC (4000–400 cm^{-1}) spectrophotometers. Electronic absorption spectra of terpolymer resins in DMF were also recorded on Perkin-Elmer Lambda 15 spectrophotometer. Proton

NMR spectra of 2,4-HADF terpolymers were recorded in DMSO-d_6 solvent on Bruker DRX-300 (300 MHz FT NMR) NMR spectrophotometer.

Ion-exchange properties

The ion-exchange properties of the 2,4-HADF terpolymer resins were determined by the batch equilibrium method.[14] The ion-exchange properties of all the four resins have been studied.

Determination of metal uptake in the presence of various electrolytes and different concentrations

The terpolymer sample (25 mg) was suspended in an electrolyte solution (25 mL) of known concentration. The pH of suspension was adjusted to the required value by using either 0.1M HNO$_3$ or 0.1M NaOH. The suspension was stirred for a period of 24 h at 25°C. To this suspension, 2 mL of a 0.1M solution of the metal ion was added and the pH was adjusted to the required value. The mixture was again stirred at 25°C for 24 h and filtered.[15,16] The polymer was washed, and the filtrate and washings were combined and estimated for the metal ion content by titration against standard ethylene diaminetetraacetic acid. A blank experiment was also carried out in the same manner without adding the
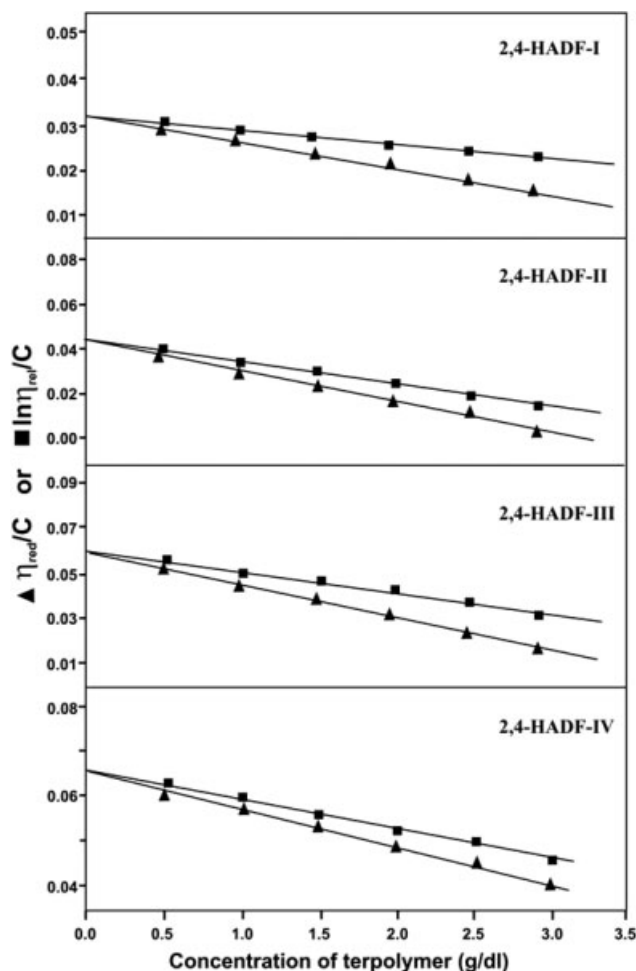

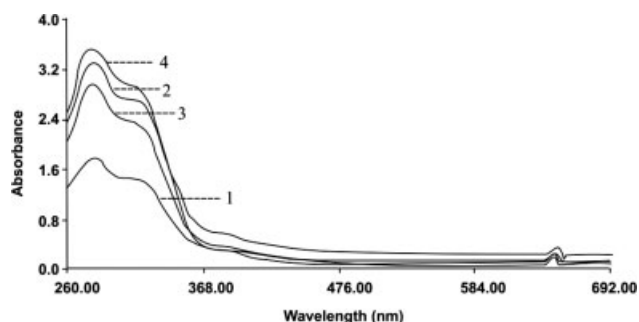**Figure 2** Viscometric plots of terpolymers.

Figure 3 Electronic spectra of terpolymers. (1) 2,4-HADF-I, (2) 2,4-HADF-II, (3) 2,4-HADF-III, (4) 2,4-HADF-IV.

polymer sample. The blank was again estimated for the metal ion content. The amount of metal ion taken up by the polymer in the presence of the given electrolyte of known concentrations results from the difference between the blank reading and the reading in the actual experiment. The experiment was repeated in the presence of several electrolytes.

The results with five different metal ions are reported in Tables V–VIII.

Evaluation of the rate of metal uptake

To estimate the time required to reach the state of equilibrium under the given experimental conditions, a series of experiments of the type described above were carried out, in which the metal ion uptaken by the chelating resins was estimated from time to time at $25°C$ (in presence of 25 mL of $1M$

$NaNO_3$ solution). It was assumed that under the given conditions, the state of equilibrium was established within 24 h. The rate of metal uptake is expressed as percentage of the amount of metal ions taken up after certain time related to that in the state of equilibrium (Tables IX–XIII).

Evaluation of the distribution of the metal ions at different pH

The distribution of each one of the five metal ions, i.e., Fe^{3+}, Cu^{2+}, Co^{2+}, Zn^{2+}, and Ni^{2+} between the polymer phase and the aqueous phase was estimated at $25°C$ and in the presence of a $1M$ $NaNO_3$ solution. The experiments were carried out as described earlier at different pH values. The distribution ratio "D" is defined by the following relationship:

$$D = \frac{\text{Weight (mg) of metal ions taken up by 1 g of terpolymer}}{\text{Weight (mg) of metal ions present in 1 mL of terpolymer}}$$

The results are presented in Tables XIV–XVIII.

RESULTS AND DISCUSSION

The resin sample was light green in color, insoluble in commonly used organic solvents, but soluble in DMSO, DMF, THF, and conc. H_2SO_4. The melting points of these resins were found to be in the range of 453–483 K. These resins were analyzed for carbon, hydrogen, nitrogen, and sulfur content (Table I).

The molecular weight ($\overline{M}_n$) of the terpolymer resins was determined by nonaqueous conductometric titration in DMF against ethanolic KOH by using 50 mg of sample. A plot (Fig. 1) of the specific conductance against the milliequivalents of potassium hydroxide required for neutralization of 100 g of ter-

polymer was made. Inspection of such a plot revealed that there were many breaks in the plot. From this plot, the first break and the last break were noted. The calculation of ($\overline{M}_n$) by this method is based on the following consideration,[7,11] (1) the first break corresponds to neutralization of the more acidic phenolic hydroxy group of all the repeating units; and (2) the break in the plot beyond which a continuous increase is observed represents the stage at which phenolic hydroxy group of all the repeating units are neutralized. On the basis of the average degree of polymerization, $\overline{DP}$ is given by the following relation.

$$\overline{DP} = \frac{\text{Total mequiv of base required complete neutralization}}{\text{Mequiv of base required for smallest interval}}$$

The number average molecular weight ($\overline{M}_n$) could be obtained by multiplying the $\overline{DP}$ by the formula weight of the repeating unit.[17] The results of the molecular weights of terpolymer samples prepared using higher proportion of two monomers (2,4-HA and D) has the highest molecular weight in the

series. The number average molecular weights are collected in Table II.

Viscosity measurements were carried out in DMF at $30°C$. The resin showed normal behavior. The intrinsic viscosity was determined by Huggin's[18] eq. (1) and Kraemer's[19] eq. (2).
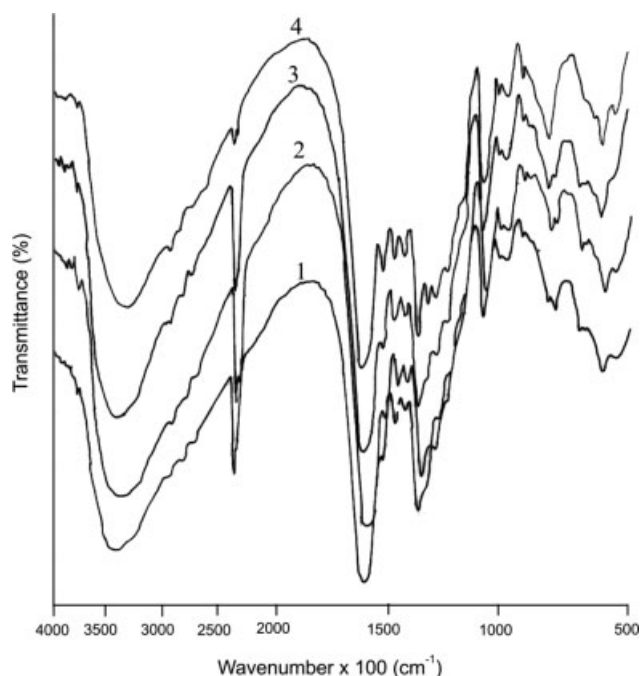
Figure 4 Infrared spectra of terpolymers. (1) 2,4-HADF-I, (2) 2,4-HADF-II, (3) 2,4-HADF-III, (4) 2,4-HADF-IV.

The viscometric plots are shown in Figure 2. In accordance with the above relations, the plots of η_{sp}/C and $1n\ \eta_r/C$ against C were linear giving as slopes K_1 and K_2, respectively. Intercepts on the axis of viscosity function gave the $[\eta]$ value in both the plots. The values of $[\eta]$ obtained from both relations were good in agreement. The values of Huggin's and Kraemer's constants K_1 (3.88) and K_2 (−3.33) were determined from the slope of graph and satisfy the condition of the relation $K_1 + K_2 = 0.55$ favorably.[19]

The UV–visible spectra of all 2,4-HADF terpolymer resins are shown in Figure 3. UV–vis spectra of all the purified resins have been recorded in pure DMF. The perusal of the UV–vis Spectra of terpolymers showed almost similar nature. The spectra of

these terpolymers exhibit two absorption maxima in the region 260–280 and 330 nm. These observed positions of the absorption bands indicate the presence of thio group processing double band which is in conjugation with the aromatic nucleus. The appearance of former band (more intense) can be accounted for $\pi \rightarrow \pi^*$ transition while the latter band (less intense) may be due to n $\rightarrow \pi^*$ electronic transition. The shift from the basic value (viz 240 and 320 nm, respectively) may be due to conjugation effect, and presence of phenolic hydroxy group (auxochrome) is responsible for hyperchromic effect, i.e., higher ε_{max}.[20–22] The ε_{max} value gradually increases in the order 2,4-HADF-I < 2,4-HADF-II < 2,4-HADF-III < 2,4-HADF-IV. This increasing order of ε_{max} values may be due to introduction of more and more chromophores (thio group) and auxochromes (phenolic —OH group) in the repeated unit of the terpolymer resins.[21,23] This observation is in good agreement with the proposed most probable structures of these terpolymer resins.

The IR spectra of all the four 2,4-HADF terpolymer resins are presented in Figure 4 and IR spectral data are tabulated in Table III. The IR spectra revealed that all these terpolymers give rise to nearly similar pattern of spectra. A broad band appeared in the region 3500–3100 cm^{-1} may be assigned to the stretching vibration of phenolic hydroxy groups exhibiting intermolecular hydrogen bonding.[24] The sharp band displayed at 1240 cm^{-1} may be due to the stretching vibrations of thio group of both thio as well as oxamide moiety.[22,24] The presence of NH in oxamide moiety may be ascribed to aromatic skeletal ring.[31] The band obtained at 802, 1220, and 1375 cm^{-1} suggested the presence of methylene bridges[25] in the polymer chain. 1, 2,3,4,5-penta substitution of aromatic ring is recognized from the bands appearing at 983, 1021, 1088, 1200, and 1295 cm^{-1}, respectively.[17,26]

^{1}H-NMR spectra of 2,4-HADF terpolymers are shown in Figure 5 and show a weak multiple signal

TABLE III
IR Spectral Data of 2,4-HADF Terpolymer Resins

| Observed band frequency (cm^{-1})					Expected band
2,4-HADF-I	2,4-HADF-II	2,4-HADF-III	2,4-HADF-IV	Assignment	frequency (cm^{-1})
3407.7 (b)	3406.1 (b)	3398.5 (b)	3314.3 (b)	—OH (phenolic)	3700–3300
3000 (w)	3000 (w)	2995 (w)	2999 (w)	>NH (Amido)	3100–2950
1225 (m)	1256 (w)	1270 (w)	1215 (w)	>C=S (thio-oxamide moity)	1250–1150
1089.9 (s)	1088.9 (s)	1088.3 (s)	1087.1 (s)	>CH$_2$ (methylene bridges)	1090
1605.0 (st)	1609.5 (st)	1609.5 (st)	1624.5 (st)	Aromatic ring	1624–1600
980 (b)	981 (b)	983 (b)	980 (b)	1, 2, 3, 4, 5-	988–970
1028 (st)	1035 (st)	1027 (st)	1021 (st)	substitution	1040–1025
1089 (s)	1088 (s)	1088 (s)	1087 (s)	in benzene	1090–1080
1193 (m)	1195 (m)	1198 (m)	1200 (m)	skeleton	1200–1180
1291 (w)	1290 (w)	1293 (w)	1295 (w)		1300–1280
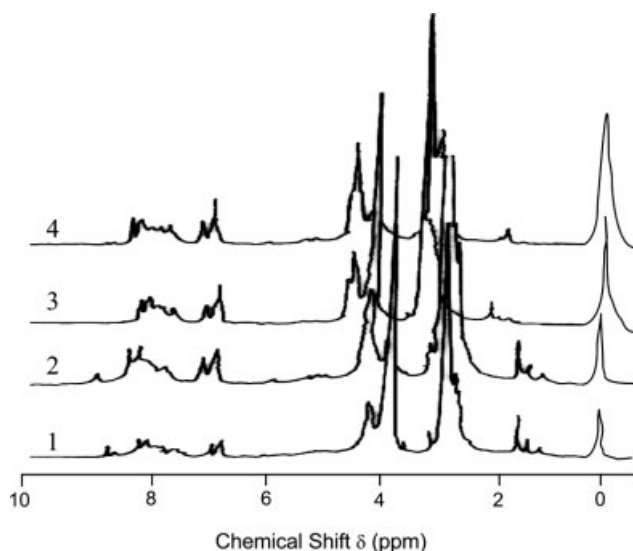
Figure 5 NMR spectra of terpolymers. (1) 2,4-HADF-I, (2) 2,4-HADF-II, (3) 2,4-HADF-III, (4) 2,4-HADF-IV.

(unsaturated pattern) in the region 6.2–8.5 (δ) ppm that is due to aromatic protons (Table IV). Triplet signal appeared in the region 3.0–4.1 (δ) ppm can be assigned to amino proton of —C—NH—CS— linkage. Intense signal appeared in the region 3.5–4.5 (δ) ppm may be due to protons of methylenic bridges (CH$_2$) of polymer chain. Weak signal in the range of 7.5–8.2 (δ) ppm is attributed to phenolic —OH proton (intramolecular H—bond). A medium singlet peak appeared at 2.5–3 (δ) ppm may be assigned to methyl protons of Ar—CO—CH$_3$ group.

Ion-exchange study

The result of the batch equilibrium study carried out with the terpolymer resin samples are presented in Tables V–XVIII. From this study with five metal ions under limited variation of experimental conditions, certain generalization may be made about the behavior of the terpolymer samples.

TABLE IV
^{1}H NMR Spectral Data of Terpolymer Resins in DMSO-d_6

Chemical shift (δ) ppm of terpolymers				
2,4-HADF-I	2,4-HADF-II	2,4-HADF-III	2,4-HADF-IV	Nature of proton assigned in spectra
3.40	3.84	3.79	3.87	Methylene proton of Ar—CH$_2$—N-linkage
3.70	3.38	3.34	3.40	Amido proton of —CH$_2$—NH—CS-linkage
7.40	7.49	7.26	7.16	Aromatic proton (unsymmetrical pattern)
2.50	2.49	2.51	2.54	Methyl proton of Ar—CO—CH$_3$ group
8.29	8.30	8.34	8.30	Proton of Ar—OH (phenolic group)

TABLE V
Effect of Electrolyte Concentration on Metal Adsorption of 2,4-HADF Terpolymer Resins

Terpolymer resin	Electrolyte concentration (mol L^{-1})	Metal ion uptake (mequiv g^{-1})				
		Cu^{2+}	Ni^{2+}	Co^{2+}	Zn^{2+}	Fe^{3+}
2,4-HADF-I	0.01	4.70	2.80	2.90	2.32	3.30
	0.05	4.20	2.50	2.63	2.10	2.31
	0.10	2.91	2.21	2.39	1.77	2.21
	0.50	2.20	1.99	1.19	1.59	1.75
	1.00	1.20	1.51	1.01	1.20	1.19
2,4-HADF-II	0.01	4.73	2.82	2.96	2.35	3.32
	0.05	4.22	2.55	2.65	2.15	2.35
	0.10	2.93	2.23	2.41	1.79	2.25
	0.50	2.22	2.01	1.22	1.62	1.78
	1.00	1.22	1.55	1.10	1.22	1.21
2,4-HADF-III	0.01	4.76	2.85	2.98	2.38	3.35
	0.05	4.25	2.57	2.68	2.16	2.38
	0.10	2.95	2.25	2.45	1.82	2.28
	0.50	2.25	2.05	1.25	1.65	1.18
	1.00	1.26	1.57	1.12	1.25	1.25
2,4-HADF-IV	0.01	4.81	2.89	2.99	2.39	3.38
	0.05	4.28	2.59	2.72	2.19	2.41
	0.10	2.96	2.29	2.47	1.86	2.30
	0.50	2.31	2.10	1.28	1.68	1.85
	1.00	1.28	1.61	1.16	1.28	1.26

Weight of polymer, 25 mg; Electrolyte, Na$_2$SO$_4$ solution (25 mL); pH of the medium, 5.5 (for Cu^{2+}, Ni^{2+}, Zn^{2+}, and Co^{2+}) and 3.0 (for Fe^{3+}).

TABLE VI
Effect of Electrolyte Concentration on Metal Adsorption Capacity
of 2,4-HADF Terpolymer Resins

Terpolymer resin	Electrolyte concentration (mol L^{-1})	Metal ion uptake (mequiv g^{-1})				
		Cu^{2+}	Ni^{2+}	Co^{2+}	Zn^{2+}	Fe^{3+}
2,4-HADF-I	0.01	2.20	2.55	2.30	2.70	2.10
	0.05	2.79	2.10	2.21	2.59	2.60
	0.10	3.49	2.00	2.10	2.19	3.00
	0.50	4.20	1.79	1.75	1.69	3.20
	1.00	4.30	1.30	1.38	1.35	3.55
2,4-HADF-II	0.01	2.25	2.57	2.31	2.72	2.12
	0.05	2.82	2.12	2.25	2.62	2.62
	0.10	3.52	2.09	2.13	2.21	3.09
	0.50	4.25	1.82	1.77	1.72	3.25
	1.00	4.38	1.31	1.39	1.38	3.56
2,4-HADF-III	0.01	2.28	2.59	2.35	2.75	2.14
	0.05	2.85	2.15	2.28	2.65	2.64
	0.10	3.53	2.12	2.15	2.25	3.12
	0.50	4.28	1.85	1.80	1.75	3.28
	1.00	4.38	1.35	1.42	1.42	3.59
2,4-HADF-IV	0.01	2.32	2.59	2.37	2.78	2.20
	0.05	2.90	2.18	2.31	2.68	2.69
	0.10	3.56	2.11	2.18	2.27	3.15
	0.50	4.31	1.87	1.82	1.78	3.31
	1.00	4.41	1.36	–	1.46	3.62

Weight of polymer, 25 mg; Electrolyte, NaNO$_3$ solution (25 mL); pH of the medium, 5.5 (for Cu^{2+}, Ni^{2+}, Zn^{2+}, and Co^{2+}) and 3.0 (for Fe^{3+}).

Effect of electrolyte and its ionic strength on metal uptake

The effect of electrolyte and its ionic strength on metal uptake by polymers was estimated at pH 5.5 for Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+} and at pH 3.0 for Fe^{3+} using four different electrolytes with five different concentrations of each (Tables V–VIII).

TABLE VII
Effect of Electrolyte Concentration on Metal Adsorption Capacity
of 2,4-HADF Terpolymer Resins

Terpolymer resin	Electrolyte concentration (mol L^{-1})	Metal ion uptake (mequiv g^{-1})				
		Cu^{2+}	Ni^{2+}	Co^{2+}	Zn^{2+}	Fe^{3+}
2,4-HADF-I	0.01	2.93	2.80	2.70	3.70	1.36
	0.05	3.70	2.30	2.31	3.42	1.80
	0.10	4.20	2.00	2.10	1.81	2.32
	0.50	4.32	1.69	1.79	1.42	3.10
	1.00	5.01	1.30	1.29	1.10	3.72
2,4-HADF-II	0.01	2.95	2.82	2.75	3.77	1.39
	0.05	3.72	2.32	2.35	3.46	1.82
	0.10	4.22	2.05	2.15	1.82	2.36
	0.50	4.38	1.72	1.81	1.46	3.13
	1.00	5.10	1.32	1.31	1.12	3.80
2,4-HADF-III	0.01	2.97	2.86	2.78	3.79	1.41
	0.05	3.78	2.37	2.38	3.47	1.85
	0.10	4.25	2.12	2.18	1.85	2.38
	0.50	4.39	1.74	1.85	1.48	3.22
	1.00	5.12	1.35	1.32	1.18	3.81
2,4-HADF-IV	0.01	2.99	2.89	2.82	3.82	1.51
	0.05	3.81	2.39	2.42	3.48	1.89
	0.10	4.28	2.15	2.21	1.88	2.42
	0.50	4.41	1.76	1.89	1.52	3.28
	1.00	5.15	1.38	1.35	1.21	3.82

Weight of polymer, 25 mg; Electrolyte, NaCl solution (25 mL); pH of the medium, 5.5 (for Cu^{2+}, Ni^{2+}, Zn^{2+}, and Co^{2+}) and 3.0 (for Fe^{3+}).

TABLE VIII
Effect of Electrolyte Concentration on Metal Adsorption Capacity of 2,4-HADF Terpolymer Resins

Terpolymer resin	Electrolyte concentration (mol L^{-1})	Metal ion uptake (mequiv g^{-1})				
		Cu^{2+}	Ni^{2+}	Co^{2+}	Zn^{2+}	Fe^{3+}
2,4-HADF-I	0.01	3.50	2.79	2.72	3.40	2.34
	0.05	4.71	2.40	2.40	3.20	3.10
	0.10	4.52	2.21	2.11	2.60	3.72
	0.50	4.98	1.79	1.79	1.80	3.99
	1.00	6.31	1.30	1.30	1.50	4.15
2,4-HADF-II	0.01	3.59	2.82	2.76	3.42	2.38
	0.05	4.73	2.42	2.42	3.25	3.14
	0.10	4.53	2.26	2.13	2.62	3.68
	0.50	4.99	1.82	1.82	1.85	4.01
	1.00	6.35	1.31	1.33	1.53	4.18
2,4-HADF-III	0.01	3.61	2.83	2.79	3.48	2.41
	0.05	4.75	2.45	2.45	3.28	3.20
	0.10	4.58	2.29	2.16	2.65	3.51
	0.50	5.12	1.85	1.83	1.88	4.12
	1.00	6.37	1.35	1.37	1.56	4.26
2,4-HADF-IV	0.01	3.65	2.87	2.81	3.52	2.51
	0.05	4.80	2.48	2.47	3.32	3.42
	0.10	4.61	2.31	2.18	2.68	3.58
	0.50	5.14	1.89	1.85	1.89	4.21
	1.00	6.38	1.39	1.42	1.59	4.38

Weight of polymer, 25 mg; Electrolyte, NaClO$_4$ solution (25 mL); pH of the medium, 5.5 (for Cu^{2+}, Ni^{2+}, Zn^{2+}, and Co^{2+}) and 3.0 (for Fe^{3+}).

We examined the influence of ClO$_4^-$, NO$_3^-$, Cl$^-$, and SO$_4^{2-}$ at various concentrations on the equilibrium of metal–resin interaction. Table V–VIII 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. In the presence of perchlorate, chloride, and nitrate ions, the uptake of Fe^{3+}, Cu^{2+}, Ni^{2+} ions increases with increasing concentration of the electrolyte, whereas in the presence of sulfate ions the amount of the aforementioned ions taken up by the terpolymer decreases with increasing concentration of the electrolyte. Moreover, the uptake of Co^{2+} and Zn^{2+} ions increases with decreasing concentration of the chloride, nitrate, perchlorate, and sulfate ions.[14,15,27,28] This may be explained on the stability constant of the complexes with those metal ions.[29]

Rate of metal ion uptake

The rate of metal adsorption was determined to find out the shortest period of time for which equilibrium could be carried out while operating as close to equilibrium conditions as possible. Tables IX–XIII 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 results show that the time taken for the uptake of the different metal ions at a given stage depends

TABLE IX
Rate of Cu^{2+} Metal Ion Uptake by 2,4-HADF Terpolymer Resins as a Function of Time

Terpolymer resin	% Attainment of equilibrium						
	Time (h)						
	1.0	2.0	3.0	4.0	5.0	6.0	7.0
2,4-HADF-I	41	53	65	82	95	–	–
2,4-HADF-II	42	55	66	83	96	–	–
2,4-HADF-III	44	56	68	88	97	–	–
2,4-HADF-IV	46	58	69	89	99	–	–

Weight of sample, 25 mg; Metal ion, 0.1M Cu(NO$_3$)$_2$ (2 mL); Electrolyte, 1.0M NaNO$_3$ (25 mL); pH of the medium, 5.5.

TABLE X
Rate of Ni^{2+} Metal Ion Uptake by 2,4-HADF Terpolymer Resins as a Function of Time

Terpolymer resin	% Attainment of equilibrium						
	Time (h)						
	1.0	2.0	3.0	4.0	5.0	6.0	7.0
2,4-HADF-I	52	62	91	96	–	–	–
2,4-HADF-II	54	63	92	96	–	–	–
2,4-HADF-III	56	65	94	98	–	–	–
2,4-HADF-IV	57	68	96	98-	–	–	–

Weight of sample, 25 mg; Metal ion, 0.1M Ni(NO$_3$)$_2$ (2 mL); Electrolyte, 1.0M NaNO$_3$ (25 mL); pH of the medium, 5.5.

TABLE XI
Rate of Co^{2+} Metal Ion Uptake by 2,4-HADF Terpolymer Resins as a Function of Time

Terpolymer resin	% Attainment of equilibrium						
	Time (h)						
	1.0	2.0	3.0	4.0	5.0	6.0	7.0
2,4-HADF-I	39	49	67	85	95	–	–
2,4-HADF-II	41	51	68	86	96	–	–
2,4-HADF-III	43	52	69	88	96	–	–
2,4-HADF-IV	45	53	71	89	98	–	–

Weight of sample, 25 mg; Metal ion, 0.1M Co(NO$_3$)$_2$ (2 mL); Electrolyte, 1.0M NaNO$_3$ (25 mL); pH of the medium, 5.5.

TABLE XII
Rate of Zn^{2+} Metal Ion Uptake by 2,4-HADF Terpolymer Resins as a Function of Time

Terpolymer resin	% Attainment of equilibrium						
	Time (h)						
	1.0	2.0	3.0	4.0	5.0	6.0	7.0
2,4-HADF-I	33	50	67	82	95	–	–
2,4-HADF-II	34	53	68	84	95	–	–
2,4-HADF-III	37	55	68	84	96	–	–
2,4-HADF-IV	38	58	69	89	97	–	–

Weight of sample, 25 mg; Metal ion, 0.1M Zn(NO$_3$)$_2$ (2 mL); Electrolyte, 1.0M NaNO$_3$ (25 mL); pH of the medium, 5.5.

TABLE XIII
Rate of Fe^{3+} Metal Ion Uptake by 2,4-HADF Terpolymer Resins as a Function of Time

Terpolymer resin	% Attainment of equilibrium						
	Time (h)						
	1.0	2.0	3.0	4.0	5.0	6.0	7.0
2,4-HADF-I	71	85	98	–	–	–	–
2,4-HADF-II	75	86	99	–	–	–	–
2,4-HADF-III	78	88	99	–	–	–	–
2,4-HADF-IV	79	91	99	–	–	–	–

Weight of sample, 25 mg; Metal ion, 0.1M Fe(NO$_3$)$_2$ (2 mL); Electrolyte, 1.0M NaNO$_3$ (25 mL); pH of the medium, 3.0.

TABLE XIV
Distribution Ratio of Cu^{2+} Ion Adsorbed by the Terpolymer Resins and Remained in the Solution at Equilibrium

Terpolymer resin	Distribution ratio (D)					
	pH of the medium					
	2.5	3.0	4.0	5.0	6.0	6.5
2,4-HADF-I	65.3	121.1	571.1	1420.2	1702.2	1901.9
2,4-HADF-II	71.4	129.3	582.6	1480.3	1742.3	1921.3
2,4-HADF-III	74.3	135.6	587.3	1491.4	1753.5	1945.4
2,4-HADF-IV	82.4	141.3	592.4	1499.3	1800.5	1972.3

Weight of polymer, 25 mg; Electrolyte, 1.0M NaNO$_3$ (25 mL).

TABLE XV
Distribution Ratio of Ni^{2+} Ion Adsorbed by the Terpolymer Resins and Remained in the Solution at Equilibrium

Terpolymer resin	Distribution ratio (D)					
	pH of the medium					
	2.5	3.0	4.0	5.0	6.0	6.5
2,4-HADF-I	50.1	101.5	560.2	650.2	1320.6	1420.21
2,4-HADF-II	55.3	115.3	568.3	661.3	1340.3	1442.32
2,4-HADF-III	58.6	118.3	569.8	669.4	1350.4	1458.42
2,4-HADF-IV	62.3	121.4	572.9	675.3	11350.4	1472.13

Weight of polymer, 25 mg; Electrolyte, 1.0M NaNO$_3$ (25 mL).

TABLE XVI
Distribution Ratio of Co^{2+} Ion Adsorbed by the Terpolymer Resins and Remained in the Solution at Equilibrium

Terpolymer resin	Distribution ratio (D)					
	pH of the medium					
	2.5	3.0	4.0	5.0	6.0	6.5
2,4-HADF-I	40.21	65.3	340.3	388.5	470.2	498.1
2,4-HADF-II	45.13	68.2	345.2	389.5	482.3	502.3
2,4-HADF-III	48.12	72.3	348.7	392.5	491.4	520.4
2,4-HADF-IV	52.13	79.4	352.8	412.3	512.3	532.1

Weight of polymer, 25 mg; Electrolyte, 1.0M NaNO$_3$ (25 mL).

TABLE XVII
Distribution Ratio of Zn^{2+} Ion Adsorbed by the Terpolymer Resins and Remained in the Solution at Equilibrium

Terpolymer resin	Distribution ratio (D)					
	pH of the medium					
	2.5	3.0	4.0	5.0	6.0	6.5
2,4-HADF-I	39.3	58.2	120.2	330.1	471.3	478.1
2,4-HADF-II	42.2	62.2	132.4	342.3	482.4	488.3
2,4-HADF-III	48.9	68.3	161.5	362.1	491.3	509.4
2,4-HADF-IV	52.3	69.8	172.3	371.3	502.3	598.3

Weight of polymer, 25 mg; Electrolyte, 1.0M NaNO$_3$ (25 mL).

TABLE XVIII
Distribution Ratio of Fe^{3+} Ion Adsorbed by the Terpolymer Resins and Remained in the Solution at Equilibrium

Terpolymer resin	Distribution ratio (D)					
	pH of the medium					
	1.5	1.75	2.0	2.5	3.0	3.5
2,4-HADF-I	30.1	201.2	399.2	520.1	–	–
2,4-HADF-II	34.2	212.5	401.5	525.2	–	–
2,4-HADF-III	36.5	225.8	415.6	530.4	–	–
2,4-HADF-IV	39.4	245.3	521.7	535.7	–	–

Weight of polymer, 25 mg; Electrolyte, 1.0M NaNO$_3$ (25 mL).

on the nature of the metal ion under given conditions. It is found that Fe^{3+} ions require about 3 h for the establishment of the equilibrium, whereas Cu^{2+}, Ni^{2+}, Co^{2+}, and Zn^{2+} ions required about 5 h. Thus, the rate of metal ion uptake fellows the order Fe^{3+} > Cu^{2+} > Ni^{2+} > Co^{2+} = Zn^{2+} for all of the terpolymers.[14,15,27,28]

Distributionn ratios of metal ion at different pH

The effect of pH on the amount of metal ions distributed between two phases can be explained by the results given in Table XIV–XVIII. The data on the distribution ratio as a function of pH indicate that the relative amount of metal ions taken up by the 2,4-HADF terpolymer increases with increasing pH of the medium.[14,15,27–29] The magnitude of increase, however, is different for different metal cations. The 2,4-HADF terpolymer resin take up Fe^{3+} ion more selectively than any other metal ions under study. The order of distribution ratio of metal ions measured in the pH range 2.5–6.5 is found to be Fe^{3+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+}. 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.[18,30] For example, the result suggest the optimum pH 6.0 for the separation of Co^{2+} and Ni^{2+} with distribution ratio "D" as 470.2 and 1320.6 for Co^{2+} and Ni^{2+}, respectively, using the 2,4-HADF-I terpolymer resin as ion-exchanger. Similarly, for the separation of Cu^{2+} and Fe^{3+} the optimum pH is 2.5, at which the distribution ratio "D" for Cu^{2+} is 65.3 and that for Fe^{3+} is 520.1. The lowering in the distribution ratio of Fe^{3+} was found to be small and, hence, efficient separation could be achieved.

CONCLUSIONS

A terpolymer, 2,4-HADF, based on the condensation reaction of 2,4-dihydroxyacetophenone and dithiooxamide with formaldehyde in the presence of acid catalyst was prepared. Since the pendent phenone group play a key role in the ion-exchange phenomena, the amount of metal adsorbed by each sample depend upon its 2,4-HA content. As the pH of the medium increase, the amounts of metal adsorbed by the polymers also increase and the trend of Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+}. The Fe^{3+} adsorption was studied in the pH range of 1.5 to 2.5 and it also increases with increasing pH. The adsorption of Cu^{2+} and Fe^{3+} increase with increasing NO_3^- and Cl^- ion concentration in the aqueous phase whereas that of Zn^{2+}, Co^{2+}, and Ni^{2+} decrease with increasing NO_3^- and Cl^- ion. From the results of distribution ratio, it can be observed that all the polymers shows highest affinity for Fe^{3+} whereas least affinity

for the Zn^{2+}. Because of the considerable difference between the adsorption capacity at different pH, rate of metal uptake, and distribution ratio at equilibrium, it may be possible to use the polymers for separation of particular metal ions from their admixture. Thus, 2,4-HADF is a selective chelating ion-exchange polymer for certain metals. The polymers showed a higher selectivity for Fe^{3+} and Cu^{2+} ions than for Co^{2+}, Ni^{2+}, and Zn^{2+} ions.

References

1. Saxena, R. S.; Gupta, K. C.; Mittal, M. L. Aust J Chem 1968, 21, 641.
2. Pal, T. K.; Kharat, R. B. Indian J Chem 1984, LXI, 490.
3. Patel, M. M.; Manavalan, R. J. Ind Chem Soc 1984, IXI, 490.
4. Patel, G. C.; Patel, M. M. J Ind Chem Soc 1991, 68, 149.
5. Gurnule, W. B.; Rahangdale, P. K.; Paliwal, L. J.; Kharat, R. B. Synth React Inorg Met-Org Chem 2003, 33, 1187.
6. Mukhmudov, T. M.; Abudullaev, S. Dokl Akad Nauk USSR 1970, 27, 34;
7. Mukhmudov, T. M.; Abudullaev, S.; Akhmedov, K. S.; Dokl Akad Nauk USSR 1971, 74, 4151a.
8. Joshi, R. M.; Patel, M. M. J Macromol Sci Chem 1983, 19, 705.
9. Gurnule, W. B.; Rahangdale, P. K.; Paliwal, L. J.; Kharat, R. B. J Appl Polym Sci 2003, 89, 886.
10. Gurnule, W. B.; Juneja, H. D.; Paliwal, L. J.; Kharat, R. B. React Funct Polym 2002, 50, 95.
11. Gurnule, W. B.; Rahangdale, P. K.; Paliwal, L. J.; Kharat, R. B. React Funct Polym 2003, 55, 255.
12. Chatterjee, S. K. J Polym Sci Part A-1: Polym Chem 1970, 8, 1299.
13. Taun, D. E. T.; Fuoss, R. M. J Phys Chem 1963, 67, 1343.
14. Patel, K. D.; Patel, M. M. Synth React Inorg Met-Org Chem 1993, 23, 299.
15. Patel, M. M.; Manavalan, R. Macromol Chem 1983, 184, 717.
16. Rath, D. K.; Nayak, P. L.; Lenka, S. J Appl Polym Sci 1994, 51, 1679.
17. Pal, T. K.; Kharat, R. B. Angew Makromol Chem 1989, 173, 55.
18. Huggins, M. L. J Am Chem Soc 1942, 74, 2715.
19. Kraemer, E. O. Ind Eng Chem 1938, 30, 1200.
20. Maron, S. H.; Reznik, R. B. J Polym Sci 1969, 2, 309.
21. Dudley, H.; Fleming, I. Spectroscopic Method in Organic Chemistry; Mc Graw-Hill: UK, 1975.
22. Silverstein, R. M.; Bassler, G. C.; Spectrometric Identification of Organic Compounds, 2nd ed.; Wiley: New York, 1967.
23. Dunn, G. E.; Mc Donald, R. C. Can J Chem 1969, 47, 4577.
24. Ballemy, I. J. The IR Spectra of Complex Molecules; Methuen and Wiley: New York, 1956 and 1958.
25. Nakanishi, K.; Infrared Absorption Spectroscopy—Practical; Nolden Day and Nankodo: Tokyo, 1967.
26. Pal, T. K.; Kharat, R. B. Indian J Chem Sect A 1989, 28, 55.
27. Patel, J. R.; Sutaria, D. H.; Patel, M. N. React Polym 1995, 25, 17.
28. Gurnule, W. B.; Juneja, H. D.; Paliwal, L. J Indian J Chem Sect A 2000, 39, 1110.
29. Pancholi, H. B.; Patel, M. M. High Perform Polym 1991, 3, 257.
30. Cotton, F. A.; Wilkinson, G. Advanced Inorganic Chemistry, 3rd ed.; Wiley: New York, 1972; pp 52–160.
31. Kemp, W.; Organic Spectroscopy; The Macmillan Press: Hong Kong, 1975.