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Preparation and Chelating Properties of 4-Bromosalicylic Acid-Formaldehyde Polymers. Part II

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Preparation and Chelating Properties of 4-Bromosalicylic Acid-Formaldehyde Polymers. Part II

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ABSTRACT

4-Bromosalicylic acid (BS) was condensed with various proportions of formaldehyde using different acid catalysts. The polymer samples have been characterized by IR spectral studies, by their number-average molecular weight ($\overline{M}_n$), and by TGA.

Viscosity measurements of selected polymer samples in DMF showed that their solutions exhibited polyelectrolyte behavior. The intrinsic viscosity $[\eta]$ of the polymer samples were measured in 80:20 (v/v) DMF/water containing 1% KBr, a medium in which the polymers exhibited normal behavior. Metal chelates of one polymer sample are characterized. Ion-exchanging properties of the same sample are studied by application of the batch equilibrium method.

INTRODUCTION

In our earlier communication [1], results of the study of the acid- and base-catalyzed polycondensations of p-aminosalicylic acid (PAS) with formaldehyde were reported. In such condensations it was found that base-catalyzed condensation accompanied decarboxylation of PAS, and the polymer was found to be similar to that formed from m-aminophenol and formaldehyde under similar conditions [1]. PAS, however, condensed with formaldehyde in the presence of acid catalyst, affording the expected PAS-F polymer which has been characterized [1]. Perusal of the literature reveals that no corresponding polymers have been prepared from 4-bromosalicylic acid and formaldehyde. The work described in the present communication is connected with the synthesis, characterization, and chelating properties of 4-bromosalicylic acid-formaldehyde polymer.

The condensation of 4-bromosalicylic acid with formaldehyde could not be effected in the presence of aqueous alkali; it could, however, be effected in the presence of acidic catalysts. The reaction was studied using different proportions of the two reactants. All the polymer samples were characterized by IR spectral studies, by estimation of the number-average molecular weight ($\overline{M}_n$) estimated by both the VPO method and by nonaqueous titration against standard tetra-n-butylammonium hydroxide, and by viscosity measurements of solutions in DMF and its mixtures with water. TGA of all the polymer samples has been carried out in CO_2 under identical conditions. The polymeric metal chelates were prepared by mixing aqueous solutions of metal nitrate and sodium salt solution of selected polymer sample, viz., BSF-2 in stoichiometric amounts. Metal:ligand (M/L) ratios, spectral characteristics, and magnetic properties of polymeric metal chelates have been studied. Thermal properties of polymeric chelates have been compared with those of the corresponding parent polymers. The batch equilibration method developed by DeGeiso et al. [2] and Gregor et al. [3] was adopted for the study of chelation ion-exchanging properties of BSF-2 polymer. It comprised a study of the effects of different electrolytes and different ionic strengths on metal ion absorption by the polymer sample, estimation of the time required to reach the state of equilibrium under given experimental conditions, and the measurement of the distribution ratio of different metal ions between the polymer phase and the solution phase over a wide pH range.

EXPERIMENTAL

Materials

The monomer, 4-bromosalicylic acid (BS), was prepared by modification of the method reported [4]. The acid BS was prepared from sodium p-aminosalicylate (Na-PAS) (obtained from Cadila Laboratories, Ahmedabad, India) by the Sandmeyer reaction. Solutions of Na-PAS (52.5 g, 0.3 mol) in 150 mL water and sodium nitrite (20.7 g, 0.3 mol) in 50 mL water were mixed and added over a period of 2.0 h to 100 mL of 98% sulfuric acid at 0.5° C. The resulting diazonium salt solution was added gradually with stirring to a hot solution (50° C) of cuprous bromide [prepared from copper sulfate pentahydrate (75.0 g, 0.3 mol)] in 120 mL of 48% hydrobromic acid. The resulting mixture was stirred for 15 min and then warmed to 70° for 1 h. The solid product was filtered, dried, and Soxhlet-extracted with benzene to extract pure 4-bromosalicylic acid. The yield was 48.0 g (75%), melting at 212-214° C ([4], mp 212°).

Benzene, acetone, ethanol, oxalic acid, glacial acetic acid, dioxane, benzil, N,N'-dimethylformamide, pyridine, and tetra-n-butylammonium hydroxide (0.1 M solution in methanol/toluene) were BDH chemicals.

Sodium hydrogen carbonate, sodium hydroxide, hydrochloric acid, hydrobromic acid, sulfuric acid, metal nitrates, and the electrolytes (sodium chloride, nitrate, chlorate, sulfate) were special chemical grade reagents and were used without purification.

Preparation of Polymers

The polycondensation of 4-bromosalicylic acid with formaldehyde could not be effected in the presence of 20% NaOH even at the reflux temperature. It is interesting to note that even salicylic acid could not be polymerized with formaldehyde under such conditions, though it has been reported that salicylic acid is resinified on reaction with formaldehyde in the presence of aqueous alkali [5]. The polycondensation of 4-bromosalicyclic acid (BS) with formaldehyde (F) was carried out under the different experimental conditions mentioned in Table 1. The details of three typical methods are presented here.

X: Condensation of 4-Bromosalicylic Acid with Formaldehyde in the Presence of 6 M H_2SO_4

A mixture of BS (0.04 mol), 37% formaldehyde solution (0.04 mol), and 6 M H_2SO_4 (60 mL) was refluxed with good stirring at 125-130° C for 6 h. The solid polymeric product was filtered and washed with a large amount of boiling water. The air-dried polymer sample was powdered and Soxhlet-extracted with benzene to remove any unreacted monomer. The polymer sample was dissolved in 1:1 (v/v) acetone/ethanol and reprecipitated by adding distilled water. The pasty mass was washed by decantation with water and dissolved in aqueous 0.4 M NaOH (100 mL). The polymer was reprecipitated by gradual addition of 5 M HCl with stirring till the medium was just acidic. The polymer was filtered, washed, and dried.

Y: Condensation of 4-Bromosalicylic Acid with Formaldehyde in the Presence of aq HCl-Oxalic Acid Mixture

A mixture of BS (0.04 mol), 37% formaldehyde solution (0.04 mol), 50 mL of 5 M HCl containing 1.1 g of oxalic acid was refluxed with

TABLE 1. Synthesis and Characterization of 4-Bromosalicylic Acid-Formaldehyde Polymer Samples; BSF-1 to 9[a]

Polymer sample	Molar ratio of reactants 4-bromosalicylic acid (BS): formaldehyde (F)	Method[b]	Yield[c]	Br[d]	By VPO,[e] $\overline{M}_n \pm 45$	Conductometric titration,[f] $\overline{M}_n \pm 45$	$[\eta] \times 10^2$ [g] dL/g
BSF-1	1:1	X	60	33.7	1470	1510	3.0
BSF-2	1:1.5	X	65	33.8	1350	1370	2.52
BSF-3	1:2	X	65	33.3	900	860	2.0
BSF-4	1:1	Y	45	33.6	1610	1600	3.25
BSF-5	1:1.5	Y	50	33.4	1260	1240	2.37
BSF-6	1:2	Y	55	33.3	980	960	2.1
BSF-7	1:1	Z	30	34.1	1600	1580	2.95
BSF-8	1:1.5	Z	35	34.1	930	960	2.15
BSF-9	1:2	Z	40	33.9	910	910	1.91

[a] Empirical formula of repeating unit: C_8H_5BrO. Molecular weight of repeating unit: 229.

[b] Method X: Condensation in presence of 6 M H_2SO_4.
Y: Condensation in presence of aq HCl-oxalic acid mixture.
Z: Condensation in presence of 6% H_2SO_4 in glacial acetic acid.

[c] After reprecipitation from NaOH/HCl.

[d] Calculated value of Br: 34.93.

[e] In dioxane at 51°C.

[f] Calculated based on method reported [7, 8].

[g] In 80:20 (v/v) DMF/water containing 1.0% KBr.

good stirring at 125-130°C for 6 h. The polymer was purified in the manner described in the above procedure.

Z: Condensation of 4-Bromosalicylic Acid with Formaldehyde in the Presence of Glacial Acetic Acid Containing 6.0 M H_2SO_4

A solution of BS (0.04 mol) in glacial acetic acid (60 mL) containing 2 mL of 98% H_2SO_4 was mixed with 37% formaldehyde solution (0.04 mol) and refluxed with good stirring at 140-145°C for 6 h. The resulting reaction mixture was transferred into a 1 L beaker and diluted with water (200 mL). The polymer separated out as a pasty mass. The supernatant liquid was decanted and the solid was washed with boiling water by decantation. It was treated further in the manner described earlier.

Preparation of Polymeric Chelate

The polymer sample BSF-2 was selected for the preparation of polymeric chelates.

Preparation of Sodium Salt Solution of 4-Bromosalicylic Acid-Formaldehyde (BSF-2) Polymer Sample, BSF-Na solution

To a solution of polymer sample (22.9 g, 0.1 mol) in 1:1 (v/v) acetone/ethanol (700 mL) was added dropwise a solution of 1.0 M NaOH (100 mL) at room temperature with stirring. During neutralization some sticky precipitates appeared. Water (100 mL) was added to dissolve the precipitates. The resulting solution was diluted to 1 L with water. This stock solution (0.1 M reagent) was used for preparing all metal chelates.

Preparation of the Polymeric Chelate of 4-Bromosalicylic Acid-Formaldehyde Polymer (BSF-2); Cu(II) Chelate of BSF-2 Polymer

To a solution of $Cu(NO_3)_2.6H_2O$ (2.22 g, 0.0075 mol) in water (100 mL) was added dropwise a 0.1 M BSF-Na solution (reagent) (150 mL containing 0.015 mol polymer) at room temperature with stirring. The pH of the resultant solution was 4.5 at this stage. A greenish blue chelate precipitated out. It was allowed to settle. The solid was filtered by decantation, washed with water, and then with ethanol (50 mL). The polymeric chelate was air dried.

The above-mentioned procedure was employed to prepare polymeric chelates like BSF-Fe(III), BSF-Co(II), BSF-Mn(II), BSF-Zn(II), and BSF-UO_2^{2+}. The properties of these polymeric chelates are presented in Table 2.

TABLE 2. Thermogravimetric Analysis of 4-Bromosalicylic Acid-Formaldehyde Polymer Samples BSF-1 to 9

Polymer sample	% Weight loss at temperature, T (°C)						
	100	200	300	400	500	600	700
BSF-1	8	8	16	30	54	65	74
BSF-2	3	5	14	52	78	98	-
BSF-3	4	8	18	40	60	96	-
BSF-4	8	9	16	28	54	64	73
BSF-5	4	6	16	54	80	98	-
BSF-6	5	9	20	60	82	98	-
BSF-7	4	7	15	20	55	65	72
BSF-8	3	6	18	50	82	98	-
BSF-9	4	7	19	50	72	98	-

Apparatus and Methods of Characterization

Elemental Analyses

The bromine content in all polymer samples and polymeric chelates was estimated by the Carius method. The analysis of the metal ions in the polymeric chelates was carried out by decomposition of a known amount of the chelate with a concentrated mineral acid, followed by dilution with distilled water, filtration, and estimation of metal ions in solution by standard method [6].

IR spectra of all polymer samples and polymeric chelates were taken in KBr on a UR-10 spectrophotometer.

The solid reflectance spectra of polymeric chelates were recorded on a Beckman DU spectrophotometer with a solid reflectance attachment. MgO was employed as the reference compound.

Vapor Pressure Osmometry

The number-average molecular weights ($\overline{M}_n$) of all polymer samples were measured with a Hewlett Packard Vapor Pressure Osmometer using dioxane as the solvent at 51°C. Benzil was used as the calibrant in the VPO experiments.

Conductometric titration of the solution of polymer samples in pyridine was carried out against standard tetra-n-butylammonium hydroxide (TBAH) in isopropanol. A Metrohm Herisau Konduktoskop E 365, Switzerland, was used for the purpose. Plots of specific conductance against mmoles of titrant base added per 100 g of polymer were made, and the $\overline{M}_n$ of all polymer samples were calculated on the basis of a reported method [7, 8].

Viscometric measurements of the solutions of polymer samples were carried out using an Ubbelohde viscometer. The viscosity of the polymer sample BSF was measured in DMF, DMF/water mixtures, and in such solvent mixtures containing KBr. Viscosity functions of all the polymer samples were measured in 80:20 (v/v) DMF/water containing 1% KBr.

Magnetic Susceptibility Measurements

These were carried out at room temperature by the Gouy method. $Hg[Co(NCS)_4]$ was used for calibration [9]. Molecular susceptibilities were corrected for diamagnetism of the component atoms by the use of Pascal's constants [9].

Thermogravimetry of all the polymer samples was carried out on a DU Pont-H 950 Thermogravimetric Analyzer in a CO_2 atmosphere at a heating rate of 10°C/min.

Ion-Exchanging Properties

Batch equilibration method has been adopted for this purpose [2, 3] to evaluate the influence of different electrolytes on the metal uptake by the polymer under equilibrium conditions, the rate of metal uptake under specified conditions, and the distribution of various metal ions at different pH values. The study has been carried out following the details described in our earlier communication [1].

RESULTS AND DISCUSSION

Polycondensation Reaction

Comparison of the yield of polymeric product formed on condensation of PAS [1], salicylic acid [10], and 4-bromosalicylic acid (BS) with formaldehyde under similar experimental conditions using an acid catalyst of the same type revealed that the yield of PAS-F, SF, and BSF polymers decrease distinctly in the stated order. This trend is also considered to show the trend in the reactivity of the three monomer acids as explained in terms of structural effects.

Characterization of Polymers

The polymer samples, BSF-1 to 9, are light brown. These polymer samples are soluble in acetone, ethanol, dioxane, tetrahydrofuran, and DMF, unlike PAS-F polymers [1] which are insoluble in common solvents. They are freely soluble in aqueous hydrogen carbonate

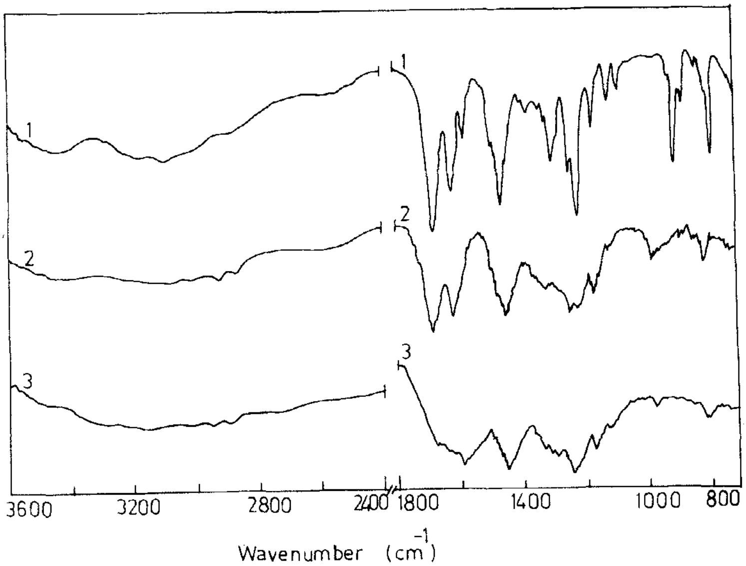

FIG. 1. IR spectra of (1) monomer acid BS, (2) polymer sample BSF-2, and (3) polychelate-BSF-Fe(III).

solution and aqueous alkali. Neutral solutions of each of these polymer samples developed a characteristic color with the Fe(III) ion.

The IR spectra of the polymer samples BSF-1 to 9 are found to be similar in all aspects. Typical spectra of monomer acid BS and polymer sample BSF-2 are shown in Fig. 1. In the spectrum of the polymer a band extending from 3600-2500 cm^{-1} is broader than the corresponding band in the spectrum of the monomer. The inflections at 2900 and 2850 cm^{-1}, a comparative broader band at 1455 cm^{-1}, and a small but sharp band at 803 cm^{-1} are observed in the spectra of all polymer samples. These are features of the CH of $-CH_2-$ bridges. The sharp band due to aromatic C=C stretching at 1450 cm^{-1} is broadened due to superposition of CH_2 scissors of $-CH_2-$ bridges. A small but distinct band observed around 867 cm^{-1} in the spectra of all the polymer samples can be attributed to the presence of an isolated aromatic hydrogen atom in the benzene ring of the repeating unit. The weak bands at 1243 and 1117 cm^{-1} observed in the spectra of all the polymers can possibly be assigned, respectively, to asymmetric and symmetric stretching of C–O–C arylalkyl ether linkages, suggesting the presence of a small number of some $-CH_2-O-CH_2-$ links in the polymer chains.

The number-average molecular weights ($\overline{M}_n$) (Table 1) of each polymer sample as estimated by the conductometric titration method

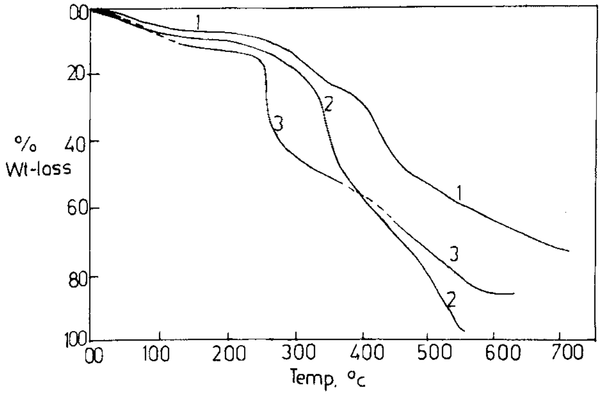

FIG. 2. TG thermograms of (1) polymer sample BSF-1, (2) polymer sample BSF-2, (3) polychelate-BSF-Cu(II).

and also by the VPO method compare well within the limits of experimental error. As expected, the polymer sample obtained using the equimolar proportion of the two monomers has the highest molecular weight.

Typical thermograms are shown in Fig. 2 and % weight loss at various stages in TG experiments are presented in Table 2. Examination of these data reveals that each polymer sample degrades in two stages (e.g., the salicylic acid-formaldehyde polymer (SF) [10]). The first stage of degradation is attributed to decarboxylation [10]. In the present cases the first stage terminates in the region from 250 to 300°C and the material loses around 17 to 25% of its weight depending upon the nature of the polymer. Each polymer suffered a 65 to 95% weight loss when heated up to 600°C depending upon the nature of the polymer. These results show that among polymer samples prepared under similar conditions, the sample prepared using equimolar proportions of the reactants is more stable.

Results of the viscometric study indicate that solutions of polymer sample BSF-2 in DMF and in 90:10 and 85:15 (v/v) DMF/water mixtures exhibit polyelectrolyte behavior. Solutions of the same polymer sample in 80:20 (v/v) DMF/water mixture showed normal behavior. With a view to finding a medium in which the actual values and normal variation of specific viscosity with concentration are high enough for more accurate estimation, the viscosity of polymer sample BSF-2 was studied in 80:20 (v/v) DMF/water mixture containing different amounts of KBr. It was found that from the above considerations a 80:20 (v/v) DMF/water mixture containing 1% KBr was a better medium for viscosity study. Hence the viscometric study of solutions of all the polymer samples was carried out in 80:20 (v/v) DMF/water mixture containing 1% KBr. Plots of reduced viscosity against concentration were made for each set of data. Values of intrinsic viscosity were measured from the slope of the corresponding linear plots. The values of intrinsic viscosity are presented in Table 1.

Characterization of Polymeric Chelates

The polymeric chelates are found to be insoluble in common organic solvents and are decomposed by mineral acids, giving the original polymeric ligands. The polymeric chelates were apparently unaffected when heated up to 360° C.

The results of metal and bromine analyses are shown in Table 3. The metal composition suggested that the metal:ligand [M:L] ratio is 1:2 for all divalent metal and 1:3 for Fe(III) ions. These results were also supported by data on the bromine content of polymeric chelates.

The IR spectra of the polymeric chelates resembled each other in general shape and relative intensity of bands. Comparison of the IR spectrum of polymeric ligand (BSF-2 polymer sample) and that of the polymeric chelate BSF-Fe(III) (Fig. 1) reveals that the broad absorptions in the region from 3500-2500 cm^{-1} in the spectrum of the polymeric ligand, due to the chelated OH group, are much less broad in the spectrum of polymeric chelate. This indicates the absence of internal H bonding due to chelation. This is also in agreement with the observation of DeGeiso et al. [10] reported earlier. A sharp band at 1675 cm^{-1} in the IR spectrum of the polymeric ligand assigned to C=O stretching is shifted to 1600 cm^{-1} in the IR spectra of polymeric chelates due to complexation. Because of the very low intensity of the bands due to metal-carbon bonds, no attempt was made to assign any band.

Magnetic moments of polymeric chelates are given in Table 3. The diffuse electronic spectrum of the Cu(II) polychelate shows two broad bands around 13,000 and 23,000 cm^{-1}. The first band may be due to a $^2T_{2g} \rightarrow {}^2E_g$ transition, while the second band may be due to charge transfer. The first band shows structures suggesting a distorted octahedral structure for the Cu(II) polychelate. The higher value of the magnetic moment of the Cu(II) polychelate supports this view. The Co(II) polychelate gives rise to two absorption bands at 23,800 and 19,040 cm^{-1} which can be assigned to $^4T_{1g} \rightarrow {}^2T_{2g}$, $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ transitions. These absorption bands and the μ_{eff} value indicate an octahedral configuration of the Co(II) polychelate. The spectrum of the Fe(III) polychelate comprised two bands at 19,000 cm^{-1} (asymmetric) and 23,000 cm^{-1}. The latter does not have a very long tail. These bands may be assigned to $^6A_1 \rightarrow {}^4T_2({}^4G)$ and $^6A_1 \rightarrow {}^4A_1({}^4G)$ transitions, respectively. The high intensities of the bands suggest that they may have some charge transfer character. The magnetic moment is found to be lower than the normal range. In the absence of low-temperature moments, it is difficult to attach any significance to this. As the spectra of the polychelates of Mn(II), UO_2^{2+} and Zn(II) are not

TABLE 3. Characterization of Polymeric Chelates of 4-Bromosalicylic Acid-Formaldehyde Polymer Sample BSF-2

Polymeric chelate	Resultant pH during preparation of polymeric chelate	Color	Molecular weight of the repeating unit in grams	% Metal content		% Bromine		μ_{eff} BM
				Calculated	Found	Calculated	Found	
BSF-Cu(II)	4.5	Greenish blue	519.54	12.23	11.5	30.95	30.6	2.17
BSF-Fe(III)	1.8	Violet blue	739.55	7.5	6.9	32.6	32.2	5.43
BSF-Co(II)	6.0	Pink	514.93	11.4	10.9	31.38	31.0	4.74
BSF-Mn(II)	5.5	Gray	510.94	10.7	10.3	31.68	31.2	5.09
BSF-Zn(II)	5.5	Pale yellow	521.37	12.53	12.0	30.89	30.5	Diamagnetic
BSF-UO_2^{2+}	2.8	Brownish yellow	726	32.8	32.5	21.93	22.2	Diamagnetic

TABLE 4. Evaluation of the Influence of Different Electrolytes in the Uptake of Several Metal (Mt) Ions [$Mt(NO_3)_2$] = 0.1 mol/L[a]

Metal (Mt) ion	pH	mol/L	Adsorption of meq × 10^1 of the metal ion on BSF-2 polymer[b] with electrolyte			
			$NaClO_4$	$NaNO_3$	NaCl	Na_2SO_4
Cu(II)	5.5	0.01	0.14	0.10	0.13	0.28
		0.05	0.17	0.12	0.16	0.26
		0.1	0.20	0.17	0.18	0.21
		0.5	0.25	0.21	0.21	0.19
		1.0	0.44	0.24	0.25	0.15
Fe(III)	2.75	0.01	0.12	0.14	-	0.23
		0.05	0.19	0.17	-	0.15
		0.1	0.25	0.18	0.1	0.1
		0.5	0.32	0.21	0.18	-
		1.0	0.35	0.24	0.25	-
UO_2^{2+}		0.01	0.20	0.16	0.16	0.26
		0.05	0.22	0.18	0.17	0.23
		0.1	0.24	0.28	0.20	0.20
		0.5	0.32	0.41	0.22	0.17
		1.0	0.52	0.48	0.25	0.11
Co(II)	5.5	0.01	0.16	0.16	0.14	0.1
		0.05	0.15	0.14	0.1	0.08
		0.1	0.10	0.11	-	-
		0.5	-	-	-	0.04
		1.0	-	0.06	0.06	-
Mn(II)	5.5	0.01	0.16	0.24	0.20	0.16
		0.05	0.14	0.20	0.19	0.10
		0.1	0.10	-	-	0.08
		0.5	-	-	-	-
		1.0	0.8	0.13	0.12	-
Zn(II)	5.5	0.01	0.16	0.11	0.15	0.14
		0.05	-	-	0.13	0.10
		0.1	0.12	0.08	-	-
		0.5	-	-	0.10	0.08
		1.0	0.08	0.06	-	-

[a] Volume of electrolyte solution: 40 mL, time: 24 h. Volume of metal ion solution: 1 mL, temperature: 25° C.

[b] Weight of polymer: 25 mg.

TABLE 5. Comparison of the Rates of Metal (Mt) Ion Uptake[a]

Time (h)	% Attainment of equilibrium state[b]			
	Fe(III)	UO_2^{2+}	Cu(II)	Mn(II)
0.5	65.0	35.0	35.0	20.0
1	80.0	65.0	50.0	45.0
2	88.0	90.0	70.0	60.0
3	98.0	98.0	80.0	75.0
4	98.0	99.0	85.0	85.0
5	-	-	93.0	90.0
6	-	-	96.0	93.0
7	-	-	99.0	98.0

[a] $[Mt(NO_3)_2]$ = 0.1 mol/L, volume = 1 mL; $[Na(NO_3)]$ = 1 mol/L, volume = 40 mL; pH = 3.0, temperature = 25° C, weight of polymer = 25 mg.

[b] Related to the amount of metal ions taken up at the state of equilibrium assumed to be established in 24 h and assumed to be 100%.

well resolved, no attempt was made to analyze them. As expected, Zn(II) and UO_2^{2+} polychelates are found to be diamagnetic and the Mn(II) chelate shows a magnetic moment lower than that required for a spin value only.

A typical TG thermogram of Cu(II) polychelate is shown in Fig. 2. Examination of the TG thermograms of all the polymeric chelates reveals that like the parent polymer, each polymeric chelate degrades above 250° C in two stages. The rate of decomposition of the chelates is more than that of the parent polymer. The polymeric chelate is comparatively thermally less stable than the parent polymer. It seems that metal ions accelerate decomposition of the polymeric chelate [11].

Ion-Exchanging Properties

Influence of Electrolytes on the Metal Uptake

Examination of the data presented in Table 4 reveals that the amount of metal ions taken up by a given amount of BSF-2 polymer depends upon the nature and concentration of the electrolyte present in the solution. The amount of each of the Fe(III), Cu(II), and UO_2^{2+} ions taken up by the polymer sample increases with an increase in

TABLE 6. Distribution Ratios, D,[a] of Different Metal Ions as a Function of the pH

	Distribution ratio,[a] mL/g, of the metal ions[b]					
pH	Cu(II)	Fe(III)	UO_2^{2+}	Co(II)	Mn(II)	Zn(II)
1.5	-	-	225	-	-	-
1.75	-	110	350	-	-	-
2.0	-	150	430	-	-	-
2.5	-	370	490	-	-	-
3.0	110	790	2255	-	130	-
4.0	210	-	-	16	210	80
5.0	475	-	-	80	280	125
6.0	2265	-	-	290	335	235

$$^{a}D = \frac{\text{meq of metal ions taken up by 1 g of polymer sample}}{\text{meq of metal ions present in 1 mL of the solution phase}}$$

$[Mt(NO_3)_2]$ = 0.1 mol/L, Volume = 1 mL; weight of polymer sample = 25 mg; $[NaNO_3]$ = 1 mol/L, Volume = 44 mL; temperature = 25°C, time = 24 h (equilibrium state).

[b] Error ± 5%.

the concentration of ions like chloride, chlorate, and nitrate but decreases with an increase in the concentration of the sulfate ions. The amount of each of the three remaining ions, Co(II), Mn(II), and Zn(II), taken by the polymer sample decreases with an increase in the concentration of chlorate, chloride, nitrate, and sulfate ions. DeGeiso et al. [2] have reported that absorption of Fe(III) ion by salicylic acid-formaldehyde (SF) polymer increases with an increase in the concentration of chloride, chlorate, and nitrate ions but decreases with an increase in the concentration of sulfate and acetate ions.

Rate of Metal Uptake

The rates of metal absorption by BSF-2 polymer were measured for Fe(III), UO_2^{2+}, Cu(II), and Mn(II) ions in the presence of 1 M $NaNO_3$ to determine the time required to reach equilibrium. All experiments were carried out at pH 3. Examination of the results presented in Table 5 shows that UO_2^{2+} and Fe(III) ions required slightly more than 3 h for the establishment of equilibrium and Cu(II) and Mn(II) ions required about 5 h for the purpose. In the experiments with solution containing UO_2^{2+} and Fe(III) ions, more than 70% of equilibrium was established in the first hour. This study reveals that the rate of uptake of metal ions follows the order: UO_2^{2+}, Fe(III) > Cu(II) > Mn(II). The rates of uptake of metal ions, viz., Zn(II) and Co(II), have been found to be very low at pH 3. Hence the values are not reported.

It is interesting to note that similar behavior was observed by DeGeiso et al. [2] in a study with SF polymer.

Distribution Ratios of Metal Ions at Different pH Values

The results described in Table 6 reveal that the amount of metal ion taken up by polymer sample BSF-2 at equilibrium increases with an increase in the pH at which the study is carried out. The selectivity of the polymer sample for UO_2^{2+} and Fe(III) ions is higher than that for the remaining metal ions. The distribution ratio for Fe(III) ions is lower than that for UO_2^{2+} by about 1550 units at pH 3. On the basis of such a study with SF polymer, DeGeiso et al. [2] reported that the distribution ratio of UO_2^{2+} ion is more than that for Fe(III) ion by about 9000 units at pH 3. The lower value of the distribution ratio for Fe(III) ions may be attributed to steric hindrance. The formation of the chelate of Fe(III) requires its attachment with proper sites on three different polymer chains and that of the UO_2^{2+} ion requires such an attachment with sites on two polymer chains [2]. Among the remaining metal ions, Cu(II) ions have high value of distribution ratio at pH 6 while the other three metal ions, Co(II), Zn(II), and Mn(II), have low distributions over the pH range from 4 to 6.

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