



Chelation Ion Exchange Properties of 2, 4-Dihydroxyacetophenone-Biuret -Formaldehyde Terpolymer Resin

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Abstract: The terpolymer resin 2, 4-HABF has been synthesized by the condensation of 2, 4-dihydroxyacetophenone (2, 4-HA) and biuret (B) with formaldehyde (F) in 1:1:2 molar ratios in presence of 2 M hydrochloric acid as catalyst. UV-Visible, IR and proton NMR spectral studies have been carried out to elucidate the structure of the resin. A terpolymer (2, 4-HABF) proved to be a selective chelating ion exchange polymer for certain metals. Chelating ion-exchange properties of this polymer were studied for Fe^{3+} , Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} ions. A batch equilibrium method was employed in the study of the selectivity of metal ion uptake involving the measurement of the distribution of a given metal ion between the polymer sample and a solution containing the metal ion. The study was carried out over a wide pH range and in media of various ionic strengths. The polymer showed highest selectivity for Fe^{3+} , Cu^{2+} ions than for Ni^{2+} , Co^{2+} , Zn^{2+} , Cd^{2+} , and Pb^{2+} ions. Study of distribution ratio as a function of pH indicates that the amount of metal ion taken by resin increases with the increasing pH of the medium.

Keywords: Terpolymer, Resin, Ion-exchange, Distribution ratio.

Introduction

Ion-exchange may be defined as the reversible exchange of ions between the substrate and surrounding medium. Ion-exchange technique can remove traces of ionic impurities for 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 analytical chemistry, hydrometallurgy, antibiotic purification and separation of radio isotopes and find large application in water treatment and pollution control^{1, 2}.

Jadhao M and coworker³ have synthesized a terpolymer resin by condensation of 2, 2'-dihydroxybiphenyl and formaldehyde in the presence of acid catalyst. They studied chelating ion-exchange properties of this polymer for Fe³⁺, Cu²⁺, Ni²⁺, Zn²⁺, Cd²⁺ and Pb²⁺ ions. A batch equilibrium method was employed in the study of the selectivity of metal ion uptake involving the measurement of the distribution of a given metal ion between polymer sample and solution containing metal ions. The study was carried out over a pH range and reported that the polymer show higher selectivity for Fe³⁺, Cu²⁺, Ni²⁺ ions than for Zn²⁺, Cd²⁺, Pb²⁺ ions.

Sykora and Dubsy⁴ have prepared a selective cation exchange polymer by reacting 2, 4-dihydroxyacetophenone and anthranilic acid with formaldehyde in alkaline media. They used the polymer for the separation of Cu²⁺ in weak alkaline media at pH 4. Copolymers have also been synthesized by condensation of a mixture of phenol or hydroxybenzoic acid, various amine and formaldehyde⁵⁻⁸. 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, biuret 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 follow:

- It must be sufficiently hydrophilic to permit diffusion of ions through the structure at a finite and usable rate.
- It must contain sufficient number of accessible ion exchangeable groups which do not undergo degradation during use, and
- The swollen material must be denser than water.

The commercially available ion exchange resins are given below.

Trade name	Functional group	Polymer matrix	Capacity, meq.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 ₆ H ₄ SO ₃ H	PS	5.0-5.2
Duolite C-3	-CH ₂ SO ₃ H	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

The chemicals 2, 4-dihydroxyacetophenone, biuret and formaldehyde (37%) used are of analytical grade and chemically pure which is purchased from Merck, India. Solvents like *N, N'*-dimethyl formamide and dimethylsulphoxide were used after distillation.

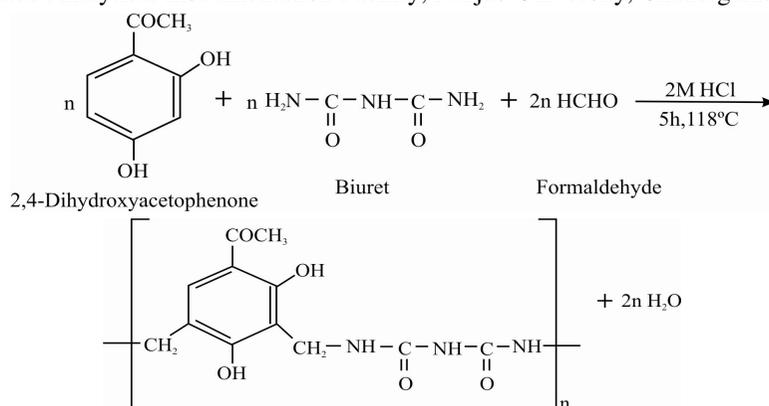
Synthesis of 2, 4-HABF terpolymer resin

The 2, 4-HABF-I terpolymer was prepared by condensing 2, 4-dihydroxyacetophenone (1.521 g, 0.01 mol) and biuret (1.3 g, 0.01 mol) with formaldehyde (7.5 mL, 0.02 mol) in the presence of 2 M HCl as a catalyst at 126±2 °C in an oil bath^{9,13} for 4 h. The cream colored solid product was washed with hot water and ether 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 2, 4- dihydroxyacetophenone-formaldehyde copolymer which might be present along with the 2, 4 - HABF-I

terpolymer. It was further purified by dissolving in 10% NaOH and then filtered. The terpolymer was then reprecipitated by drop wise addition of 1:1 (v/v) conc. HCl / water with constant stirring and filtered. The process was repeated thrice. The resulting polymer sample was washed with boiling water and dried in a vacuum at room temperature. The purified terpolymer was finely ground to pass through 300 mesh size sieve and kept in a vacuum over silica gel. The yield of the terpolymer was found to be about 80%.

Apparatus and procedure

The terpolymer resins were subject to micro analysis for carbon, hydrogen and nitrogen on Elemental Vario EL III Carlo Erba 1108 Elemental Analyzers at Sophisticated Analytical Instrumentation Facility, Punjab University, Chandigarh. The number average molecular weights (\bar{M}_n) were determined by conductometric titration in DMF using ethanolic KOH as the titrant. The molecular weight (\bar{M}_n) of the terpolymer resin was determined by non-aqueous conductometric titration in DMF against ethanolic KOH by using 25 mg of sample. Electronic absorption spectra of the terpolymers in DMSO were recorded on Perkin-Elmer Lambda 15 spectrophotometer. Infrared spectra of 2, 4-HABF terpolymers were recorded on Perkin-Elmer 983 spectrophotometer in KBr pallets in the wave number region of 4000-400 cm^{-1} at SAIF Punjab University, Chandigarh. $^1\text{H-NMR}$ spectra were recorded on Bruker Advance-II 400 MHz proton NMR spectrometer DMSO- d_6 was used as a solvent at Sophisticated Analytical Instrumentation Facility, Punjab University, Chandigarh.



Scheme 1. Reaction and suggested structure of representative 2, 4-HABF-I terpolymer resin.

Ion-exchange properties

The ion-exchange properties of the 2, 4-HABF terpolymer resins were determined by the batch equilibrium method¹⁴. The ion-exchange properties of all the four resins have been studied. However, only the data for the 2, 4-HABF-I terpolymer resins have been presented in this report.

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 0.1 M HNO_3 or 0.1 M NaOH. The suspension was stirred for a period of 24 h at 25 $^\circ\text{C}$. To this suspension 2 mL of a 0.1 M solution of the metal ion was added and the pH was adjusted to the required value. The mixture was again stirred at 25 $^\circ\text{C}$ for 24 h and filtered^{11,12}. The terpolymer was washed and the filtrate and washings were combined and estimated for the

metal ion content by titration against standard ethylene diamine tetraacetic acid. A blank experiment was also carried out in the same manner without adding the 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 seven different metal ions are reported in Table 1.

Table 1. Evaluation of the effect of different electrolytes on the uptake of several metal ions^a.

Metal ion	Electrolyte mol l ⁻¹	pH	Weight of metal ion (mg) taken up in the presence of			
			NaNO ₃	NaCl	NaClO ₄	Na ₂ SO ₄
Zn ²⁺	0.01	5.5	2.72	4.03	3.62	2.59
	0.05		2.61	3.72	3.29	2.21
	0.10		2.31	1.91	2.84	2.02
	0.50		2.02	1.62	2.10	1.81
	1.00		1.62	1.41	1.82	1.79
Cd ²⁺	0.01	5.5	2.60	2.91	2.62	2.91
	0.05		2.41	2.69	2.31	2.52
	0.10		2.39	2.42	2.10	2.11
	0.50		1.91	2.10	1.69	1.61
	1.00		1.60	1.77	1.55	1.49
Pb ²⁺	0.01	5.5	2.91	2.72	2.22	-
	0.05		2.82	2.61	2.07	-
	0.10		2.71	2.43	1.72	-
	0.50		2.30	2.10	1.61	-
	1.00		1.92	1.87	1.42	-
Fe ³⁺	0.01	2.5	2.32	1.51	2.31	3.73
	0.05		2.81	2.02	3.30	2.71
	0.10		3.12	2.82	3.51	2.62
	0.50		3.32	3.31	3.90	2.10
	1.00		3.78	4.08	4.22	1.57
Cu ²⁺	0.01	5.0	2.02	2.42	2.92	4.62
	0.05		2.71	3.31	3.42	3.91
	0.10		3.32	3.91	3.81	3.15
	0.50		3.43	4.52	4.31	2.30
	1.00		4.62	4.71	5.71	1.41
Ni ²⁺	0.01	5.5	2.31	2.40	3.21	4.15
	0.05		3.20	2.92	3.42	3.61
	0.10		3.91	3.71	3.71	2.81
	0.50		4.69	4.21	3.89	2.15
	1.00		5.82	4.82	4.75	1.51
Co ²⁺	0.01	5.5	2.74	3.11	3.10	3.05
	0.05		2.39	2.40	2.61	2.50
	0.10		2.19	2.31	2.31	2.21
	0.50		1.18	2.15	2.10	1.72
	1.00		1.01	1.75	1.60	1.51

Mt (NO₃)₂=0.1 mol l⁻¹; volume= 2 mL; volume of electrolyte solution= 25 mL, weight of resin= 25 mg; time= 24 h; room temperature.

Evaluation of the rate of metal uptake

In order 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 up taken by the chelating resins was estimated from time to time at 25 °C (in presence of 25 mL of 1 M NaNO₃ 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 (Table 2).

Table 2. Composition of the rates of metal (M) ion uptake^a.

Metal ion	pH	Percentage of metal ion uptake ^b at different times, h						
		1	2	3	4	5	6	7
Zn ²⁺	5.5	47	61	70	86	97	-	-
Cd ²⁺	5.5	22	45	62	65	82	92	-
Pb ²⁺	5.5	29	42	58	64	82	92	-
Fe ³⁺	2.5	78	93	98	-	-	-	-
Cu ²⁺	5.0	56	67	79	94	97	-	-
Ni ²⁺	5.5	49	63	78	92	97	-	-
Co ²⁺	5.5	45	62	76	92	94	-	-

^a $Mt(NO_3)_2=0.1\text{ mol l}^{-1}$; volume= 2 mL; $NaNO_3=1\text{ mol l}^{-1}$; volume= 25 mL; room temperature.

^b
$$\frac{\text{Amount of metal ion absorbed} \times 100}{\text{Amount of metal ion absorbed at equilibrium}}$$

Evaluation of the distribution of the metal ions at different pH

The distribution of each one of the seven metal ions *i.e.* Fe³⁺, Cu²⁺, Co²⁺, Zn²⁺, Cd²⁺, Pb²⁺ and Ni²⁺ between the polymer phase and the aqueous phase was estimated at 25 °C and in the presence of a 1 M NaNO₃ solution. The experiments were carried out as described above at different pH values. The results are presented in Table 3. The distribution ratio 'D' is defined by the following relationship: D = Weight (mg) of metal ions taken up by 1 g of terpolymer / weight (mg) of metal ions present in 1 mL of solution.

Table 3. Distribution ratio D^a of different metal ions as a function of the pH^b.

Metal ion	Distribution ratio of the metal ion at different pH									
	1.5	1.75	2.0	2.5	3.0	3.5	4.0	5.0	6.0	6.5
Zn ²⁺	-	-	-	41.2	62.1	81.1	125.1	334.1	475.2	482.1
Cd ²⁺	-	-	-	-	36.2	48.2	61.2	72.1	422.1	523.6
Pb ²⁺	-	-	-	38.1	57.2	73.5	119.2	325.2	428.2	458.1
Fe ³⁺	33.2	205.1	401.3	523.2	-	-	-	-	-	-
Cu ²⁺	-	-	-	68.2	124.2	293.2	573.2	1424.1	1707.2	1912.2
Ni ²⁺	-	-	-	53.2	105.2	254.2	563.2	654.2	1325.2	1424.21
Co ²⁺	-	-	-	42.3	68.2	124.3	342.5	391.2	474.1	504.2

^a
$$D = \frac{\text{Amount of metal ion absorbed} \times 100}{\text{Amount of metal in the solution}} \times \frac{\text{volume of solution (mL)}}{\text{weight of resin (g)}}$$

^b $Mt(NO_3)_2 = 0.1\text{ mol l}^{-1}$; volume= 2 mL; $NaNO_3=1\text{ mol l}^{-1}$; volume= 25 mL; room temperature; time= 24 h (equilibrium state).

Results and Discussion

The newly synthesized purified 2, 4-HABF resin was found to be cream in colour and soluble in DMF, DMSO, THF and conc. H₂SO₄. Analytical data for C₁₂H₁₃N₃O₅ as per numerical calculations and experimental evidence are mentioned below respectively. Theoretically calculated C=51.61%, H=4.65% and N=15.65%. Experimentally found C=52.12%, H=4.12% and N=15.58%. Decomposition temperature of the polymer was found to be above 360 °C.

The molecular weight (\overline{M}_n) of the terpolymer resin was determined by non-aqueous conductometric titration in DMF against ethanolic KOH by using 50 mg of sample. A plot of the specific conductance against the milliequivalents of potassium hydroxide required for neutralization of 100 g of terpolymer was made. Inspection of such a plot revealed that there were many breaks in the plot. From this plot the first break at 392 milliequivalent of base and the last break at 1456 milliequivalent of base were noted. The calculation of \overline{M}_n by this method is based on the following consideration^{5,12}, (1) the first break corresponds to neutralization of the more acidic phenolic hydroxy group of all the repeating units; and (2) the last 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, is found to be 3.71. On the basis of the average degree of polymerization, \overline{DP} is given by the following relation: $\overline{DP} = (\text{Total meq. of base required for complete neutralization}) / (\text{meq. Of base required for smallest interval})$. The number average molecular weight (\overline{M}_n) is 1035 as obtained by multiplying the \overline{DP} by the formula weight of the repeating unit^{17,18}.

The UV-Visible spectra of all the 2, 4-HABF terpolymer samples in pure DMF were recorded in the region 190-700 nm at a scanning rate of 100 nm min⁻¹ and at a chart speed of 5 cm min⁻¹. The perusal of the UV-Visible spectra of terpolymers showed almost similar nature. The spectra of these terpolymers exhibit two absorption maxima in the region 280 nm and 304 nm. These observed positions of the absorption bands indicate the presence of carbonyl group (ketonic) having a carbon-oxygen double bond 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 later band (less intense) may be due to $n \rightarrow \pi^*$ electronic transition. The shift from the basic value (*viz.* 240 nm and 320 nm respectively) may be due to conjugation effect, and presence of phenolic hydroxy group (auxochromes) is responsible for hyperchromic effect i.e. ϵ_{\max} higher values¹⁵⁻¹⁷. The ϵ_{\max} value gradually increases in the order: 2, 4-HABF-I < 2, 4-HABF-II < 2, 4-HABF-III < 2, 4-HABF-IV. This increasing order of ϵ_{\max} values may be due to introduction of more and more chromophores (carbonyl group) and auxochromes (phenolic-OH groups) in the repeat unit of the terpolymer resins^{11,18}. This observation is in good agreement with the proposed most probable structures of these terpolymer resins.

From the IR spectral studies it has been revealed that all the 2, 4-HABF terpolymer give rise to nearly similar pattern of spectra. A broad band appearing in the region 3415-3361 cm⁻¹ to the stretching vibration of phenolic -OH group^{19,30,31}. The sharp band displayed at 1627 cm⁻¹ may be on account of the stretching vibrations of carbonyl group (>C=O) of biuret moiety^{17,20}. Presence of >NH has been indicated by the medium band at 2365-2363 cm⁻¹ which is merged with broad intense peak due to hydroxyl group^{18,20}. The spectra show bands at 800.2-800, 1373-1372, 1438-1432 cm⁻¹ which may be ascribed to methylene groups¹⁹. The sharp peak at 1520-1510 cm⁻¹ may be due to breathing modes of aromatic skeletal ring. 1, 2, 3, 4, 5- penta substitution are indicated by the peaks at 994-990, 1094-1090, 1198-1189, 1283-1279 and 1373-1330 cm⁻¹.^{20,21}

The NMR spectra of all four terpolymers were scanned in DMSO- d_6 . From the spectra it is revealed that all 2, 4-HABF terpolymers gave rise to different patterns of ^1H NMR spectra, since each of the 2, 4-HABF terpolymer possesses sets of protons having different electronic environment.

Except for 2, 4-HABF-I, the remaining three terpolymers *viz.* 2, 4-HABF-II, 2, 4-HABF-III and 2, 4-HABF-IV exhibit singlet signal in the region δ 2.3-2.7 ppm which are due to methylene protons of the Ar-CH₂-Ar bridges^{16,17,19}. The weak multiplet signal (unsymmetrical proton) in the region δ 7.4-7.7 ppm are due to aromatic protons. The methylenic proton of the Ar-CH₂-N moiety may be recognized as signal appearing in the region δ 3.3-3.4 ppm^{16,17,19}. The signal in the region δ 5.1-5.4 ppm are attributed to the protons of -NH- bridges. The methyl proton of the Ar-CO-CH₃ moiety may be identified by the intense peak at δ 4.3-4.5 ppm. The signal in the range of δ 8.9-9.0 ppm is attributed to phenolic hydroxy proton. This significant downfield chemical shift of the protons of the phenolic OH group clearly indicates intramolecular hydrogen bonding of OH with the carbonyl group present at the adjacent ortho position^{16,17,19}.

Effect of electrolytes on metal uptake

We examined the influence of ClO_4^- , NO_3^- , Cl^- and SO_4^{2-} at various concentrations on the position of the equilibrium of metal-resin interactions. Examination of the data given in Table 1 reveals that the amount of Fe^{3+} , Cu^{2+} and Ni^{2+} ions taken up by the 2, 4-HABF terpolymer sample increases with increasing concentrations of ClO_4^- , NO_3^- and Cl^- and decreases with increasing concentrations of SO_4^{2-} whereas the uptake of Co^{2+} , Zn^{2+} , Pb^{2+} and Cd^{2+} ions by above terpolymer increases with decreasing concentrations of ClO_4^- , NO_3^- , Cl^- and SO_4^{2-} . This may be explained in terms of the stability constants of the complexes which Cu^{2+} , Ni^{2+} , Co^{2+} , Cd^{2+} , Zn^{2+} , Fe^{3+} and Pb^{2+} ions form with these anions²². SO_4^{2-} might form rather strong complexes with Fe^{3+} , Cu^{2+} and Ni^{2+} ions, while ClO_4^- , NO_3^- and Cl^- might form weak complexes and, therefore, might not be expected to influence the position of the Fe^{3+} , Cu^{2+} and Ni^{2+} chelates equilibrium as much as SO_4^{2-} . ClO_4^- , NO_3^- , Cl^- and SO_4^{2-} might form rather strong chelates with Co^{2+} , Zn^{2+} , Pb^{2+} and Cd^{2+} and, therefore, might be expected to influence the position of the Co^{2+} , Zn^{2+} , Pb^{2+} and Cd^{2+} chelates equilibrium. This type of trend has also been observed by other investigators in this field^{23,24,28,29}.

Rate of metal 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. Table 2 shows the dependence of the rates of metal ion uptake on the nature of the metal. Fe^{3+} ion required almost 3 h for the establishment of equilibrium, while Cu^{2+} , Ni^{2+} , Co^{2+} and Zn^{2+} ions required about 5 h for equilibrium. Cd^{2+} and Pb^{2+} ions required almost 6 h for equilibrium. The rate of metal uptake follows the order $\text{Fe}^{3+} > \text{Cu}^{2+}$, Ni^{2+} , Co^{2+} , $\text{Zn}^{2+} > \text{Cd}^{2+}$ and Pb^{2+} .

Distribution ratios of metal ions at different pH

The effect of pH on the amount of metal ions distributed between two phase can be explained by the results shown in Table 3. The results indicate that the relative amount of metal ions taken up by the terpolymer increases with increasing pH of the medium. The study was carried out up to a definite pH value for the particular metal ion to prevent hydrolysis of the metal ions at higher pH. The Fe^{3+} ion is taken up more selectively than any other metal ions under study. Zn^{2+} and Pb^{2+} ions have a low distribution ratio in the range of

pH 4-6. This could be attributed to the low stability constant, *i.e.* weak ligand stabilization energy, of the metal complexes^{25,26}. The possible order of selectivity of a cation exchange resin for divalent metal ions is²⁷: Cu > Ni > Co > Zn > Cd > Fe. In the present study the observed order of distribution ratios of divalent ions was found to be Cu²⁺ > Ni²⁺ > Co²⁺ > Zn²⁺ > Pb²⁺ > Cd²⁺, which well with that reported. The results of this study are helpful in selecting the optimum pH for the selective uptake of a metal ion from a mixture of different ions. For example, for the separation of Cu²⁺ and Fe³⁺ ions the optimum pH is 2.5, at which the distribution ratio D for Cu²⁺ is 68.2 and that for Fe³⁺ is 523.2.

In order to assess the potential for separation of metal ions such as Fe³⁺ from other metal ions the following combinations of metal solutions were prepared: (1) Fe³⁺ and Cu²⁺, (2) Fe³⁺ and Ni²⁺, (3) Fe³⁺ and Co²⁺ and (4) Fe³⁺ and Zn²⁺. The solutions for separation were prepared by mixing 1 mL of 1.0 M solution of Fe³⁺ with 1 mL of 1.0 M solution of Cu²⁺, Ni²⁺, Co²⁺ or Zn²⁺. Selective uptake of the metal ions was studied by adjusting the optimum pH of 2.5. The lowering in the distribution ratios of Fe³⁺ is found to be small and, hence, efficient separation could be achieved. A similar trend has also been observed by earlier investigators³².

Conclusions

- A terpolymer 2, 4-HABF based on the condensation reaction of 2, 4-dihydroxyacetophenone and biuret with formaldehyde in the presence of acid catalyst has been prepared.
- 2, 4-HABF is a selective chelating ion exchange polymer for certain metals.
- The terpolymer showed a higher selectivity for Cu²⁺ and Fe³⁺ ions than for Co²⁺ and Zn²⁺ ions.

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