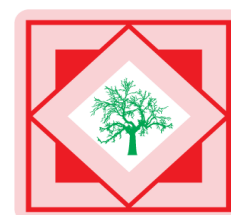




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Ion-exchange properties of terpolymer resin-II derived from p-hydroxybenzaldehyde, urea and ethylene glycol

Amit N. Gupta

Department of Applied Chemistry, JD College of Engineering and Management, Nagpur, India

ABSTRACT

Ion-exchange resin abbreviated as HBUE-II was synthesized by polycondensation of p-hydroxybenzaldehyde (0.2M) and urea (0.1M) with ethylene glycol (0.4M) in the presence of polyphosphoric acid as a catalyst. The chelating ion-exchange property of resin was studied by batch equilibrium method. The metal ions were estimated spectrophotometrically over a wide pH range and in media of various ionic strengths. The HBUE-II resin was found to be higher selective chelating ion-exchange resin for Sb^{3+} , Bi^{3+} and Zn^{2+} than Mg^{2+} ions.

Keywords: ion-exchange; batch equilibrium method; distribution ratio.

INTRODUCTION

Chelating polymers have been more significance, due to their applications in water technology such as ravage water treatment, metal recovery from dilute solutions, pollution control, antibiotic purification and separation of radioisotopes [1-2]. In the earlier communication from this department a number of such terpolymers have been reported [3-5]. However, no work has been carried out on terpolymer resin from p-hydroxybenzaldehyde, urea and ethylene glycol monomers.

MATERIALS AND METHODS

A terpolymer resin abbreviated as HBUE-II was prepared by polycondensation of monomers p-hydroxybenzaldehyde (0.2M), urea (0.1M) and ethylene glycol (0.4M) in presence of polyphosphoric acid as a catalyst in oil bath at 120 ± 2 °C temperature for 5 hrs. The reddish brown solid crude product was separated, washed, filtered dried and squeezed with ether so as to remove impurity. 82 % yield was found.

RESULTS AND DISCUSSION

Elemental analysis has been carried out by analytical functional testing Vario MICRO CHN elemental analyzer. The elemental analysis of HBUE-II terpolymer resin as follows- Found: C, 67.31; H, 6.01; N, 6.77 Calc. for $C_{23}H_{25}O_5N_2$: C, 67.48; H, 6.11; N, 6.85%. Molecular weight of repeating unit and degree of polymerization of HBUE-II were found to be 409 and 18 respectively. The number average molecular weight was found to be 7362 by non-aqueous conductometric titration in DMSO using 0.1M KOH in absolute alcohol as titrant [6].

IR spectrum of HBUE-II terpolymer resin is shown in Figure 1. IR absorption of HBUE-II terpolymer resin was as follows: $\nu_{\max}/\text{cm}^{-1}$ 3570m (N-H stretching - secondary amide group), 3430b (phenolic -OH group with intermolecular hydrogen bonding), 2744w and 2916m (-C-H- stretching in the aldehyde, doublet due to Fermi resonance), 1685m (C=O amide, amide-I band), 1655s (C=O band, aldehyde), 1598m (aromatic ring), 1561m (N-H bending), 1344m (aldehydic C-H bending), 1298w and 1284m (C-N stretching band in -CONH- group), 1220m, 1095m and 961w (1, 2, 3, 5- tetra substitution of aromatic ring), 830w ($\text{-CH}_2\text{-}$ wagging) [7].

Inset of Figure 1 shows ultraviolet-visible spectra of HBUE-II terpolymer sample. The HBUE-II terpolymer sample displayed two characteristic broad bands at 280-320 and 210-265 nm. Observed positions for the absorption bands indicate the presence of a carbonyl ($>\text{C=O}$) group having a carbon-oxygen double bond which is in conjugation with aromatic nucleus. The latter band (more intense) can be accounted for by a $\pi-\pi^*$ transitions while the former band (less intense) due to $n-\pi^*$ transitions. The bathochromic shift (shift towards longer wave length) from the basic values of the C=O group viz. 320 and 240 nm respectively due to the combined effect of conjugation and phenolic hydroxyl group (auxochrome) [8].

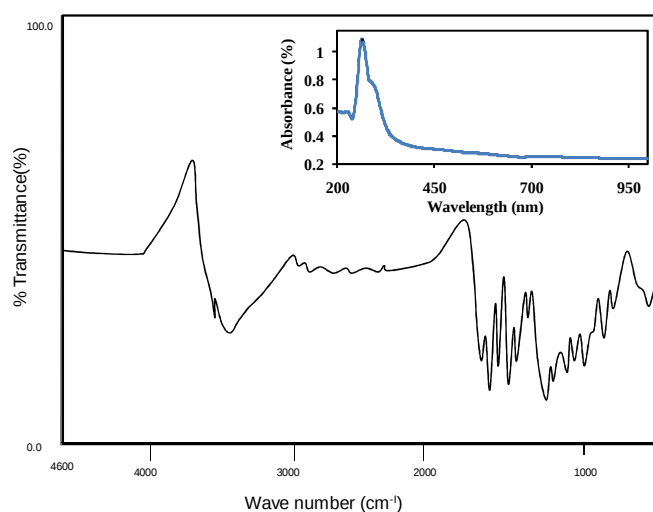


Figure 1 IR-spectra of HBUE-II terpolymer resin and inset shows UV-Visible spectra

The ^1H NMR spectrum of HBUE-II terpolymer is presented in Figure 2. The δ in the range 1.3 ppm was of $\text{-CH}_2\text{-}$ in HBUE-II. The signal at 2.48 δ ppm was due to $\text{-CH}_2\text{-NH}$ in polymer resin. The signal at 2.60 δ ppm was due to DMSO solvent. Signal at 3.40 δ ppm was assigned to secondary amine proton in terpolymer. Signal at 3.80 δ ppm was attributed to CH-OH moiety. The signal at 6.95 δ ppm was due to aromatic ring protons in HBUE-II. Signal at 7.2 δ ppm was due to C-NH in HBUE-II terpolymer. Weak signal 9.4 δ ppm was due the aldehydic proton [8].

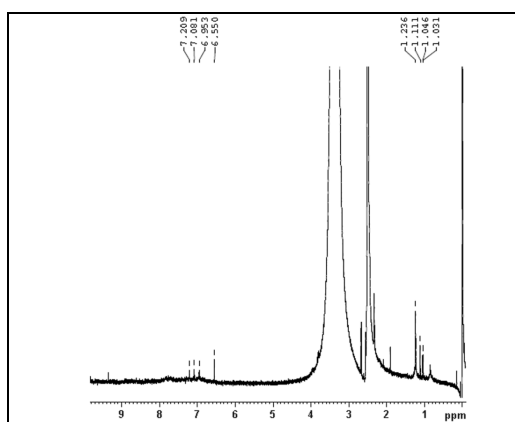


Figure 2 ^1H NMR spectra of HBUE-II terpolymer resin

To ascertain the selectivity of HBUE-II, The ion-exchange properties of resin were studied with reference to the influence of various electrolytes, the rate of metal ions uptake and distribution of metal ions between the resin and solution. The results of ion-exchange properties of HBUE-II terpolymer resin is presented in table 1 and in Figure 3.

Effect of electrolyte on metal ions uptake is summarized in table 1. The inspection of the data reveals that the amount of metal ions taken up in the presence of NaNO_3 is larger than NaCl , Na_2SO_4 and NaClO_4 . For the metal ions Sb^{3+} , Bi^{3+} , Mg^{2+} , Zn^{2+} , the exchange capacity increases with increases in the concentration of NO_3^- , ClO_4^- and Cl^- , whereas it decreases with increases in concentration of SO_4^{2-} . This is due to the fact that metal ions under study form kinetically more inert compound with respect to SO_4^{2-} as compared to metal-resin interaction. On a contrary increase in the metal exchange capacity of metal resin in the presence of NO_3^- , ClO_4^- and Cl^- attributed to high kinetically inert metal-resin interaction as compared to metal-electrolyte interactions [9].

Table 1 Effect of different electrolytes on the uptake of several metal ions on HBUE-II resin

Metal ions	Electrolyte		NaNO_3	NaCl	Na_2SO_4	NaClO_4
	Conc.					
Sb^{3+}	0.25		19.25	20.62	23.56	17.46
	0.50		20.54	22.17	22.24	17.75
	0.75		22.93	23.23	20.85	18.88
	1.00		23.97	24.12	19.42	20.16
	1.25		25.86	24.82	17.97	21.79
	1.50		26.62	25.97	16.31	22.46
Bi^{3+}	0.25		10.83	11.78	14.81	9.92
	0.50		11.11	12.43	13.53	11.37
	0.75		12.26	13.56	12.55	12.71
	1.00		13.74	14.28	10.33	13.54
	1.25		15.74	15.51	9.30	15.62
	1.50		17.62	16.97	8.49	16.56
Mg^{2+}	0.25		7.58	6.92	9.03	6.74
	0.50		7.94	7.58	8.52	7.29
	0.75		8.49	8.10	7.68	7.76
	1.00		9.07	8.68	7.15	8.29
	1.25		9.54	9.23	6.93	8.85
	1.50		9.98	9.51	6.75	9.11
Zn^{2+}	0.25		2.81	1.30	7.65	2.50
	0.50		4.60	3.26	7.24	3.99
	0.75		6.21	4.64	6.98	5.50
	1.00		8.00	6.24	6.68	7.72
	1.25		9.75	7.50	6.24	9.32
	1.50		10.85	9.01	6.04	10.19
Metal nitrate solution = 0.1 Mol/l, 5ml; Electrolyte= 25 ml; Equilibrium state= 24hrs; Wt. of resin=25 mg; Temperature = Room Temperature; Metal ions were estimated spectrophotometrically; Error= $\pm 1.5\%$.						

It was assumed that the equilibrium state was established within 24 hrs. The rate of metal ions uptake was expressed in terms of percent metal ions uptake related to a state of equilibrium by the formula (1). Here metal ion uptake was estimated as a function of time in hrs in the presence of 1.5 M NaNO_3 solution (25 ml).

$$\% \text{ metal uptake} = \frac{\text{mg of metal sorbed in given time}}{\text{mg of metal sorbed in 24hrs}} \times 100 \quad \dots (1)$$

From the graph present in figure 3, initially the rate of metal uptake was steeply increased, become gradual and finally remain constant as the time passes for all metal ions. For Sb^{3+} and Mg^{2+} the equilibrium was reached within 7 hours whereas for Bi^{3+} and Zn^{2+} , the time required to reach equilibrium was 6 hrs. The rates of metal ions uptake for trivalent metal ions (Bi^{3+} and Sb^{3+} ions) were higher than divalent metal ions (Mg^{2+} and Zn^{2+} ions) [10]. The order of the rate of metal ion uptake was as $\text{Bi}^{3+} > \text{Sb}^{3+} > \text{Zn}^{2+} > \text{Mg}^{2+}$.

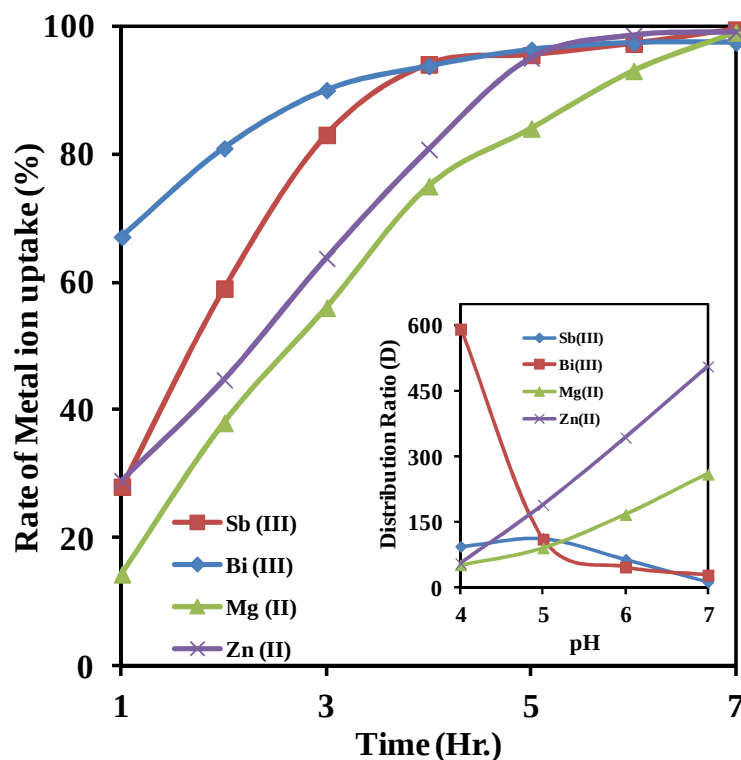


Figure 3 Rate of metal ion uptake as a function of time. Inset shows distribution ratio as function of pH

The resin sample (25 mg) of HBUE-II was allowed to swell for 24 hours in 1.5 M NaNO_3 solution. The pH was adjusted to the required value using 0.1 M HNO_3 or 0.1M NaOH solution. 5mL of 0.1 M metal nitrate solution was added. The pH was maintained again and stirred for 24 hrs. Metal ions were estimated spectrophotometrically to determine the distribution ratio between polymer phase and solution phase [10]. The distribution ratio (D) was calculated by the formula (2),

$$D = \frac{\text{weight (mg) of metal ions taken up by 1gm of polymer}}{\text{weight (mg) of metal ions present in 1ml of solution}} \quad \text{..... (2)}$$

The effect of pH on a distribution ratio of metal ions between resin and solution phase can be explained by inset graph of figure 3. The study was carried out in the limit of higher pH in order to prevent hydrolysis of metal ions. Distribution ratios for Mg^{2+} and Zn^{2+} ions were found to increase with increases in pH values. However reverse effect of pH was observed on distribution ratios for Sb^{3+} and Bi^{3+} ions.

The order of distribution ratio values decreases as $\text{Bi}^{3+} > \text{Sb}^{3+} > \text{Zn}^{2+} > \text{Mg}^{2+}$ at pH 4.0. At pH 5.0, the order of distribution ratio as follows $\text{Zn}^{2+} > \text{Sb}^{3+} > \text{Bi}^{3+} > \text{Mg}^{2+}$. At pH 6.0 and at pH 7.0, HBUE-II resin was the same order as $\text{Zn}^{2+} > \text{Mg}^{2+} > \text{Bi}^{3+} > \text{Sb}^{3+}$.

CONCLUSION

The data of elemental analysis, UV-Visible spectra, IR spectra and ^1H NMR spectra supports the structure of HBUE-II terpolymeric resin. Among the electrolytes such as NaNO_3 , NaCl , NaClO_4 and Na_2SO_4 , the NaNO_3 are found to be more suitable electrolyte supporting to the ion exchange of metal ion under study by HBUE-II resin. Trivalent metal ion shows comparatively higher rates of metal ions uptake than divalent. This may be due to electrostatic assistance to ion exchange process. HBUE-II terpolymer resin is a selective chelating ion exchange resin for metals as Bi^{3+} ions at pH 4 and Zn^{2+} ions at pH 5 to 7 in the mixture of Sb^{3+} , Bi^{3+} , Mg^{2+} and Zn^{2+} metal ions. The HBUE-II resin may be used to separate Zn^{2+} and Bi^{3+} metal ions. Similarly it may be used to preconcentrate Sb^{3+} from the solution containing Sb^{3+} and Bi^{3+} .

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