Synthesis of Resin IV: Salicylic Acid, Diaminonaphthalein, and Formaldehyde Terpolymer and Its Ion Exchange

Dhanraj T. Masram,[1] Narayan S. Bhave,[1] Kiran P. Kariya[2]

[1]Department of Chemistry, Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur 440033, India
[2]Department of Chemistry, VMV Commerce JMT Arts & JJP Science College, Nagpur 440008, India

ABSTRACT: This article reports the synthesis, characterization, and ion exchange properties of a terpolymer. The terpolymer resin salicylic acid-diaminonaphthalein-formaldehyde (SDNF) was synthesized by the condensation of salicylic acid and diaminonaphthalein with formaldehyde in the presence of a hydrochloric acid catalyst. Terpolymer resin was characterized by elemental analysis, infrared (IR) spectroscopy, nuclear magnetic resonance spectroscopy, and UV–Visible spectral studies. The number average molecular weight of the resin was determined by nonaqueous conductometric titration. Chelation ion exchange properties have also been studied for Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+} ions employing a batch equilibrium method. It was employed to study the selectivity of metal ion uptake involving the measurements of distribution of a given metal ion between the polymer sample and a solution containing the metal ion. The study was carried out over wide pH range and in a media of various ionic strengths. The terpolymer showed higher selectivity for Fe^{3+}, Cu^{2+}, and Ni^{2+} ions than for Co^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} ions. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 315–321, 2010

Key words: chelation; batch equilibrium; metal ion uptake; degree of polymerization

INTRODUCTION

Synthesis, characterization, and ion exchange studies of polymeric resins deserve to be investigated because of their varied characteristics and beneficial properties. Ion exchangers are widely used in hydrometallurgy, antibiotic purification, analytical chemistry, separation of radioisotopes, and also find large scale application in water treatment and pollution control.[1–4] Terpolymers are found to exhibit better thermal and electrical properties than those of phenol-formaldehyde type copolymer. These terpolymers can be used as high energy materials, ion exchangers, semiconductors, bonding agent/additives, molding material, fungicides in plant and living tissues, biosensors, and controlled release devices for pharmaceuticals.[5,6,7–11] Nowadays renewed interest has been evidenced in the context of obtaining materials with high temperature resistance and ion exchangers. Patel and Lad[12] reported the novel terpolymers: poly(keto-amine-ureas) and studied the glass reinforcement of such terpolymer- epoxy systems. Michael and coworkers have reported the synthesis, structural,

and thermal degradation of a polymer derived from salicylic acid, guanidine, and formaldehyde.[13] Synthesis, characterization, and ion exchange properties of 4-hydroxyacetophenone, biuret, and formaldehyde terpolymer resin were studied by Gurnule et al.[14] Ion exchange resin derived from semicarbazone and oximes of 2-hydroxy acetophenone-substituted benzoic acid-formaldehyde studied by Nayak and coworkers.[15,2] The synthesis and characterization of 2, 4- dihyroxyacetophenone with 1, 4-butanediolcopolymer and its ion exchange properties have been reported.[16] Chelation ion exchange resins derived from 2-hydroxy-4-methoxyacetophenone and thiourea with trioxane was investigated by Pancholi et al.[17] Patel and coworkers[18,19] reported the ion exchange properties of resacetophenone (2, 4 dihydroxy Acetophenone) -formaldehyde and resacetophenone oxime-formaldehyde resins. In our laboratory, extensive research work was carried out on synthesis and characterization of terpolymers and their ion exchange properties.[20–22] However, the literature studies have revealed that no terpolymer has been synthesized using the monomers salicylic acid, diaminonaphthalein, and formaldehyde. Therefore, in this communication we report synthesis, characterization, and ion exchange properties of a salicylic acid-diaminonaphthalein-formaldehyde (SDNF) terpolymer resin.

Correspondence to: D. T. Masram (Dhanraj_masram27@rediffmail.com).

EXPERIMENTAL SECTION

Chemicals

All Chemicals were AR grade or chemically pure grade. Salicylic acid, diaminonaphthalein were purchased from Aldrich Chemical Co. Formaldehyde from RANKEM, Ranbaxy, India, dimethylformamide (DMF) and dimethylsulfoxide (DMSO) (HPLC grade) were used.

Instruments used

C, H, and N were analyzed on Carlo Erber Elemental Analyzer Fourier Transform. Infrared spectra in the region 400–4000 cm^{-1} were recorded on a Perkin-Elmer with KBr pellets. The electronic spectrum of the terpolymer was recorded in DMF at room temperature with a UV-240 Shimadzu double beam spectrophotometer. The nuclear magnetic resonance (NMR) was scanned at 300 MHz with dueterated DMSO solvent at RSIC, Chandigarh.

Synthesis of SDNF terpolymer resin

Condensation of salicylic acid (S) and diaminonaphthalein (DN) with formaldehyde (F)

A mixture of salicylic acid (6.9 g,0.05 mol),diaminonaphthalein(7.9 g,0.05 mol), formaldehyde (3.0 mL, 0.05 mol) and 2M hydrochloric acid was taken in a round bottom flask fitted with water condenser and heated in an oil bath at 120°C for 7 h with occasional shaking. The temperature of electrically heated oil bath was controlled with the help of dimmer stat. The resinous solid product obtained was immediately removed from the flask as soon as the reaction period was over and then purified.

   The resinous product so obtained was repeatedly washed with cold distilled water, dried in air and powdered with the help of agated mortar and pestle. The powder was washed many times with hot water to remove unreacted monomers. The air-dried powder was extracted with diethyl ether and then petroleum ether was used to remove salicylic acid diaminonaphthalein copolymer, which might be present along with SDNF terpolymer. It was further purified by dissolving in 8% sodium hydroxide solution, filtered and reprecipeted by gradual drop wise addition of 1 : 1 (v/v) hydrochloric acid with constant and rapid stirring to avoid lump formation.[16,21,22] The SDNF terpolymer resin so obtained was filtered, washed several times with hot water and dried (yield = 14 g; mp = 178°C). Analytical data for C19H18N2O3H2O as per numerical calculations and experimental evidences are mentioned below, respectively. Theoretically calculated C = 67.45%, H = 8.25%, N = 5.32%. Experimentally found C = 67.62%, H = 8.54%, N = 5.47%.
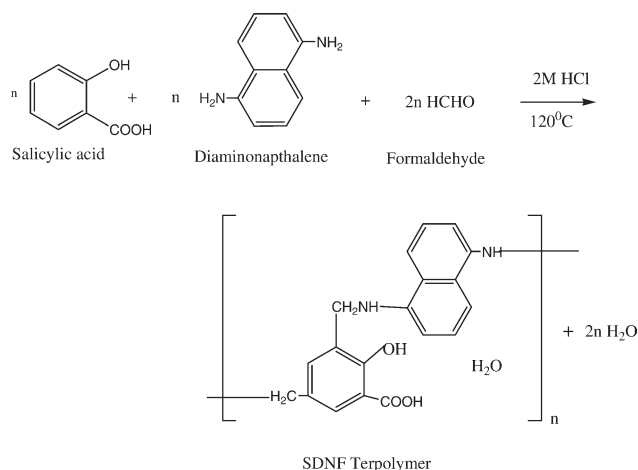
Synthesis of SDNF terpolymer resin.

Ion exchange properties

The purified SDNF resin sample was finely powdered and used in all experiments carried out in the ion exchange study.

Determination of metal ion uptake in the presence of electrolytes of different concentration

A total of 25 mg of the finely powdered terpolymer resin was suspended in an electrolyte solution (25 mL) of known concentration. The pH of the solution was adjusted to required value by using either 0.1M HNO_3 or 0.1M NaOH. The suspension was stirred for a period of 24 h at room temperature. To this suspension 2 mL of 0.1M solution of electrolyte 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 polymer was washed, and the filtrate and washings were combined and estimated for the metal ion content by titration against standard ethylenediaminetetraacetic acid. A blank experiment was also carried out in the same manner without adding the polymer sample to estimate the metal ion content. The amount of metal ion taken up by the terpolymer in the presence of given electrolyte of known concentration was determined from the difference between the blank reading and the reading in the actual experimental.[16,21,22] The experiment was repeated in the presence several electrolytes of known concentration with seven different metal ions such as Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}. The results with seven different metal ions are reported in Table III.

Evaluation of the rate of metal uptake

To determine the time required to reach the state of equilibrium under given experimental conditions,
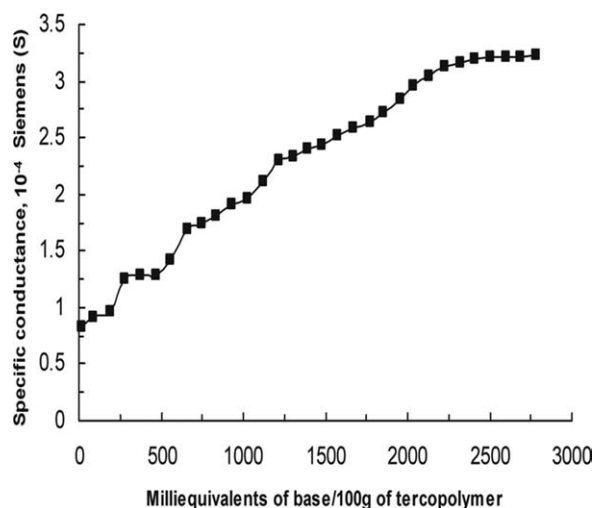
Figure 1 Conductometric titration curve of SDNF terpolymer.

series of experiments of the type described above were carried out, in which the metal ion uptake by the chelating resins was estimated from time to time at room temperature at 25°C. It was assumed that under given conditions, the state of equilibrium is established in the 24 h. The rate of metal ion uptake is expressed as percentage of the amount of metal ions taken up after a certain time related to that in state of equilibrium as Table IV.[16,21,22]

Evaluation of distribution of metal ions at different pH values

The distribution of each of the metal ions Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+} between the resin phase and aqueous phase was estimated at 25°C using $1M$ $NaNO_3$ solution. The experiments were carried out as described above at different pH values.

The distribution ratio "D" was determined by the following equation[16,21,22]:

$$D = \frac{\text{Weight of metal ions taken up by 1 g of resin}}{\text{Weight of metal ions present in 1 mL of solution}}$$

The results are presented in Table V.

RESULTS AND DISCUSSION

The terpolymer resin was soluble in DMF and DMSO; however, it is insoluble in common organic solvents. The composition of the polymeric unit was assigned on the basis of a detailed study of the elemental analysis of the polymer, ultraviolet-visible (UV–Visible), IR, and NMR spectral studies.

Characterization of terpolymer

Determination of molecular weight by conductometric titration

Molecular weight (M_n) of the terpolymer 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 milieqvivalents of potassium hydroxide required for neutralization of 100 g of terpolymer was made. Inspection of such a plot revealed the breaks in the plot. The first break at 270 milliequivalent of base and the last break at 2430 milliequivalent of base were noted. The calculations of (M_n) by this method is based on the following considerations[16,22,23]: (1) the first break corresponds to neutralization by the more acidic phenolic hydroxy group of all the repeating units; (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. Based on the average degree of polymerization (DP) is given by the following relation.

DP

$$= \frac{\text{Total meq of base required for complete neutralization}}{\text{meq of base required for smallest interval}}$$

The DP, which is given by the following relation, is found to be 9 and the number average molecular weight (M_n) is 3042 as obtained by multiplying the DP by the formula weight of the repeating unit.[16,22,23]

UV–Visible studies

The electronic spectrum of the SDNF terpolymer is shown in Figure 2. The spectra depicted two characteristic bands in the region of 305 nm and 350 nm. The band at 305 nm indicates the presence of a
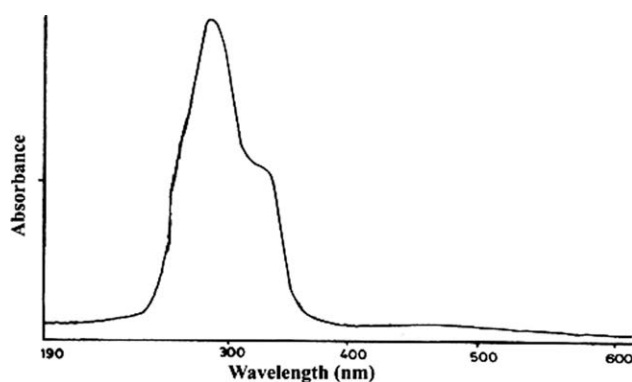

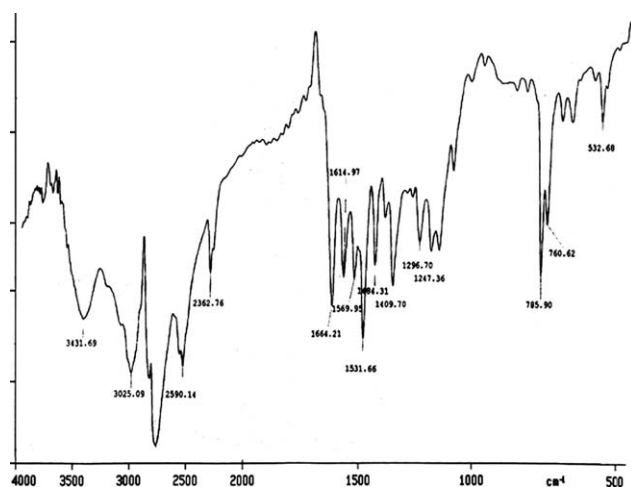**Figure 2** Electronic spectra of SDNF terpolymer.

Figure 3 Infrared spectra of SDNF terpolymer.

carbonyl (>C═O) group containing a carbon oxygen double bond in conjugation with an aromatic nucleus and was characteristic of a $\pi \rightarrow \pi^*$ transition, whereas the latter band (less intense) may be due to $n \rightarrow \pi^*$ electronic transition. The additional shift of absorption to the longer wavelength region, i.e. bathochromic shift from the basic value may be because of conjugation effect and phenolic hydroxyl group (auxochrome) is more effective for hyperchromic effect i.e. higher ε_{max} value.[24–26]

Infra red studies

The IR spectra of the newly synthesized SDNF terpolymer resins are depicted in Figure 3 and IR values are mentioned in Table I. The assignment of vibrational frequencies is mainly based on the data available in the literature. A broad band appeared at 3431.6 cm^{-1} [27–29,30,31] might be due to the stretching vibrations of phenolic hydroxyl group exhibiting intermolecular hydrogen bonding, which exists between ─OH groups of different polymer chains. The band observed at 3025 cm^{-1} may be due to the stretching vibrations of ─NH (imide).[29,32–34] The inflections around 1484.3 cm^{-1}, 1296.7 cm^{-1}, and 785.9 cm^{-1} suggest the presence of bending, wagging, rocking vibrations of methylene (─CH$_2$─) bridges in polymeric chains.[27,29,33,35] The medium broad band at 1614.9 cm^{-1} may be ascribed to aromatic ring. The broad band at 1664.2 cm^{-1} may be due to the stretching vibrations of >C═O.[29,35] The broad bands at 1569.9 cm^{-1}, 760.6 cm^{-1}, and 700 cm^{-1} are because of ─NH─ bending, wagging, and deformation out of plane vibrations in terpolymer resin respectively.[29,33,35] The band at 1376.6 cm^{-1} may be due to phenolic >C─O stretching modes of vibration.[29,35] The presence of band at 900 cm^{-1}–1150 cm^{-1} suggests that the aromatic ring is 1, 2, 3, 5-tetrasubstituted.[29,35] This fact is further supported by the presence of band at 836.9 cm^{-1} for tetra-substituted benzene ring.[27]

NMR studies

The NMR spectrum of the SDNF terpolymer shown in Figure 4 depicted signal in the region of 7.9 δ (ppm), which is ascribed to the proton of the aromatic ring (Ar─H), and the signal at 8.2 δ (ppm) may be assigned to the phenolic─OH proton involved in intermolecular hydrogen bonding.[29,35,31] The signal displayed at 7.5 δ (ppm) may be due to the carboxylic proton of Ar─COOH.[35] The presence of a signal around 6.8 δ (ppm) may be attributed to ─NH bridges.[29,36] A methylene proton Ar─CH$_2$─N moiety was inferred by the appearance of a signal at 3.7–4.2 δ (ppm).[29,35,37] The spectral data is as tabulated in Table II.

TABLE I
IR Spectral Data of SDNF Terpolymer

| Assignment	Observed band frequency (cm^{-1})	Expected band frequency (cm^{-1})
Phenolic ─OH	3431.6	3500–3000
─NH stretch	3025	3500–2800
>C═O stretching	1664.2	1680–1630
Phenolic C─O	1409.7	1410–1310
Methylene bridge (─CH$_2$) mode		
Wagging	1296.7	1300–1200
Bend	1484.3	1460
Rock	785.9	775
1,2,3,5- substitution on aromatic ring	900–1150	900–1200
Tetra substitution benzene ring	830	~830
N─H wagging	760.6	650–800
N─H bending	1569.9	1490–1570
N─H deformation out of plane	700	800–600
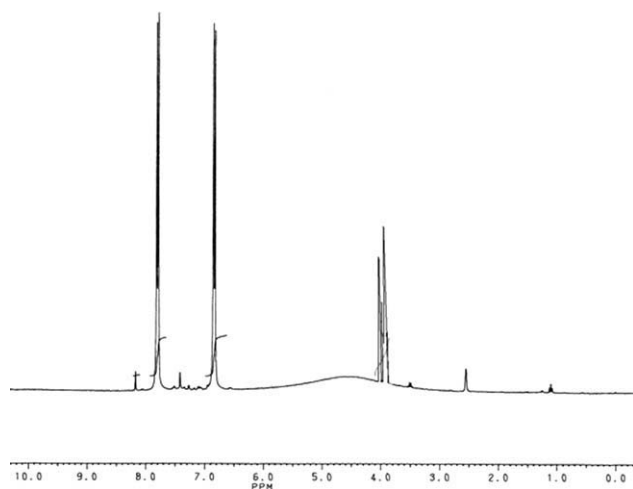
Figure 4 NMR spectra of SDNF terpolymer.

Ion-exchanging properties

To ascertain the selectivity of SDNF, we have studied the influence of various electrolytes, the rate of metal uptake and the distribution of metal ions between the resin and solution. The results of the batch equilibrium study carried out with resin sample SDNF are presented in Tables III, IV and V.

Effect of electrolyte on metal uptake

The data presented in Table III reveals that the amount of metal ions taken up for a given amount of resin sample depends on the nature and concentration of electrolyte present in the solution. In presence of chloride and nitrate ions, the amount of Cu^{2+}, Fe^{3+} and Ni^{2+} ions taken up by the terpolymer sample increases, whereas in presence of sulphate ions the amount of above mentioned ions taken up by the resin samples decreases with increasing concentration of electrolyte. Moreover, the amount of Co^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} ions taken up by the terpolymer samples decreases with increasing concentration of the chloride, nitrate, and sulphate ions. This may be explained on the basis of stability constant of the complexes with Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} metal cations.[38–40]

TABLE II
^{1}H NMR Spectral Data of SDNF Terpolymer

Nature of proton	Chemical shift, δ (ppm)	Expected chemical shift, δ(ppm)
Aromatic (Ar—H)	7.8–8.0	7.3–8.8
Phenolic (Ar—OH)	8.2	7.5–12
Carboxylic (Ar—COOH)	7.45	7.41
—NH bridging	6.9	5.0–8.5
Ar—CH$_2$—N moiety	3.7–4.1	2.5–4.5

TABLE III
Evaluation of the Effect of Different Electrolytes on the Uptake of Several Metal Ions^a of SDNF Terpolymer

Metal ion	Electrolyte conc. (mole/lit)	Weight of metal ion (mg) taken up in presence of		
		NaNO$_3$	NaCl	Na$_2$SO$_4$
Fe^{3+}	0.01	1.82	1.79	2.56
	0.05	2.01	1.96	2.43
	0.1	2.13	2.11	2.08
	0.5	2.41	2.41	1.92
	1	2.62	2.58	1.79
Cu^{2+}	0.01	0.56	0.54	1.41
	0.05	0.78	0.73	1.32
	0.1	1.07	0.98	1.01
	0.5	1.32	1.25	0.72
	1	1.58	1.43	0.53
Ni^{2+}	0.01	0.86	0.81	1.71
	0.05	0.93	0.90	1.36
	0.1	1.13	1.04	0.92
	0.5	1.51	1.41	0.76
	1	1.92	1.88	0.68
Co^{2+}	0.01	1.73	1.65	1.68
	0.05	1.46	1.41	1.38
	0.1	1.13	1.05	1.03
	0.5	0.98	0.92	0.93
	1	0.86	0.83	0.81
Zn^{2+}	0.01	1.33	1.31	1.28
	0.05	1.18	1.26	1.21
	0.1	0.94	0.85	0.90
	0.5	0.74	0.68	0.66
	1	0.65	0.61	0.57
Cd^{2+}	0.01	1.26	1.17	1.03
	0.05	1.14	1.01	0.94
	0.1	0.94	0.83	0.67
	0.5	0.81	0.64	0.58
	1	0.62	0.58	0.42
Pb^{2+}	0.01	1.24	1.03	0.86
	0.05	1.03	0.76	0.59
	0.1	0.85	0.62	0.51
	0.5	0.68	0.52	0.34
	1	0.59	0.34	0.11

^{a} [M(NO$_3$)$_2$] = 0.1 mol/L; Volume = 2 mL; Volume of electrolyte solution = 25 mL; time = 24 h; room temperature.

Rates of metal uptake

The rates of metal adsorption by the SDNF terpolymer were measured for Fe^{3+}, Cu^{2+}, Ni^{2+} Co^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} ions to know the equilibrium time required. The term "rates" refers merely change in the concentration of metal ion in the aqueous solution, which is in contact with given terpolymer resins. The experimental results which are given in Table IV, shows that the time taken for the uptake of the metal ions at a given stage depends on the nature of the metal ion under the given conditions. As the size of the metal ion increases, time taken for the uptake metal ion also increases. The experimental results indicate that Fe^{3+} ions required less time of 4 h for the establishment of equilibrium. Cu^{2+},

<div align="center">

TABLE IV
Comparison of the Rates of Metal Ion Uptake of SDNF Terpolymer

</div>

Metal ions	Percentage of the metal ion uptake[a] at different times (h)						
	0.5	1	2	3	4	5	6
Fe^{3+}	53	62	76	81	92	–	–
Cu^{2+}	29	40	61	68	81	91	–
Ni^{2+}	16	29	42	61	72	91	–
Co^{2+}	10	24	39	53	69	90	–
Zn^{2+}	08	15	25	51	68	89	–
Cd^{2+}	09	20	51	62	69	81	91
Pb^{2+}	08	15	29	60	71	81	90

[a] Metal ion uptake $= \dfrac{\text{Amount of metal ion absorbed} \times 100}{\text{Amount of metal ion absorbed at equilibrium}}$

$[M^+(NO_3)_2] = 0.1$ mole/l; Volume = 2, $NaNO_3 = 0.1$ mol/l; Volume of electrolyte solution = 25 mL; time = 24 hr (equilibrium state), room temperature.

Ni^{2+}, Co^{2+}, Zn^{2+}, ion required 5 h, whereas Cd^{2+} and Pb^{2+} ions required about 6 h reaching for the establishment of equilibrium. It is further revealed that the rates of metal ion uptake follow the order: $Fe^{3+} > Cu^{2+} \sim Ni^{2+} \sim Co^{2+} \sim Zn^{2+} > Cd^{2+} \sim Pb^{2+}$ for all the terpolymers.[41,42]

Evaluation of distribution coefficient of the metal ions over wide pH range

The results of the effect of pH on the amount of metal ion distributed between two phases are incorporated in Table V. Examination of the data indicates that the relative amount of metal ions taken up by the resin samples at equilibrium increases with increasing pH of the medium.[3,38,40,41,43] The study was carried out only up to pH = 6.5 to prevent hydrolysis of the metal ions at higher pH.

Perusal of data given in Table V the selectivity of resin samples for Fe^{3+} is higher than that of other metal ions. The lower distribution ratio of Fe^{3+} because of sterric hindrance imposed by polymer matrix.[40,42] Among the other metal ions Cu^{2+} and Ni^{2+} ions are taken up more selectively by terpolymer resin. The other metal ions Co^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} have distribution ratio, 'D' over the pH range of 4–6.5. This could be attributed to the low stability constant i.e. the weak ligand stabilization energy of the metal complexes.[44,45] The possible order of selectivity of a cation-exchange resin for divalent metal ions is[46]: Pd > Cu > Ni > Co > Zn > Cd > Fe > Mn > Mg. Comparison of the values of distribution coefficients of a given metal ion for all the four molar ratio of terpolymer reveals that there is no much difference in the values. Thus, in this study the observed order of distribution ratio of metal ions measured in the range of 1.5–6.5 pH was found to be $Fe^{3+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+} > Cd^{2+} > Pb^{2+}$. Earlier workers have also suggested this order of selectivity for a salicylic acid containing polymer.

<div align="center">

TABLE V
Distribution Ratio D[a] of the Metal Ion as a Function of the pH[b] of SDNF Terpolymer

</div>

Metal ion	Distribution ratio of the metal ion at different pH								
	1.5	2.0	2.5	3.0	4.0	4.5	5.0	6.0	6.5
Fe^{3+}	157.8	226.3	490.7	–	–	–	–	–	–
Cu^{2+}	–	–	–	72.6	130.4	298.3	501.1	885.7	1039.3
Ni^{2+}	–	–	–	61.2	92.1	119	182.4	355.7	798.3
Co^{2+}		–	–	34.6	71.3	87.1	128.5	189.6	330.2
Zn^{2+}	–	–	–	21.3	39.5	58.6	118.8	187.4	283.6
Cd^{2+}	–	–	–	16.3	38.8	55.6	109.2	148.1	229
Pb^{2+}	–	–	–	29.2	44.3	61.2	96.3	155.4	243.2

[a] $D = \dfrac{\text{Weight of metal ions taken up by 1 g of resin}}{\text{Weight of metal ions present in 1 mL of solution}}$

[b] Metal ion uptake $= \dfrac{\text{Amount of metal ion absorbed} \times 100}{\text{Amount of metal ion absorbed at equilibrium}}$

$[M^+(NO_3)_2] = 0.1$ mole/l; Volume = 2, $NaNO_3 = 0.1$ mol/l; Volume of electrolyte solution = 25 mL; time = 24 hr (equilibrium state), room temperature.

CONCLUSIONS

A resin SDNF based on the condensation reaction of salicylic acid and diaminonaphthalein with formaldehyde in the presence of HCl catalyst has been prepared. The results of ion exchange study are helpful in selecting the optimum pH for a selective uptake of a particular metal ion from a mixture of a different metal ion. For example, the results suggest the optimum pH 2.5 for the separation of Cu^{2+} and Fe^{3+} at which the distribution ratio D of Fe^{3+} is 586.3 SDNF terpolymer resin, whereas Cu^{2+} does not show the distribution ratio. Thus, SDNF is a selective chelating ion exchange resin for certain metals. The resin showed a higher selectivity for Fe^{3+}, Cu^{2+}, and Ni^{2+} ions than Co^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} ions.

References

1. Kunin, R. Ion Exchange Resin, 3rd ed; Wiley: New York, 1958.
2. Samal, U. K.; Nayak, P. L.; Lenka, S. J Appl Polym Sci 1993, 47, 1315.
3. Zagorodni, A. Ion Exchange Materials, Properties and Applications; Elsevier: Amsterdam, 2006.
4. Gurnule, W. B.; Juneja, H. D.; Paliwal, L. J. React Funct Polym 2001, 50, 95.
5. Das, A. P.; Lenka, S.; Nayak, P. L. J Appl Polym Sci 1987, 34, 2139.
6. Gurnule, W. B.; Juneja, H. D.; Paliwal, L. J. React Funct Polym 2002, 50, 95.
7. Yu, G.; Zhongguo, J. 1995, 4, 1.(Ch). C.A. 124, 233746S (1996).
8. Nakam Shinichi. Jpn kokai Tikkyo koho 08 143, 750 996, 143750 (1996); Ci. C08L61/04 C.A. 125116385h (1996).
9. Zinger, B. J Electronal Chem 1988, 244, 115.
10. Trivedi, Y.; Kariya, K. P.; Bhave, N. S. Macromolecules 2007, 3, 71.
11. Gurnule, W. B.; Juneja, H. D.; Paliwal, L. J. Ultra Sci 1999, 11, 325.
12. Patel, H. S.; Lad Manohar, J. High Perform Polym 1996, 8, 225.
13. Michael, P. E.; Lingala, P. S.; Juneja, H. D.; Paliwal, L. J. J Appl polym Sci 2004, 92, 2278.
14. Gurnule, W. B.; Juneja, H. D.; Paliwal, L. J. React Funct Polym 2003, 55, 255.
15. Bastia, T. K.; Lenka, S.; Nayak, P. L. J Appl Polym Sci 1992, 46, 739.
16. Masram, D. T.; Kariya, K. P.; Bhave, N. S. e-Polymers 2007, 075, ISSN 1618.
17. Pancholi, H. B.; Patel, M. M.; Patel, M. R. High Perform Polym 1991, 3, 257.
18. Parmar, J. S.; Patel, M. M.; Patel, M. R. Angew Makromol Sci Chem 1981, 105, 11.
19. Parmar, J. S.; Patel, M. M.; Patel, M. R. Angew Makromol Sci Chem 1982, 105, 75.
20. Gurnule, W. B.; Juneja, H. D.; Paliwal, L. J.; Asian J Chem 2000, 12, 51.
21. Gurnule, W. B.; Juneja, H. D.; Paliwal, L. J. Res J Chem Environ 1999, 3, 23.
22. Jadhao, M.; Paliwal, L. J.; Bhave, N. S. J Appl Polym Sci 2005, 96, 1605.
23. Jadhao, M.; Paliwal, L. J.; Bhave, N. S.; Indian J Chem 2005, 44, 1110–1113.
24. Maron, S. H.; Reznik, R. B. J Polym Sci 1938, 2, 1200.
25. Dudley, H.; Fleming, I. Spectroscopic Methods in Organic Chemistry; McGraw-Hill: UK, 1975.
26. Silverstein, R. M.; Bassler, G. C. Spectrometric Identification of Organic Compounds; 2nd ed; Willy: New York, 1967.
27. Kemp, W. Organic Spectroscopy; The Macmillan Press, Hong Kong Press: 1975.
28. Dunn, G. E.; Mcdonald, R. C. Can J Chem 1969, 47, 4577.
29. Nakanishi, K. Infrared Absorption Spectroscopy Practical; Nolden Day and Nankod: Tokyo, 1967.
30. Meenakshi, S.; Vishwnathan, N. J Colloid Interface Sci 2007, 308, 438.
31. Singh, B.; Sharma, N. J Polym Degrad Stab 2007, 1, 19.
32. Willard, H. H.; Merrit, L. I.; Dean, J. A.; Seattle, F. A. Instrumental Methods of Analysis; CBS: New Delhi, 1986.
33. Kalsi, P. S. Spectroscopy of Organic Compounds, 2nd ed.; New Age International: New Delhi, 1995.
34. Ballemy, I. J. The IR Spectra of Complex Molecules; Methuen and Wiley: NewYork, 1956 and 1958.
35. Dyer, J. R. Application of Absorption Spectroscopy of Organic and biological Chemistry; MIR: Moscow, 1975.
36. Vogel, A. I. Textbook of Practical Organic Chemistry; Longman Scientific and Technical: UK, 1989.
37. Pal, T. K.; Kharat, R. B.; Indian J Chem 1989, 22, 55.
38. Joshi, R. M.; Patel, M. M. J Makcromol Chem 1983, 19, 705.
39. Gurnule, W. B.; Juneja, H. D.; Paliwal, L. J.; Indian J Chem 2000, 39, 1110.
40. Manavalan, R.; Patel, M. M. Makromol Sci Chem 1983, 184, 717.
41. Pancholi, H. B.; Patel, M. M.; Patel, M. R. React Polym 1992, 17, 353.
42. Savitha, P.; Sathyanarayana, D. N. J Polym Sci Part A: Polym Chem 2005, 43, 3040.
43. Deshkhun, A.; Young, G.; Choi, U. React Funct Polym 2007, 67, 312.
44. Cotton, F. A.; Wilkinson, G. Advanced Inorganic Chemistry; 3rd ed; Wiley: New York, 1972.
45. Davadov, S. L.; Plate, N. A. Coord Chem Rev 1975, 16, 195.
46. Irving, H.; Williams, R. J. J Chem Soc 1953, 320.
47. Nagai, K.; Kawaski, T.; Takeo, C.; Yayabe, F. Jpn Kokai Takkyo Koho 0827226 (1996); Ci.C08F 20/58/30 Appl 94/160, 382/ C.A. 124 (1994).