

Chelation ion-exchange properties of 2,2'-dihydroxybiphenyl-urea-formaldehyde (2:1:3) resin

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The resin 2,2'-dihydroxybiphenyl-urea-formaldehyde [BPhUF], has been synthesized by the condensation of 2,2'-dihydroxybiphenyl [BPh] and urea [U] with formaldehyde [F] in 2:1:3 molar ratio in presence of 2M HCl as a catalyst. UV-Vis, IR and NMR spectral studies have been carried out to elucidate the structure of resin. Ion exchange properties of this resin have been studied by batch equilibrium method for Fe³⁺, Cu²⁺, Ni²⁺, Co²⁺, Zn²⁺, Cd²⁺ and Pb²⁺ ions over the pH range, 1.5 to 6.5 and in media of various ionic strengths. In presence of chloride and nitrate ions, the uptake of Fe³⁺, Cu²⁺ and Ni²⁺ ions increases with increasing concentration of electrolyte while for Co²⁺, Zn²⁺, Cd²⁺ and Pb²⁺ ions, it decreases with increasing concentration of chloride, nitrate and sulphate ions. The resin shows a higher selectivity for Fe³⁺ ion over any other ion. Study of distribution ratio as a function of pH indicates that the amount of metal ion taken up by resin increases with the increasing pH of the medium.

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The study of polymeric resins has attracted the attention of many researchers because of their versatile practical applications, viz., as ion exchangers, high-energy materials, electronic devices, etc. Among these, ion exchangers play an important role in pollution control, in antibiotic purification, analytical chemistry, hydrometallurgy, separation of radioisotopes and in large-scale water treatment. Various polymers derived from hydroxy compounds, urea and formaldehyde have been reported in literature^{1,2}. In our laboratory, extensive work on synthesis and characterization of polymeric resins and their application as ion-exchanger, high energy material, coordination polymer etc. have been undertaken^{3,4}. In continuation to our earlier work, we report herein the synthesis, characterization and ion exchange properties of 2,2'-dihydroxybiphenyl-urea-formaldehyde resin.

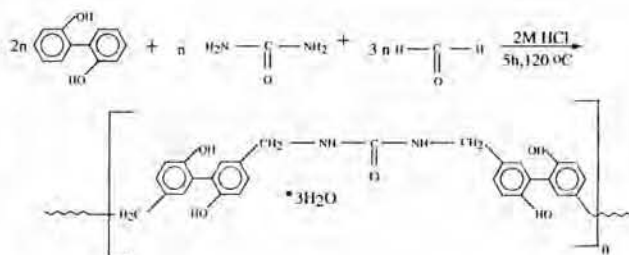
Experimental

The chemicals used were of AR or chemically pure grade. DMF and DMSO were used after double distillation.

Preparation of BPhUF resin

The BPhUF resin was prepared by condensing 2,2'-dihydroxybiphenyl (7.6 gm, 0.04 mol) with urea (1.252 gm, 0.02 mol) and formaldehyde (5.1 ml of 35% solution, 0.06 mol) in presence of 2 M HCl (100 ml) as a catalyst at 120 ± 2°C in an oil bath for 5 h^{4,5} (Scheme 1). The faint pink coloured resin 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 resin was purified by dissolving in 8% NaOH solution and filtered. The polymer 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 resin was finely ground to pass through a 300-mesh size sieve and kept in vacuum over silica. The yield of resin was found to be 89%.

The resin was subject to microanalysis for C, H, N on a Perkin-Elmer analyzer. The number average molecular weight ($\bar{M}_n$) was determined by conductometric titration in DMF using KOH in 50% (v/v) DMF alcohol mixture as the titrant^{4,6}. Electronic absorption spectrum of the resin in DMF was recorded on a Shimadzu double beam spectrophotometer in the range of 190-700 nm. Infrared spectrum of the BPhUF resin was recorded on a Nicolet Magna 550 IR spectrophotometer in KBr



Scheme 1

pellets in the region of 4000-400 cm^{-1} . ^1H NMR spectrum was recorded on a Varian - VXR - 300S 300 MHz proton NMR spectrophotometer using $\text{DMSO}-d_6$ as a solvent.

The ion-exchange properties of the BPhUF resin were determined by the batch equilibrium method^{2,4}.

Determination of metal uptake in the presence of various electrolytes

The resin 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 0.1 M HNO_3 or 0.1 M NaOH . The suspension was stirred for 24 h at 25°C. To this suspension, 2 ml of 0.1 M solution of the metal ion was added and the pH was adjusted. The mixture was again stirred at 25°C for 24 h and filtered. The solid was washed and the filtrate and washings were combined. The metal ion content was determined by titration against standard EDTA. The amount of metal ion uptake of the polymer was calculated from the difference between a blank experiment without polymer and the reading in the actual experiments. The experiment was repeated in the presence of several electrolytes.

Rate of metal uptake

In order to estimate the time required to reach the state of equilibrium under the given experimental conditions, a series of experiments were carried out, in which the metal ion uptake by the chelating resins was determined at time intervals of 1 hour at 25°C (in the presence of 25 ml of 1 M NaNO_3 solution). It was assumed that under the given conditions, the state of equilibrium was established within 24 h. The rate of metal uptake is expressed as percentage of the amount of metal ions taken up after a certain time related to that at the state of equilibrium.

Distribution of metal ions at different pH

The distribution of each one of the seven metal ions studied, i.e. Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , Cd^{2+} , Pb^{2+} and Fe^{3+} , between the polymer phase and the aqueous phase was determined at 25°C in the presence of a 1 M NaNO_3 solution. The experiments were carried out as described above at different pH values. The distribution ratio (D) is defined by the following relationship: $D = [\text{Wt. (in mg) of metal ions taken up by 1 g of polymer}] / [\text{Wt. (in mg) of metal ions present in 1 mL of solution}]$.

Results and discussion

The resin, which has been used in the present investigation, was prepared by the reaction as shown in Scheme 1.

The newly synthesized purified BPhUF resin was found to be faint pink in colour, and soluble in DMF, DMSO and insoluble in almost all organic solvents and concentrated acids. The resin was analysed for carbon, hydrogen and nitrogen contents. [Found (calc) %: C = 64.43(64.37); H = 5.73 (5.75); N = 5.40 (5.36)]. Decomposition temperature of the polymer was found to be above 400°C.

Characterisation of resin

The molecular weight ($\bar{M}_n$) of the resin was determined by non-aqueous conductometric titration in DMF against KOH in 50% (v/v) DMF alcohol mixture using 50 mg of sample⁶. A plot of the specific conductance versus the milliequivalents of potassium hydroxide required for neutralization of 100 g of polymer shows that there are many breaks in the plot. The first and the last break were noted at 5 and 560. $\bar{M}_n$ was calculated based on the following considerations^{4,14}: (i) the first break corresponds to neutralization of the more acidic phenolic hydroxy group of all the repeating units, and, (ii) the break in the plot beyond which a continuous increase is observed represents the stage at which phenolic hydroxy groups of all repeating units are neutralized. On the basis of the average degree of polymerization, D_p , is given by the following relation: $D_p = (\text{Total meq of base required for complete neutralization}) / (\text{meq of base required for smallest interval})$.

The average molecular weight ($\bar{M}_n$) was obtained by multiplying the D_p by the formula weight of the repeating unit and found to be 58464.

The UV-visible spectrum of BPhUF resin in pure DMF was recorded in the region 190-700 nm at a scan rate of 100 nm min^{-1} and chart speed of 5 cm min^{-1} . The resin sample displayed two characteristic bands at 295 and 330 nm. The intense band at 295 nm is due to ($\pi \rightarrow \pi^*$) allowed transition of biphenyl moiety, which readily attains coplanarity, and the shoulder-merging (loss of fine structure) band at 330 nm may be due to ($n \rightarrow \pi^*$) forbidden transition in saturated aliphatic carbonyl compounds⁷. The bathochromic shift from the basic value, viz., 252 nm and 270 nm respectively, may be due to combined effect of conjugation and phenolic hydroxy group (auxochrome)⁷, or it may be due to conversion of phenol to corresponding anion.

IR spectral study, shows a broad band in the region $3750\text{--}3200\text{ cm}^{-1}$ which may be assigned to the stretching vibrations of phenolic hydroxy group, -NH groups and intermolecular hydrogen bonding existing between different polymer chains^{7,8}. The band at 1645 cm^{-1} may be due the stretching vibrations of $>\text{C}=\text{O}$ group of substituted urea or amide moiety^{7,8}. The bands at 1500 cm^{-1} and 635 cm^{-1} may be assigned to -NH-stretching, bending and deformation out-of-plane vibrations of the urea moiety in the resin respectively^{7,8}. The band at 1581 cm^{-1} may be ascribed to aromatic skeletal ring^{7,8}. The bands at 2936 cm^{-1} , 1442 cm^{-1} , 1347 cm^{-1} and 761 cm^{-1} may be assigned to stretching, bending, wagging, and rocking vibrations respectively of methylene bridges (-CH₂-) in the polymeric chain^{7,8}. The band at 1225 cm^{-1} may be due to $>\text{C}=\text{O}$ stretch of polymeric phenol⁷. The band at 900 cm^{-1} may be due to one isolated H-atom situated between two substituents.

¹H NMR of the resin in DMSO-*d*₆ shows a triplet in the region 6.9-7.20 δ ppm which may be due to aromatic protons^{7,9}. Since the resin possesses three benzenoid hydrogen, three types of coupling are exhibited: (i) hydrogen adjacent to OH group gives a doublet due to *o*-coupling. The *p*-coupling is very small in this case and thus it manifest itself only a small broadening of doublet; (ii) the hydrogen flanked between two substituents is at lowest field and gives doublet due to small metacoupling; and, (iii) the third hydrogen atom adjacent to -CH₂- substituent on ring displays double of doublet due to simultaneous coupling to both H-atom (*o*-coupling and *m*-coupling).

A weak doublet appears in the region 6.2-6.4 (δ) ppm which may be assigned to proton of phenolic -OH group involved in hydrogen bonding or intermediate proton exchange reaction or Ar-OH polymeric association^{7,10}. A broad signal at 9.0-9.2 (δ) ppm shows intramolecular hydrogen bonding of -NH-CO-group or intermediate proton exchange of reaction of both phenolic -OH group^{7,10}. A weak signal at 5.8-5.9 (δ) ppm may be due to protons of -NH-bridge^{7,10,11}. The signal at 4.1 to 4.2 (δ) ppm may be assigned to methylenic protons of Ar-CH₂-NH-CO-moiety^{7,10}. A signal in the region 3.8-3.9 (δ) ppm may be due to methylenic protons of Ar-CH₂-Ar. On the basis of the nature and reactive positions of the monomers, elemental analysis, electronic, IR, NMR spectra and molecular weight, the most probable structures have been proposed for resins as shown in Scheme 1.

Table 1—Influence of different electrolytes on the uptake of several metal ions on BPhUF resin at room temperature. $[\text{M}(\text{NO}_3)_2] = 0.1\text{ mol/l}$, vol. = 2 ml; vol. of electrolyte solution = 25 ml; wt of resin = 25 mg; time = 24 h. pH: Fe³⁺ = 2.5; Cu²⁺, Ni²⁺, Pb²⁺ = 4.5, Co²⁺, Zn²⁺ = 5, Cd²⁺ = 6].

Metal ion	Electrolyte (mol L ⁻¹)	Metal ion uptake (mg) in presence of		
		NaCl	NaNO ₃	Na ₂ SO ₄
Fe ³⁺	0.01	0.37	1.18	2.47
	0.05	0.82	1.59	2.36
	0.1	1.70	1.90	1.41
	0.5	2.10	2.31	0.98
	1.0	2.82	2.62	0.59
Cu ²⁺	0.01	2.92	1.52	4.85
	0.05	3.33	2.34	3.98
	0.1	3.97	3.63	2.81
	0.5	4.79	4.38	1.99
	1.0	5.20	5.11	0.29
Ni ²⁺	0.01	3.13	1.25	4.54
	0.05	4.27	2.21	3.53
	0.1	4.43	3.4	2.28
	0.5	5.08	4.82	1.46
	1.0	5.99	5.89	0.62
Co ²⁺	0.01	2.06	1.97	1.85
	0.05	1.30	1.31	1.53
	0.1	1.19	1.68	1.15
	0.5	0.55	1.01	0.83
	1.0	0.49	0.51	0.28
Zn ²⁺	0.01	2.83	2.28	1.8
	0.05	2.29	1.86	1.68
	0.1	1.62	1.51	0.90
	0.5	0.90	0.96	0.66
	1.0	0.36	0.66	0.42
Cd ²⁺	0.01	1.87	2.1	1.86
	0.05	1.03	1.35	1.55
	0.1	0.96	1.28	1.15
	0.5	0.62	0.97	0.57
	1.0	0.45	0.53	0.26
Pb ²⁺	0.01	1.49	1.90	-
	0.05	1.41	1.52	-
	0.1	1.30	1.14	-
	0.5	0.90	0.76	-
	1.0	0.61	0.32	-

Table 2—Comparison of the rate of metal ion uptake of BPhUF resin at room temperature. $[\text{M}(\text{NO}_3)_2] = 0.1\text{ mol/L}$, vol. = 2 ml; $\text{NaNO}_3 = 1.0\text{ mol/l}$, vol. of $\text{NaNO}_3 = 25\text{ ml}$

Metal ion	Metal ions uptake (%) up at different times (h)						
	1	2	3	4	5	6	7
Fe ³⁺	68	83	91	98	-	-	-
Cu ²⁺	48	61	66	84	96	-	-
Ni ²⁺	37	58	64	83	94	-	-
Co ²⁺	38	57	64	84	94	-	-
Zn ²⁺	38	58	63	83	94	-	-
Cd ²⁺	-	25	30	47	63	76	86
Pb ²⁺	-	-	21	32	41	64	84

Metal ion uptake = $\frac{(\text{amount of metal ion absorbed} \times 100)}{\text{amount of metal ion at equilibrium}}$

Table 3—Distribution ratio (D) of different metal ions as a function of the pH of BPhUF resin at room temperature. [(M(NO₃)₂) = 0.1 mol/L, vol. = 2 ml; NaNO₃ = 1.0 mol/L, vol. = 25 ml; time = 24 h (equilibrium state)]

Metal ion	D at different pH s									
	1.5	1.75	2.0	2.5	3.0	3.5	4	5	6	6.5
Fe ³⁺	22.64	162.72	304.2	426.0						
Cu ²⁺					122.9	226.1	415.4	627.3	1477.9	1793.0
Ni ²⁺					147.4	309.4	442.2	715.2	1488.8	1532.6
Co ²⁺					67.6	128.4	177.0	232.4	304.0	310.8
Zn ²⁺					58.7	130.4	163.0	202.1	391.2	286.9
Cd ²⁺					50.8	47.8	116.0	210.3	232.0	232.0
Pb ²⁺					38.0	67.5	101.2	181.4	223.6	227.8

Effect of electrolytes on the metal uptake

We examined the influence of varying concentrations of NO₃⁻, Cl⁻ and SO₄²⁻ on the equilibrium of metal resin interaction. Table 1 shows that the amount of metal ions taken up by a given amount of resin depends on the nature and concentration of the electrolyte present in the solution. In the presence of chloride and nitrate ions, the uptake of Fe³⁺, Cu²⁺ and Ni²⁺ ions increases with increasing concentration of the electrolytes, whereas in presence of sulphate ions, the amount of the above mentioned ions taken up by resin decreases with increasing concentration of electrolyte. Moreover, the amount of Co²⁺, Zn²⁺, Cd²⁺ and Pb²⁺ ions decreases with increasing concentration of chloride, nitrate and sulphate ions^{12,13,14}. This may be explained on the basis of stability constants of metal ion complex formed¹⁵.

Rate of metal ion uptake

The rate of metal adsorption was determined to find the shortest time period required to attain equilibrium. Rate refers to the change in the concentration of the metal ions in the aqueous solution which is in contact with the given polymer. The results (Table 2) show that the time taken for the uptake of the different metal ions at a given stage depends on the nature of the metal ion. It is found that Fe³⁺ requires about 4 h to reaching equilibrium, whereas Cu²⁺, Ni²⁺, Co²⁺ and Zn²⁺ require about 5 h. The rate of metal ion uptake follows the order: Fe³⁺ > Cu²⁺ > Ni²⁺ = Co²⁺ = Zn²⁺ > Cd²⁺ > Pb²⁺ for BPhUF resin.

Distribution ratio of metal ion at different pH

Studies on the effect of pH on the amount of metal ions distributed between two phases indicate that the relative amount of metal ions taken up by the BPhUF resin increases with increasing pH of the medium¹²⁻¹⁵

(Table 3). The magnitude of increase, however, is different for different metal ions. The BPhUF resin takes up Fe³⁺ more selectively than any other metal ions under study. The order of distribution ratio of metal ions measured in the pH range 2.5 to 6.5 is found to be: Fe³⁺ > Cu²⁺ > Ni²⁺ > Co²⁺ > Zn²⁺ > Cd²⁺ > Pb²⁺.

Results given in Table 3 are helpful in selecting the optimum pH for a selective uptake of a particular metal ion from a mixture of different metal ions. For example, the results suggest the optimum pH 3 for the separation of Pb²⁺ and Ni²⁺ using the resin with the distribution ratio 38.0 and 147.4 respectively.

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