

Synthesis, Characterization, Morphology and Chelation Ion-Exchange Properties of a Copolymer Resin-II

W. B. Gurnule
Department of Chemistry
Kamla Nehru Mahavidyalaya
Nagpur-440024
E-mail: wbgurnule@yahoo.co.in

Vaishali R. Bisen
Department of Chemistry
Kamla Nehru Mahavidyalaya
Nagpur-440024
E-mail: vrbisen@yahoo.com

Mudrika Ahamed
Department of Chemistry
Govt. Polytechnic
Nagpur, India
E-mail: mudrika_ahmed@rediffmail.com

Abstract— Pthalic acid-melamine-formaldehyde (TMF-II) copolymer resin was synthesized by an eco-friendly technique in dimethyl formamide medium. The resin was characterized by elemental analysis, UV-Visible, FTIR, ^1H NMR, ^{13}C -NMR and viscometric measurement. The surface morphology of the copolymer resin was established by scanning Electron Microscopy. The number average molecular weight was determined by non-aqueous conductometric titration. One of the important applications of these types of polymer is their capability to act as chelating ion-exchanger. The chelation ion-exchange properties of the copolymer showed a powerful adsorption towards specific metal ions like Fe^{3+} , Cu^{2+} , Ni^{2+} , Co^{2+} , Cd^{2+} , Pb^{2+} and Zn^{2+} . A batch equilibrium method was adopted to study the selectivity of the metal ion uptake involving the measurement of the distribution of the given metal ion between the polymer sample and a solution containing the metal ion over a wide range of concentrations and pH of different electrolytes.

Keywords: Polycondensation, Polymer, Chelation, Metal ion uptake, morphology

INTRODUCTION

Although recent years there have been considerable interest shown in sulphur containing compounds [1]. Dithioamide 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, 6]. Their ion exchange properties and semiconducting properties have been studied. However a literature survey revealed that no terpolymers have been synthesized from pthalic acid, melamine and formaldehyde. Therefore, we have carried out synthesis and characterization of these terpolymer and results of our studies are reported in the present paper.

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

- 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	$-\text{N}^+(\text{CH}_3)_3 \text{Cl}^-$	PS	3.5
Amberlite IRA-45	$-\text{NR}_2, -\text{NHR}, -\text{NH}_2$	PS	5.6
Dowex-3	$-\text{NR}_3, -\text{NHR}, -\text{NH}_2$	PS	5.8
Allasian AWB-3	$-\text{NR}_2, -\text{N}^+\text{R}_3$	Epoxy-Amine	8.2
Amberlite IR-120	$-\text{C}_6\text{H}_4\text{SO}_3\text{H}$	PS	5.0-5.2
Duolite C-3	$-\text{CH}_2\text{SO}_3\text{H}$	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

EXPERIMENTA

Materials

Solvents like N, N-dimethyl formamide and dimethyl sulphoxide were used after distillation. Pthallic acid, melamine and formaldehyde (37 %) were purchased from market and are from Merck. All other chemicals used were of chemically pure grade.

Preparation of TMF-II terpolymer resin

The TMF-II terpolymer resin was prepared by condensing phthalic acid (T) and melamine (M) with formaldehyde (F) with the mole ratio of 2:1:4 in the presence of 2M HCl as catalyst. The mixture was heated at 126 ± 2 °C in an oil bath for 5 h [7]. 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 phthalic acid - formaldehyde copolymer which might be present along with TMF-II 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 resin was finally ground well to pass through a 300 mesh size sieve and kept in vacuum over silica gel. The yield of this terpolymer resin was found to be 76 %.

DETERMINATION OF METAL UPTAKE IN THE PRESENCE OF ELECTROLYTES OF DIFFERENT CONCENTRATIONS

The terpolymer sample (25 mg) was suspended in an electrolyte solution (25 ml) of known concentration. The pH of the suspension was adjusted to the required value by using either 0.1N HNO₃ or 0.1N NaOH. The suspension was stirred for a period of 24 h 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. The terpolymer was washed, and the filtrate and washing were combined and estimated for the metal ion content by titration against standard ethylenediamine-tetraacetic acid. A blank experiment was also carried out in the same manner without adding the terpolymer 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 concentration 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.

Evaluation of the rate of metal uptake

In order to estimate the time required to reach the state of equilibrium under the given pH, experiments of the type described above were carried out, in which the metal ion taken up by the chelating terpolymer was estimated from time to time at 25 °C in the presence of 25 ml of 1M NaNO₃ solution. It is assumed that under the given conditions, the state of equilibrium is established within 24 h. The rate of metal uptake is expressed as the percentage of the amount of metal ion taken up after a certain time related to that in the state of equilibrium.

The distribution of each one of the seven metal ions i.e. Cu²⁺, Ni²⁺, Co²⁺, Cd²⁺, Zn²⁺, Fe³⁺ and Pb²⁺, between the terpolymer phase and the aqueous was estimated at 25 °C and in the presence of a 1M NaNO₃ solution. The experiments were carried out as described above at different pH values. The distribution ratio D is defined by the following relationship.

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

RESULTS AND DISCUSSION

The TMF-II terpolymer resins are pinkish white in colour. The purified resins are soluble in DMF, DMSO, aqueous sodium and potassium hydroxide. The melting points of these resins were found to be in the range 300 to 425 °C.

These resins were analyzed for carbon, hydrogen and nitrogen content.

UV-Visible spectra of the purified resin has 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 210-240 and 310 nm. These observed positions of the absorption bands indicate the presence of carbonyl group (ketonic) processing 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 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} values [8].

The IR spectra shows a broad band containing several inflections appearing in the region $2600-3500\text{ cm}^{-1}$ may be assigned to the stretching vibration of -OH of the polymeric associated phenolic group and the intermolecular bonding between the hydroxyl groups in a polymeric chain [9]. The bands at $800, 1200$ and 1300 cm^{-1} suggest the presence of methylene bridges. A sharp peak at about 1595 cm^{-1} may be ascribed to aromatic skeletal ring breathing modes. 1, 2, 3, 5 -tetra substitution of the aromatic acid ring is recognized from bands appearing at $920, 1060, 1125$ and 1230 cm^{-1} , respectively [9]. The presence of -NH in melaminet is difficult to assign as the region for the stretching vibration of -NH is rendered complex due to chelated -OH. However, the medium broad band at nearly 3000 cm^{-1} may be due to -NH of melamine unit.

- ^1H NMR spectra of TMF-II terpolymer show a weak multiply signal (unsymmetrical pattern) in the region $7.10 - 7.13$ (δ) ppm which is due to aromatic protons. Triplet signal appeared in the region $3.32-3.42$ (δ) ppm can be assigned to amino proton of -C - NH - CO - linkage. The singlet signal appearing at $8.62 - 8.86$ (δ) ppm may be due to amido proton of -CO - NH - CO -

linkage [10]. Weak signal in the range of $4.15 - 4.25$ (δ) ppm is attributed to phenolic -OH proton of carboxylic acid. Triplet signal appeared in the region $6.99-7.09$ (δ) ppm can be assigned to amino proton of -C - NH - CO - linkage.

With a view to ascertain the selectivity of the TMF-II terpolymer for the selected metal ions, we have studied the influence of various electrolytes on the selectivity of metal ions, the rate of metal uptake, and the distribution ratio of metal ions between the terpolymer and the solution containing the metal ions.

3.1. 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 TMF-II 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 anions [18]. 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 [11].

3.2. 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 6 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+} (Table 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 [12]. The possible order of selectivity of a cation exchange resin for divalent metal ions is [13]: $\text{Pd} > \text{Cu} > \text{Ni} > \text{Co} > \text{Zn} > \text{Cd} > \text{Fe} > \text{Mn} > \text{Mg}$. In the present study the observed order of distribution ratios of divalent ions was found to be $\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+} > \text{Pb}^{2+} > \text{Cd}^{2+}$, 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 Cu^{2+} and Fe^{3+} ions the optimum pH is 2.5, at which the distribution ratio D for Cu^{2+} is 66.1 and that for Fe^{3+} is 522.1.

In order to assess the potential for separation of metal ions such as Fe^{3+} from other metal ions the following combinations of metal solutions were prepared: (1) Fe^{3+} and Cu^{2+} , (2) Fe^{3+} and Ni^{2+} , (3) Fe^{3+} and Co^{2+} and (4) Fe^{3+} and Zn^{2+} . The solutions for separation were prepared by mixing 1 ml of 1.0 M solution of Fe^{3+} with 1 ml of 1.0 M solution of Cu^{2+} , Ni^{2+} , Co^{2+} or Zn^{2+} . Selective uptake of the metal ions was studied by adjusting the optimum pH of 2.5. The lowering in the distribution ratios of Fe^{3+} is found to be small and, hence, efficient separation could be achieved.

CONCLUSIONS

A terpolymer TMF-II based on the condensation reaction of phthalic acid and melamine with formaldehyde in the presence of acid catalyst has been prepared. TMF-II is a selective chelating ion exchange terpolymer for certain metal. The terpolymer showed a higher selectivity for Cu^{2+} and Fe^{3+} ions than for Ni^{2+} , Co^{2+} , Zn^{2+} and Pb^{2+} ions.

ACKNOWLEDGEMENT

The authors are pleased to express their gratitude to the Technology Principal Priyadarshani college Engineering Nagpur, for providing laboratory facility. Authors are also thankful to the Director, STIC analysis for spectral analysis.

REFERENCES

- [1]. M.R Lutfor and S Silong, Md Wan Zin W. M., Ab M. Z Rahman., M. Ahmad J. and Haron. "Preparation and characterization of poly(amidoxime) chelating resin from polyacrylonitrile grafted sago starch", *European Polymer Journal*, **36**, 2105-2110, 2000.
- [2]. S. A., Patel, B. S Shah and R.M Patel, P.M. Patel "Synthesis, characterization and ion exchange properties of acrylic copolymers derived from 8-quinolinyl methacrylate". *Iranian Polymer Journal*, **13 (6)**, 445 2004.
- [3]. D.B. Patle. and W. B. Gurnule. "Study of chelation ion-exchange properties of new copolymer resin derived from o-aminophenol, urea and formaldehyde", *Scholars Research Library, Archives of Applied Science Research*, **2 (1)**, 261-276, 2010.
- [4]. S. S. Rahangdale, A. B Zade. and W. B Gurnule.: "Terpolymer resin II: Synthesis, characterization, and ion-exchange properties of 2, 4-dihydroxyacetophenonedithiooxamide-formaldehyde terpolymers". *J. Appl. Polym. Sci.*, **108 (2)**, 747-756 2008.
- [5]. K. A. K. Ebraheem, J. A. Al-duhan and S. T Hamdi. "Polycondensates of some phenolic chelants and formaldehyde Synthesis, characterization and properties," *European Polymer Journal*, **21**, 97,1985.
- [6]. W. B Gurnule, P. K. Rahangdale, L. J. Paliwal and R. B. Kharat, "Chelation ion-exchange properties of copolymer derived from 2-hydroxyacetophenone, oxamide and formaldehyde", *Synth. React. Inorg. Met. Org. Chem.* **33(7)**, 1187, 2003.

[7]. W. B. Gurnule, P. K. Rahangdale, L. J. Paliwal, R. B. Kharat, "Ion exchange properties of 4-hydroxyacetophenone-biuret-formaldehyde terpolymer," Prog. Cryst. Grow. Charact. Mat. **45**, 127, 2002.

[8]. S. Lenka, A. Parija and P. L. Nayak "Synthetic resins: XV. Chelation ion exchange properties of 2,4-dinitrophenylhydrazone of resacetophenone-formaldehyde resin", Polymer International, **29(2)**, 103-106, 2007.

[9]. M. A. Kapadia, M. M. Patel, G. P. Patel and J. D. Joshi "Synthesis, Characterization, and Ion-Exchange Study of Benzophenone Based Resin and Its Polychelates with Lanthanides(III)", International Journal of Polymeric Materials, **56(5)**, 549-563, 2007.

[10]. W. B. Gurnule, P. K. Rahangdale, L. J. Paliwal and R. B. Kharat "Chelation ion-exchange properties of copolymer resin derived from 4-hydroxyacetophenone, oxamide, and formaldehyde", J. Appl. Polym. Sci., **89**, 787, 2003.

[11]. A. B. Shah, A. V. Shah, M. P. Shah, "Synthesis, characterization and Analytical applications of o-substituted benzoic acid chelating resin", Iran Polym J, **15**, 809-819, 2006.

[12]. F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd ed., Wiley:New York, 1972.

[13]. M. M. Patel, M. A. Kapadiya, G. P. Patel and J. D. Joshi "Synthesis, characterization, ionexchange and antimicrobial study of poly[(2-hydroxy-4-methoxybenzo- phenone) ethylene] resin and its polychelates with lanthanides(III)". React. Funct. Polym., **67(8)**, 746-757, 2007.

Table5
Evaluation of the effect of different electrolytes on the uptake of several metal ions^a

Metal ion	Electrolte (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	2.62	3.82	3.52	2.41
	0.05		2.51	3.61	3.22	2.10
	0.10		2.21	1.82	2.72	1.82
	0.50		1.92	1.52	1.72	1.74
	1.00		1.52	1.32	1.71	1.70
Cd ²⁺	0.01	5.5	2.52	2.82	2.52	2.82
	0.05		2.31	2.42	2.22	2.41
	0.10		2.21	2.22	2.10	2.02
	0.50		1.82	1.92	1.64	1.52
	1.00		1.51	1.52	1.52	1.32
Pb ²⁺	0.01	5.5	2.84	2.61	2.21	-
	0.05		2.71	2.56	1.92	-
	0.10		2.61	2.35	1.62	-
	0.50		2.18	1.92	1.51	-
	1.00		1.89	1.71	1.32	-
Fe ³⁺	0.01	2.5	1.92	1.21	1.82	3.22
	0.05		2.35	1.62	2.81	2.28
	0.10		2.75	2.42	3.15	2.15
	0.50		2.92	2.82	3.42	1.62
	1.00		3.35	3.62	3.84	1.12
Cu ²⁺	0.01	5.0	2.05	1.92	2.52	4.21
	0.05		2.61	2.91	3.04	3.52
	0.10		3.15	3.42	3.42	2.62
	0.50		3.52	4.68	3.96	1.82
	1.00		3.62	4.31	5.21	1.02
Ni ²⁺	0.01	5.5	1.82	2.01	2.72	3.62
	0.05		2.45	2.52	2.92	3.02
	0.10		3.35	3.35	3.32	2.45
	0.50		3.82	3.82	3.42	1.62
	1.00		4.10	4.42	4.25	1.08
Co ²⁺	0.01	5.5	2.38	2.74	2.52	2.52
	0.05		1.92	2.05	2.21	2.15
	0.10		1.84	1.82	1.92	1.75
	0.50		1.42	1.72	1.61	1.22
	1.00		1.21	1.31	1.25	1.09

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

Table 6
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	41	52	64	78	92	-	-
Cd ²⁺	5.5	27	39	52	61	75	88	-
Pb ²⁺	5.5	24	36	52	61	78	89	-
Fe ³⁺	2.5	73	90	95	-	-	-	-
Cu ²⁺	5.0	54	62	74	84	97	-	-
Ni ²⁺	5.5	45	57	72	88	94	-	-
Co ²⁺	5.5	41	57	68	87	89	-	-

^a Mt (NO₃)₂=0.1 mol l⁻¹; volume, 2 ml; NaNO₃=1 mol l⁻¹; volume, 25 ml; room temperature.

Table3

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⁺	-	-	-	40.1	60.2	80.2	123.8	332.5	472.3	480.3
Cd ²⁺	-	-	-	-	34.1	47.1	59.8	70.2	420.5	521.5
Pb ²⁺	-	-	-	37.5	56.1	72.8	117.1	323.1	426.1	457.2
Fe ³⁺	32.1	204.2	400.3	522.1	-	-	-	-	-	-
Cu ²⁺	-	-	-	66.1	123.1	292.3	572.5	1422.0	1700.3	1910.1
Ni ²⁺	-	-	-	51.1	101.1	252.1	562.3	653.1	132.1	1422.1
Co ²⁺	-	-	-	42.1	67.5	123.1	341.7	389.1	470.1	501.8

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

^bMt (NO₃)₂ = 0.1 mol l⁻¹; volume, 2ml; NaNO₃ = 1 mol l⁻¹; volume, 25 ml; room temperature; time, 24 h (equilibrium state).