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p-Hydroxybenzoic Acid-Urea-Formaldehyde Copolymers and Their Ion-Exchange Properties

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ABSTRACT

Copolymers (PUF) were synthesized by the condensation of p-hydroxybenzoic acid (P), urea (U), and formaldehyde (F), in the presence of different acidic catalysts and using varied molar ratios of reacting monomers. One of the copolymers having the highest molecular weight was fractionated. Copolymer compositions have been determined on the basis of their elemental analysis and conductometric titrations in the nonaqueous phase. Molecular weights (\bar{M}_n) have been estimated by VPO.

Copolymer prepared by using the stoichiometric properties of the monomers and HCl as catalyst furnished the highest molecular weight (\bar{M}_n). The viscosity measurements carried out in DMF indicate normal behavior. TGA and DSC data were analyzed to compare the relative thermal stability and estimate the characteristic parameters. IR spectra were studied to elucidate the structure. Chelation ion-exchange properties have also been studied employing the batch equilibration method. The order of selectivity of metal ions by the copolymers is $\text{UO}_2^{2+} > \text{Fe}^{3+} > \text{Cu}^{2+} > \text{Co}^{2+}$.

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INTRODUCTION

Various hydroxybenzoic acid-formaldehyde copolymers have been reported to find use as ion exchangers [1-4]. A survey of the literature has revealed that copolymers can be prepared from a mixture of phenols or hydroxybenzoic acid, various amines, and formaldehyde [5-9]. However, no systematic work on the synthesis and characterization of these types of copolymers seems to have been done. Taking into account the useful ion-exchange properties of these types of polymers, we earlier prepared and characterized salicylic acid-urea-formaldehyde copolymers (SUF) [5]. The ion-exchange studies of these copolymers have indicated that the presence of urea moiety in SUF copolymers improves the stability of ion-exchange resin in the presence of basic electrolytes. This led us to prepare new copolymers from *p*-hydroxybenzoic acid, urea, and formaldehyde.

The present report describes the synthesis and characterization along with the ion-exchange capacity of PUF copolymers. Condensation reactions of (P) and (U) with (F) have been investigated with a view to ascertaining the favorable conditions under which the condensation could be best effected. The condensation of (P) and (U) with formaldehyde was carried out in the presence of different acidic catalysts using varied molar proportions of the reactants. Copolymer sample PUF-1 was fractionated by fractional precipitation. The copolymer compositions have been determined by elemental analysis and conductometric titration in nonaqueous medium [10]. Copolymers were also characterized by molecular weight (\bar{M}_n),

intrinsic viscosity in DMF, and thermal (TGA, DSC) studies. IR spectra have been studied with a view to assigning the probable structure. The ion-exchange properties of selected copolymers have been investigated by the batch equilibration method [11]. The effect of various electrolytes on the selectivity of metal ions by the resin, the rate of metal uptake, and the distribution ratio of a given metal ion between the copolymer sample and a solution containing the metal ions were studied.

EXPERIMENTAL

Materials

All the chemicals used were of chemically pure grade or obtained from Sarabhai Merck Co. (India). DMF was used after distillation.

Preparation of Copolymers

The variations attempted in the condensation of (P) and (U) with (F) have been summarized in Table 1. Details of three typical methods are described below.

TABLE 1. Synthesis of Copolymers, Compositions of Copolymers, and IR Data

Copolymer	Mole ratio of reactant method ^b (P:U:F) ^a	Method	N% ^c by elemental analysis	Copolymer composition		Average molecular weight of repeating unit	Important IR frequencies	
				(P) unit	(U) unit		Wave number (cm ⁻¹)	Probable assignment
PUF-1	1:1:2	A	10.35 (11.76) ^d	0.552	0.448	114.75	1674(m) ^f	ν C=O
PUF-2	1.5:1:2.5	A	9.58 (8.84)	0.588	0.412	117.8	3200-3400(b) 1208(m)	Chelated -OH -OH bending (in plane)
PUF-3	2:1:3	A	8.24 (9.13)	0.654	0.345	122.94	900-1000(wb)	OH deformation (out of plane)
PUF-4	3:1:4	A	5.09 (5.93)	0.740	0.259	129.64	1545(w)	δ NH
PUF-4a	Fraction 1	-	10.50 (9.43)	0.569	0.430	116.31	2825, 2845(w)	ν CH of -CH ₂ -
PUF-4b	Fraction 2	-	9.52 (8.84)	0.588	0.411	117.79	1445, 1480(w)	δ CH of -CH ₂ -
PUF-4c	Fraction 3	-	8.14 (8.84)	0.635	0.365	121.38	940, 1135(w)	1, 3, 4, 5 substitution (in-plane bending)
PUF-5	1:1:1	A	8.14 (9.13)	0.614	0.385	119.8	851(m)	1, 3, 4, 5 substitution (out-of-plane bending)

(continued)

TABLE 1 (continued)

Copolymer	Mole ratio of reactant method ^b (P:U:F) ^a	Method	N% ^c by elemental analysis	Copolymer composition ^e		Average molecular weight of repeating unit	Important IR frequencies	
				(P) unit	(U) unit		Wave number (cm ⁻¹)	Probable assignment
PUF-6	1:1:4	A	8.83 (8.00)	0.634	0.365	121.38		
PUF-7	1:1:2	B	11.43 (12.34)	0.534	0.466	113.65		
PUF-8	1:1:2	C	10.96 (11.47)	0.516	0.483	112.17		

^a P = p-hydroxybenzoic acid, U = Urea, F = formaldehyde.

^b A = Condensation in the presence of 2 M HCl. B = Condensation in the presence of 2 M H₂SO₄. C = Condensation in the presence of glacial acetic acid.

^c N% by micro-Kjeldahl method; an error of nearly 2% in the reported value has been noted on an average.

^d N% by conductivity in pyridine against 0.02 M TBAH in pyridine.

^e Compositions are expressed in mole (m) ratios and obtained by the use of "N" estimation.

^f b = broad, m = medium, w = weak, wb = weak broad.

(A) Condensation of p-hydroxybenzoic acid and urea with formaldehyde in the presence of 2 M HCl: A mix of p-hydroxybenzoic acid (0.2 mol), urea (0.2 mol), 37% aq formaldehyde (0.4 mol), and 2 M HCl (200 mL) was heated at 100°C on an oil bath for 5 h with stirring. The solid product obtained was immediately removed from the flask as soon as the reaction period was over. It was washed with cold water, dried, and powdered. The powder was repeatedly washed with hot water to remove unreacted monomers. The air dried copolymer was Soxhlet extracted with ether to remove excess of (P) and p-hydroxybenzoic acid-formaldehyde (PF) copolymer which might be present along with PUF copolymer. For further purification it was dissolved in 8% NaOH and filtered (~30% insoluble). The yellowish product was precipitated by gradual addition of 1:1 (v/v) conc HCl/water with constant stirring. The copolymer was filtered, washed with hot water, dried in air, and kept in vacuum over silica gel; yield, 20.0 g.

(B) Condensation of p-hydroxybenzoic acid and urea with formaldehyde in the presence of 2 M H₂SO₄: A mix of p-hydroxybenzoic acid (0.03 mol), urea (0.03 mol), 37% aq formaldehyde (0.06 mol), and 2 M H₂SO₄ (30 mL) was heated on an oil bath for 5 h with stirring. The copolymer thus obtained was worked out and purified in the manner indicated above.

(C) Condensation of p-hydroxybenzoic acid and urea with formaldehyde in the presence of glacial acetic acid: A mix of p-hydroxybenzoic acid (0.1 mol), urea (0.1 mol), 37% aq formaldehyde (0.2 mol), and glacial acetic acid (120 mL) was heated on an oil bath for 5 h under stirring. Here glacial acetic acid acts as a solvent and catalyst. During the reaction period, no solid product appeared. The resulting solution was transferred into a 1-L beaker and it was just neutralized by aq NaHCO₃ to yield a yellowish brown product. It was filtered and washed with cold and then hot water. The product was purified in a manner similar to that described above in (A).

Fractionation

Copolymer sample PUF-1 (Table 1) was fractionated at 35°C by fractional precipitation method. Copolymer (10.0) was dissolved in DMF (500 mL). The solution was filtered through a sintered glass Grade-2 funnel into a 1-L round-bottom flask and in this solution 1 M aq HCl was added slowly with constant stirring. The turbid solution was allowed to set for 1 h and then heated to just dissolve the turbidity and cooled to room temperature. 1M HCl was again added in slight excess. The flask was then kept by a thermostat at 35°C for overnight. The pasty mass thus obtained was separated by filtration and dissolved in 8% NaOH and again filtered through a sintered G-2 funnel. The fraction was reprecipitated by adding 1:1 (v/v) conc HCl/water, washed with water, and dried to yield 2.8 g. The second and third fractions were collected in a similar manner by adding about 375

and 450 mL of 1 M HCl to the first and second filterings, respectively. The second and third fractions collected were 3.5 and 2.3 g, respectively.

Ion-Exchanging Properties

The purified copolymer samples PUF-1 and PUF-4 were finely powdered to pass a 300-mesh screen and used in all experiments carried out in an ion-exchange study. We have adopted the batch equilibration method [11]. The details of the procedure for different types of studies in the selectivity of different metal ions by the above copolymers are similar to those reported earlier from this laboratory [12].

Measurements

Copolymer compositions of all the copolymers per 100 g of copolymer were determined by nitrogen estimation and conductometric titration in nonaqueous medium [10]. The number-average molecular weights (\bar{M}_n) of the copolymers have been estimated with a Hewlett Packard vapor pressure osmometer using DMF as a solvent and benzil as a calibrant at 71°C. The intrinsic viscosities of the copolymers were measured in DMF at 35°C using an Ubbelohde viscometer. The TG and DSC thermograms were recorded on a Linseis Thermal Analyser (West Germany) and a Du Pont Analyzer (U.S.A.), respectively. IR spectra in KBr disks were run on a UR-10 spectrophotometer.

RESULTS AND DISCUSSION

All the copolymers were yellow to brown in color. The purified copolymers were soluble in DMF, pyridine, aq hydrogen carbonate, and aq sodium and potassium hydroxide. The melting points of copolymers were found to be in the range 210-250°C. The results obtained for copolymer composition by nitrogen estimation and conductometric method [10] were in good agreement (Table 1). On the basis of N % in the copolymers, copolymer compositions can be calculated if the comonomer does not contain N. With the known N %, the total number of moles (P) of urea repeating unit (A) in 100 g of copolymer is given by

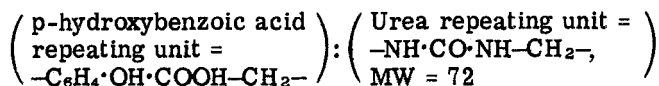
$$P = N \% + 28$$

Therefore, % of urea repeating unit in the copolymer is $P \times 72\%$

and % of comonomer repeating unit in the copolymer is $100 - (P \times 72)\%$. Thus it can be said that, the number of moles (Q) of p-hydroxybenzoic acid unit (B) would be

$$\frac{100 - (P \times 72)}{\text{molecular mass of B}}$$

Hence copolymer composition can be given by the molar proportion:



per 100 g of copolymer. Conductometric titrations were carried out in pyridine against standard tetra-n-butylammonium hydroxide in pyridine. The results are presented in Table 1. Plots of specific conductance vs mmole of titrant base added for 100 g of copolymer were made. The plot showed a specific neutralization giving distinct breaks [10]. The last peak gave the mole composition of p-hydroxybenzoic acid unit per 100 g of copolymer, which can be utilized to determine the copolymer composition by a method of calculation similar to that described above. The results of mole compositions established by quantitative analysis and conductometric titration are in close agreement. Thus meq/100 g of copolymer obtained by conductometric titration and copolymer composition by "N" estimation are comparable within limits of experimental error (Tables 1 and 2). It has been revealed from copolymer composition results that the copolymers prepared in the presence of dilute HCl or dilute H₂SO₄ and having molar ratios of 1:1 and 3:2 of p-hydroxybenzoic acid to urea have almost the same composition.

The results of conductometric titration were used to determine the number-average molecular weights of the copolymers. Examination of the conductometric titration curves revealed that there were several breaks in the plot of specific conductance against mmoles of titrant base added for 100 g of copolymer. From these plots, the first breaks and the last breaks (Table 2) were noted. The first break was the smallest of all the breaks observed in a given plot. It was assumed that this corresponded to a stage in titration when on an average one COOH group of each chain was neutralized. The titration curves indicated a sharp stepwise increase in the conductance till the stage of neutralization of all the COOH groups. Beyond this stage there was almost a continuous increase in the conductance. The degrees of polymerization (\overline{DP}) of the copolymer samples were obtained from the ratio of total milliequivalents of base for neutralization of all COOH groups to the milliequivalents for neutralization

TABLE 2. Molecular Weight Determination

Copolymer	Conductometric titration ^a					VPO ^c	
	First stage of neutralization (meq/100 g of copolymer)	Final stage of neutralization (meq/100 g of copolymer) obs (calc) ^b	DP	Molecular weight ($\bar{M}_n \pm 5\%$)	$\bar{M}_n \pm 5-10\%$		DP
PUF-1	35	465 (480)	13.28	1525	1670	14.55	
PUF-2	50	515 (500)	10.30	1213	1126	9.55	
PUF-3	55	510 (530)	9.27	1140	1030	8.37	
PUF-4	70	765 (570)	8.07	1046	950	7.32	
PUF-4a	27	505 (490)	18.70	2175	2346	20.17	
PUF-4b	50	515 (500)	10.30	1213	1135	9.63	
PUF-4c	65	515 (520)	7.92	961	1012	8.33	
PUF-5	50	510 (510)	10.20	1222	1235	10.30	
PUF-6	45	530 (520)	11.77	1430	1538	12.67	
PUF-7	40	455 (470)	11.37	1293	1415	12.45	
PUF-8	45	470 (460)	10.40	1172	1240	11.05	

^aIn pyridine against 0.02 M tetrabutylammonium hydroxide in pyridine.

^bCalculated from N estimation.

^cIn DMF at 71°C.

of first COOH group (first break). The value of \overline{DP} was multiplied by the average molecular weight of the repeating unit (Table 1) to give the number-average molecular weight (Table 2).

With a view to providing additional support to the results of conductometric titration used for molecular weight, the molecular weights of copolymers were also estimated by vapor pressure osmometry. Examination of these data presented in Table 2 reveals that the molecular weights of samples estimated by conductometric titration and the VPO method are comparable within the limits of experimental error.

The estimation of the number-average molecular weight (\overline{M}_n) of copolymers (Table 2) revealed the following trends:

1. The copolymers synthesized from equimolar proportions of (P) and (U) have comparatively higher molecular weight in the series. The use of formaldehyde more or less than the stoichiometric proportion gave low molecular weight copolymers.
2. There is no significant difference in the molecular weights of the copolymers prepared in the presence of dilute HCl or H₂SO₄.
3. Glacial acetic acid catalyzed copolymer has the lowest molecular weight among the copolymers prepared. The results of viscosity measurements (Table 3) indicate the normal behavior for all the copolymers.

The viscometric measurements were carried out at five different concentrations ranging from 3 to 1.52%. The reduced viscosity of a 3% solution of copolymer sample 1 is 0.0875 dL/g; it is decreased by about 12.14% when the concentration of the solution is reduced to 1.152%. Intrinsic viscosities ($[\eta]$) were determined by the following Huggin (Eq. 1) and Kramer (Eq. 2) relations:

$$\eta_{sp}/c = [\eta] + k_1[\eta]^2C \quad (1)$$

$$\ln \eta_r/c = [\eta] - k_2[\eta]^2C \quad (2)$$

The values of $[\eta]$ obtained from both the relations were in good agreement. The values of constants k_1 and k_2 determined from the slope of the respective graphs in most of the cases satisfy the condition of the relation $k_1 + k_2 = 0.5$ favorably [13]. To examine the behavior of copolymers in solution, the intrinsic viscosities and molecular weights of copolymer PUF-1 and its fractions were correlated by the Mark-Houwink equation, $[\eta] = k\overline{M}^\alpha$. The relation established is

$$[\eta] = 9.66 \times 10^{-6} [\overline{M}_n]^{1.275}$$

TABLE 3. Molecular Weight and Viscometric Data

Copolymer	Intrinsic viscosity, [η] $\times 10^2$ ^a (dL/g)	Huggin constant, k_1	Kramer constant, k_2	$k_1 + k_2$
PUF-1	8.75	0.658	-0.122	0.536
PUF-2	7.30	0.680	-0.133	0.547
PUF-3	7.15	1.224	-0.627	0.596
PUF-4	7.05	0.716	-0.168	0.548
PUF-4a	16.60	0.266	-0.281	0.547
PUF-4b	7.30	0.863	-0.314	0.548
PUF-4c	6.70	0.904	-0.332	0.572
PUF-5	6.95	0.585	-0.080	0.505
PUF-6	8.65	0.629	-0.074	0.554
PUF-7	8.25	1.085	-0.495	0.590
PUF-8	7.50	1.100	-0.61	0.49

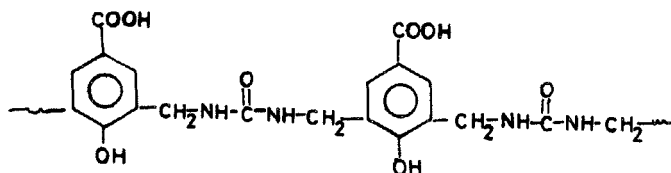
^aIn DMF at 35°C.

The copolymer having higher M_n in the series indicated higher intrinsic viscosity.

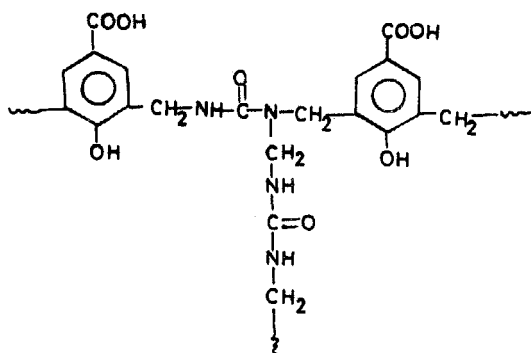
From IR spectral studies it has been revealed that all the copolymers give rise to nearly similar spectra. The IR spectral data for typical copolymer PUF-1 are listed in Table 1. A broad band containing several inflections appearing in the region $2400-3400\text{ cm}^{-1}$ may be assigned to the stretching vibration of $-\text{OH}$ of the polymeric associated phenolic group [14] and the intermolecular bonding between the hydroxyl group of $-\text{COOH}$ from different acid units in a polymeric chain. The absorption bands at 1445 and 1480 cm^{-1} represent $-\text{CH}$ bending modes of the $-\text{CH}_2-$ bridge. The bands obtained in the range $1200-1300\text{ cm}^{-1}$ also confirm the $-\text{CH}_2-$ bridge [14]. Since the region $2800-3000\text{ cm}^{-1}$ is overlapped by the stretching frequency of $-\text{OH}$ and aromatic ring stretching vibrations, it is rather difficult to interpret this region with respect to the $-\text{CH}_2-$ bridge. However, inflections obtained at 2825 and 2845 cm^{-1} may be due to stretching of $-\text{CH}$ of the $-\text{CH}_2-$ bridge. A sharp peak at 1600 cm^{-1} may be ascribed to aromatic skeletal ring breathing modes. The band displayed at 1675 cm^{-1} may be due to the stretching vibration of $\text{C}=\text{O}$ of both the acid and urea molecules. 1,2,3,5-tetrasubstitution [14] of the aromatic acid ring is recognized from bands appearing at 940 , 1134 , 1172 , and 1220 cm^{-1} due to the bending mode of $-\text{CH}$ (in-plane) and 851 cm^{-1} due to the bending mode of $-\text{CH}$ (out-of-plane). The presence of $-\text{NH}$ in urea is difficult to assign as the region for the stretching vibration of $-\text{NH}$ is rendered complex due to chelated $-\text{OH}$. However, the medium broad band at ~ 3400 may be due to $-\text{NH}$ of urea unit.

The copolymers in the present study contain two repeating units; hence it is rather difficult to assign an exact structure to them. However, taking into account all the above evidence and considering the linear structure of p-hydroxy benzoic acid-formaldehyde polymer and the linear branched structure of urea-formaldehyde polymer, the most probable structure for the copolymers may be a linear or a sparse-branched linear structure as shown on the following page.

To evaluate the thermal stability and ascertain the characteristic parameters, TGA and DSC measurements of selected copolymers have been carried out (Table 4). The copolymers prepared from a higher molar ratio of (p) showed a lower rate of decomposition, indicating higher thermal stability of copolymers prepared from equal molar ratios. This may be due to the possibility of an almost linear structure in the copolymer having a higher molar ratio of (p) which may give rise to a stable configuration to the polymer chain. This is supported by the higher melting point value of the copolymer. Weight loss in all the copolymers starts after $\sim 60^\circ\text{C}$ and occurs in two stages. The initial and final decomposition ranges are summarized in Table 4. Parts of the initial losses may be due to solvent or moisture entrapped in the copolymer. The Broido method [15] was applied to the TG data to determine the energy of activation and the order of the reaction. The comparative values of glass transition temperatures (T_g) and melting points (Table 4) of the copolymers show



OR



(1)

the highest values for PUF-3. All the copolymers have two glass transition temperatures and a melting point. Most of the copolymer samples start decomposing just after melting.

Ion-Exchanging Properties

With a view to ascertaining the selectivity of the copolymers (PUF-4 and PUF-1) for the selected metal ions, we have studied the influence of various electrolytes on the selectivity of metal ion, the rate of metal uptake, and the distribution ratio of metal ion between the copolymer and solution containing metal ions.

Effect of Electrolytes on the Metal Uptake

We examined the influence of ClO_4^- , NO_3^- , Cl^- , and SO_4^{2-} at various concentrations on position of the equilibrium of metal polymer interaction. Perusal of the data given in Table 5 reveals that the amount of Cu^{2+} , UO_2^{2+} , and Fe^{3+} taken up by PUF-1 and PUF-4 copolymer samples increases with increasing concentration of ClO_4^- , NO_3^- , and Cl^- and decreases with increasing concentration of SO_4^{2-} .

TABLE 4. TG^a and DSC^b Analysis of Copolymers

Copolymer	Weight loss at temperature T (°C), %					Decomposition temperature range (°C)	Energy of activation ^c E* (kcal/mol)	Order of reaction (n)	DSC		
	100	200	300	400	500				600	T _{g1} (°C)	T _{g2} (°C)
PUF-1	10.10	42.42	60.60	78.78	80.80	80.80	6.640	1	87	179	212
						160-280	2.830	1			
						280-480	4.915	1			
PUF-2	8.03	18.75	37.94	46.87	58.03	70.08	1.849	1	90	188	234
						180-300	4.714	1			
						300-620	2.773	1			
PUF-3	1.58	8.73	31.37	46.82	63.49	67.46	5.832	1	81	204	243
						240-560	3.399	1			
PUF-5	2.23	8.95	20.15	66.41	82.83	82.83	4.648	1	88	176	206
						300-640	9.152	1			
PUF-6	6.08	12.17	26.08	50.43	61.73	81.73	2.953	1	86	161	206
						180-620	5.07	1			
PUF-8	5.58	11.76	22.05	52.94	61.76	61.76	6.795	1	-	-	-
						300-460	4.172	1			

^a Heating rate, 10°C/min in air.^b Heating rate, 20°C/min.^c Brodico method.^d T_g, glass transition temperature.

TABLE 5. Evaluation of the Effect of Different Electrolytes in the Uptake of Several Metal Ions. $Mt(NO_3)_2 = 0.1 \text{ mol/L}^a$

Metal ion	Electrolyte (mol/L)	pH	Weight in meq $\times 10$ of the metal ion uptake in the presence of			
			NaClO ₄	NaNO ₃	NaCl	Na ₂ SO ₄
Cu ²⁺	1.00	5.0	0.2 ^b (0.15) ^c	0.16 (0.13)	0.18 (0.12)	0.11 (0.09)
	0.50		0.18 (0.14)	0.16 (0.12)	0.17 (0.12)	0.12 (0.09)
	0.10		0.13 (0.12)	0.13 (0.10)	0.15 (0.10)	0.15 (0.11)
	0.05		0.12 (0.10)	0.11 (0.09)	0.12 (0.10)	0.16 (0.12)
UO ₂ ²⁺	1.00	4.0	0.30 (0.23)	0.25 (0.16)	0.27 (0.19)	0.16 (0.10)
	0.50		0.29 (0.21)	0.23 (0.15)	0.27 (0.18)	0.17 (0.12)
	0.10		0.24 (0.20)	0.18 (0.13)	0.23 (0.15)	0.23 (0.15)
	0.05		0.22 (0.18)	0.17 (0.12)	0.20 (0.13)	0.24 (0.15)
Fe ³⁺	1.0	2.0	0.29 (0.2)	0.20 (0.14)	0.21 (0.15)	0.12 (0.11)
	0.5		0.27 (0.19)	0.19 (0.12)	0.20 (0.14)	0.15 (0.13)
	0.10		0.25 (0.15)	0.14 (0.09)	0.15 (0.11)	0.19 (0.14)
	0.05		0.21 (0.14)	0.12 (0.08)	0.12 (0.09)	0.19 (0.15)
Co ²⁺	1.0	5.5	0.03 (-)	- (-)	0.03 (-)	0.01 (-)
	5.0		0.03 (0.03)	0.03 (0.02)	0.04 (0.03)	0.03 (0.02)
	0.10		0.07 (0.05)	0.05 (0.04)	0.07 (0.05)	0.04 (0.03)
	0.05		0.095 (0.07)	0.07 (0.06)	0.08 (0.06)	0.075 (0.06)

^aVolume of electrolyte solution: 44 mL, volume of metal ion solution: 0.1 mol/L, 1 mL; time: 24 h, room temperature.
^bPUF-4.
^cPUF-1.

TABLE 6. Comparison of the Rates of Metal (Mt) Ion Uptake^a

Metal ion	Percentage of metal ion uptake ^b at different times (h)							
	0.5	1	2	3	4	5	6	7
Cu ²⁺	60 ^c (58) ^d	64 (63)	70 (70)	73 (72)	85 (82)	90 (93)	97 (96)	97 (96)
UO ₂ ²⁺	55 (58)	49 (60)	65 (65)	70 (73)	80 (82)	84 (85)	96 (97)	96 (97)
Fe ³⁺	40 (43)	53 (52)	60 (63)	67 (70)	75 (78)	80 (85)	95 (96)	95 (96)
Co ²⁺	28 (23)	30 (35)	45 (48)	65 (65)	72 (75)	84 (85)	98 (97)	98 (97)

^aMt(NO₃)₂ = 0.1 mol/L; volume: 1 mL; NaNO₃ = 1 mol/L; volume: 44 mL for Cu²⁺, Fe³⁺ and UO₂²⁺ ions. NaNO₃ = 0.01 mol/L; volume: 44 mL for Co²⁺ ion. pH: 5 for Cu²⁺; 2.0 for Fe³⁺; 4.0 for UO₂²⁺ and 5.5 for Co²⁺. Room temperature.

^b Amount of metal ion adsorbed × 100

Amount of metal ion adsorbed at equilibrium

cPUF-4.

dPUF-1.

TABLE 7. Distribution Ratios D^a of Different Metal Ions as a Function of the pH

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	5.5	
Cu^{2+}	-	-	-	-	-	55.6 ^b (36.7) ^c	178.0 (114.8)	368.6 (280.9)	-	-
UO_2^{2+}	-	-	74.0 (36.7)	-	245.4 (156.5)	450.0 (199.9)	648.9 (293.0)	-	-	-
Fe^{3+}	192 (74.9)	275 (156.5)	395.1 (317.6)	599 (395.1)	-	-	-	-	-	-
Co^{2+}	-	-	-	-	-	-	36.7 (36.7)	114.8 (55.6)	156.5 (114.8)	-

^a Amount of metal on the copolymer \times $\frac{\text{volume of solution}}{\text{weight of copolymer}}$.

$D = \frac{\text{Amount of metal in the solution}}{\text{Amount of metal on the copolymer}}$.

$\text{M}(\text{NO}_3)_2 = 0.1 \text{ mol/L}$; volume: 1 mL; $\text{NaNO}_3 = 1 \text{ mol/L}$; volume: 44 mL for Cu^{2+} , UO_2^{2+} , and Fe^{3+} ; $\text{NaNO}_3 = 0.01 \text{ mol/L}$; volume 44 mL for Co^{2+} . Room temperature. Time: 24 h (equilibrium state).

^b PUF-4.

^c PUF-1.

[3], whereas uptake of Co^{2+} ion by the above copolymers increases with decreasing concentration of ClO_4^- , NO_3^- , Cl^- , and SO_4^{2-} . This may be explained in terms of stability constants [12] of the chelates with these copolymers. Sulfate might form rather strong chelates with Fe^{3+} , UO_2^{2+} , and Cu^{2+} ions, while perchlorate, nitrate, and chloride might form weak chelates and therefore might not be expected to influence the position of the Fe^{3+} , UO_2^{2+} , and Cu^{2+} chelates equilibrium as much as sulfate. This type of trend has also been observed by other investigators in this field [3, 12]. The amount of metal uptake is more in PUF-4 than in PUF-1. However, in comparison to the molar ratios of P:U in both the copolymers, the amount adsorbed by PUF-4 is relatively lower than what should be adsorbed. This may be explained by assuming the possibility of a chain structure branched to some extent which would help in bringing the chelating groups of [P] units nearer, thereby adsorbing more metal ions than expected.

In the case of Co^{2+} ion selectivity, it was observed that the higher pH was not suitable when concentrated electrolytes were used. The effect was much more predominant in PUF-4 than in PUF-1 copolymer. Hence it can be said that a copolymer containing a higher molar ratio of P:U is less stable with respect to solubility in concentrated electrolyte solution at higher pH. Thus it may be concluded that the higher the concentration of urea in a copolymer improves, to some extent, the stability of the copolymer when used as an ion-exchanger.

Rate of Metal Uptake

Table 6 shows the dependence of the rate of metal ion uptake on the nature of the metal. Keeping in view the stability of copolymers under study, it was not possible to study the rate of metal uptake at higher pH and in the same concentration of electrolytes. The rate of uptake of Cu^{2+} during the first hour in both copolymers is more than of other metal ions in the study. The shortest time to reach equilibrium is ~ 5 h for Cu^{2+} , Fe^{3+} , and UO_2^{2+} while Co^{2+} requires ~ 6 h for equilibration. The rate of metal ion uptake follows the order $\text{Cu}^{2+} > \text{UO}_2^{2+} > \text{Fe}^{3+} > \text{Co}^{2+}$ for both copolymers.

Distribution Ratios of Metal Ions at Different pH

The effect of pH on the amount of metal ion distributed between two phases can be explained by the results shown in Table 7. The results indicate that the relative amount of metal ions taken up by the copolymer 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. Both copolymers take up UO_2^{2+} more selectively than any other metal ion under study. The order of selectivity of metal ions by the copolymers is $\text{UO}_2^{2+} >$

$\text{Fe}^{3+} > \text{Cu}^{2+} > \text{Co}^{2+}$. The results of this type of study are helpful in selecting the optimum pH for a selective uptake of a particular metal ion from a mixture of different metal ions.

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