New cation exchanger of poly(N-substituted phenylmaleimide) type

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Four gel type cation exchange resins have been prepared from the condensation product of maleic anhydride and *p*-aminobenzoic acid, i.e., 4-(2,5-dioxopyrrolin-1-yl) benzoic acid (DPBA): homopolymer of DPBA (A), copolymer with styrene (B), cross-linked polymer with divinyl benzene (DVB, 10wt%) (C) and condensation product of 4-aminobenzoic acid with poly (maleic anhydride-co-styrene) (D). The adsorption behaviour of these polymers has been investigated with different cations under various experimental conditions.

Ion exchangers are widely used in analytical chemistry, hydrometallurgy, antibiotic purification, and separation of radioisotopes, and finds large scale applications in water treatment and pollution control[1,2]. Various commercial exchangers have a polymeric base (styrene, acrylic acid, phenol-formaldehyde, etc.) with cationic or anionic units as the site of exchange. In view of rising costs of the polymers, the need exists for either preparing new, cheaper exchangers or finding an efficient substitute that can atleast partly replace the polymeric content of commercial ion exchangers without affecting properties like thermal stability and ion exchange capacity. The present work is an attempt in this direction.

Little attention seems to have been paid to the preparation of ion-exchange resins containing various ion-exchangeable groups on poly(N-phenylmaleimide) base. In an earlier publication[3], we had reported the synthesis and characterization of the cation-exchange resins having −COOH as functional group on poly(N-phenylmaleimide) matrix. The present work describes detailed ion-exchange study of the synthesized polymers (A-D) with transition metal ions.

Experimental

The polymers, viz. poly (DPBA) (A), poly (DPBA-co-styrene) (B), poly(DPBA-co-DVB) (C) and poly(DPBA-co-styrene-co-maleic anhydride) (D) were prepared as reported earlier[3]. A batch type equilibration procedure was used to determine the metal uptake from aqueous solution by the resin. The dried resin was ground to 100-150 mesh size powder and stirred with aqueous metal ion solution for a specified period of time under various conditions. The amount of metal ions in the supernatant was substracted from the amount initially added to give the amount of metal ion adsorbed by the resin[4].

Results and discussion

Table 1 summerizes the properties of various polymers. These polymers, containing −COOH as a functional group, were prepared by various routes. Polymers (A, B & D) are soluble in solvents like DMF, DMSO and aq. alkali, etc. To impart chemical stability, polymerization was carried out using DVB as cross-linking agent. The polymer with 10% DVB content was only found to be hydrolytically stable, and so it was studied in detail along with others.

Optimum pH of metal ion uptake

The effect of pH on the capacities of polymers (A-D) for the transition metal ions is shown in Fig.

Table 1 — Properties of polymers (A-D)

Polymer	Colour	N (%) [Expt.]	Softening point (°C)	Solubility	η, (DMF, 0.1M NaNO$_3$) dl.g^{-1} (30°C)
A	Cream	6.3	300	DMF, DMSO, dioxane, aq. alkali	0.02
B	Cream	3.99	230-240	DMF, DMSO, aq. alkali	0.20
C	Cream	3.79	300	Swells in DMF, aq. alkali	—
D	Light brown	4.9	191-210	DMF, cyclo-hexanone, aq. alkali	0.415

(1a-d). A mixture of polymer (50 mg), 40 ml of an electrolyte solution (1.0 M, NaNO$_3$) and 2 ml metal ion (0.1 M) solution was equilibrated for 24 hr at room temperature. The pH of the test solutions was adjusted prior to equilibration with the resin sample by adding dil. HNO$_3$ or NaOH. After equilibration and filtration, concentration of metal ion remaining in solution was determined by chelatometric titration[5].

From Fig. (1a-d), it can be seen that the adsorption of metal ion on the resin increases with the increase in pH of the solution with maxima in the pH range, 4-5. Under the experimental conditions, the selective adsorption of the various metal ions on polymers (A-D) at the pH 4.5 is in the following order:

A: $Cd^{2+} > Cu^{2+} > Ni^{2+} > Zn^{2+} > Pb^{2+}$

B: $Cd^{2+} > Ni^{2+} > Cu^{2+} > Pb^{2+} > Zn^{2+}$

C: $Cd^{2+} > Pb^{2+} > Ni^{2+} > Cu^{2+} > Zn^{2+}$

D: $Cd^{2+} > Pb^{2+} > Ni^{2+} > Cu^{2+} > Zn^{2+}$

The above trend suggests that all the polymers (A-D) selectively adsorb Cd^{2+} ion over other metal ions and polymer A has the highest metal exchange capacity. The resins B and C are more brittle and harder than resins A and D, since both contain higher content of benzene units in the backbone chain. As a result, resins B and C undergo lesser swelling in aqueous solution as compared to resins A and D, and thus possess lower metal adsorption capacity. This clearly suggests that adsorption capacity of metal ions is not only affected by the ion exchange capacity of the resins but also by the extent of swelling in aqueous media.

Influence of contact time on adsorption

A mixture of polymer (50 mg), 40 ml of an electrolyte solution (1.0 M NaNO$_3$) and metal ion (2 ml, 0.1 M) was equilibrated for different periods of time and then capacity was determined in each case. The metal ion adsorbed was calculated in % against the time, (hr) for all the metal ions under study. It is seen that the time needed for almost complete saturation
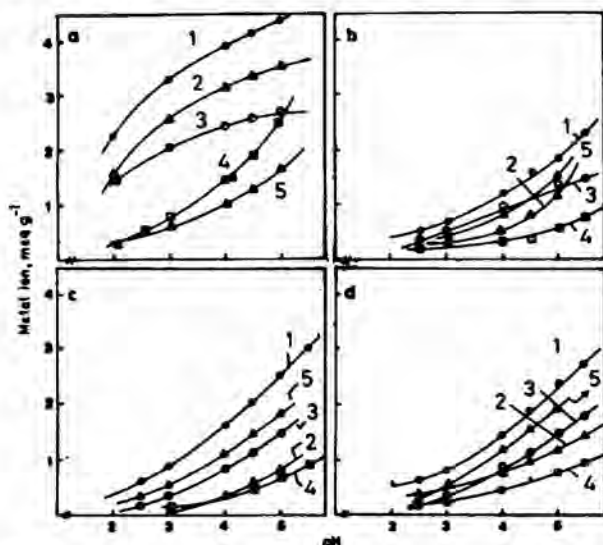

Fig. 1—Effect of pH on the capacities of the polymers for the heavy metal ions: (a), polymer A; (b), polymer B; (c) polymer C; and (d), polymer D [1, ●, Cd^{2+}; 2, △, Cu^{2+}; 3, ○, Ni^{2+}; 4, □, Zn^{2+}; 5, ▲, Pb^{2+}].

Table 2—Comparison of the rates of cation uptake by polymer A-B[a]

Time, hr	Polymer	Metal ion adsorbed[b], %					
		Ni^{2+}	Cu^{2+}	Zn^{2+}	Pb^{2+}	Cd^{2+}	Fe^{3+}
0.5	A	16	7	15	56	29	47
	(B)	(23)	(29)	(9)	(35)	(20)	(58.5)
1	A	23	14	22	72	36	56
	(B)	(29)	(37)	(14)	(59)	(34)	(70.2)
2	A	31	29.5	55	81	80	80
	(B)	(46)	(53)	(37)	(73)	(52)	(87.2)
3	A	46	41	72	90	87	97
	(B)	(69)	(59)	(54)	(83)	(69)	(100)
5	A	79	70	89	97	98	100
	(B)	(78)	(69)	(73)	(97)	(86)	—
7	A	100	90	100	100	100	—
	(B)	(88)	(83)	(100)	(100)	(98)	—
9	A	100	100	100	100	100	—
	(B)	(99)	(95)	(100)	(100)	(100)	—

[a]Me(NO$_3$)$_2$ = 0.1 mol/1,2 ml; NaNO$_3$ = 1 mol/lit, 40 ml; pH = 2.5 for Fe^{3+} and pH = 4.5 for all other cations.
[b]Related to the amount of metal ions in the state of equilibrium, 24 hr (100%).

Table 3—Comparison of the rates of cation uptake by polymer C-D[a]

Time, hr	Polymer	Metal ion adsorbed[b], %					
		Ni^{2+}	Cu^{2+}	Zn^{2+}	Pb^{2+}	Cd^{2+}	Fe^{3+}
0.5	C	9.4	23	8.3	53.5	21.5	29.3
	(D)	(20.5)	(29.5)	(14.5)	(55.3)	(22.1)	(35.2)
1.0	C	20.0	36.7	13.7	73.0	54.0	40.2
	(D)	(37.0)	(37.5)	(35.1)	(69.5)	(45.6)	(62.8)
2.0	C	37.1	53.5	22.1	94.8	73.0	61.2
	(D)	(52.9)	(55.3)	(69.5)	(90.0)	(69.5)	(78.2)
3.0	C	56.5	72.2	55.3	98.0	86.0	100
	(D)	(72.2)	(83.8)	(86.5)	(98.0)	(86.8)	(98.9)
5.0	C	79.9	88.0	83.1	100	95.0	—
	(D)	(88.5)	(98.5)	(100)	(100)	(99.0)	—
7.0	C	97.0	90.1	97.7	100	100	—
	(D)	(98.0)	(100)	(100)	(100)	(100)	—

[a]$Me(NO_3)_2 = 0.1$ mol/lit, 2 ml; $NaNO_3 = 1$ mol/lit, 40 ml; $pH = 2.5$ for Fe^{3+} and $pH = 4.5$ for all other cations
[b]Related to the amount of metal ions in the state of equilibrium, 24 hr (100%).

Table 4—Distribution ratio (D) of metal ions as a function of pH for polymer-C.

pH	Distribution ratio, $D (mlg^{-1})$			
	Ca^{2+}	Ni^{2+}	Pb^{2+}	Cd^{2+}
3.0	19.8	89.9	62.2	107.2
4.0	60.6	137.9	152.2	205.4
4.5	71.1	166.7	200.0	279.3
5.0	81.0	211.8	225.6	305.1

Table 5—Separation of metal ions, using polymer-C

$Pb^{2+}:Ca^{2+}$	Amount of metal ions adsorbed, (mg)	
	Pb^{2+}	Ca^{2+}
0 :10	—	20.1
4 :6	52.1	16.5
5 :5	89.1	10.1
6 :4	120.2	5.4
10 :0	160.1	—

Polymer = 300 mg, metal ion solution = 50 ml, Conc. of total metal ions = 1.2 mmol

of the capacity of the polymer for metal ions is about 5-7 hr (Tables 2 and 3).

Distribution ratio of metal ions

The distribution of each metal ion, between polymer phase and aqueous phase, was determined at various pH and in presence of 1.0 M $NaNO_3$ solution at 30°C. The experiments were carried out as described earlier. Adsorbability of a metal ion on the resin can be expressed in terms of the distribution ratio, D, which is defined as:

$$D = \frac{\text{meq. of metal on the resin}}{\text{meq. of metal in the solution}} \times \frac{\text{volume of solution (ml)}}{\text{weight of resin (g)}}$$

Adsorption of cations generally increased with increasing pH studied upto pH 3.5 for Fe^{3+} and 5.5 for other metal ions to avoid hydroxide formation. This study is useful in selecting the optimum pH for selective adosrption of a particular metal ion from a mixture of metal ions. For example, from Table 4 it could be seen that at pH 4.5 the Pb^{2+} ions (D = 200) can be selectively separated from mixture with Ca^{2+} ion (D = 71.1).

It is reported that[6] using standard procedures, Pb^{2+} and Ca^{2+} ions could be separated from their mixture. Following this procedure the separation of Ca^{2+} ions from a mixture of Ca^{2+}-Pb^{2+} was carried out (Table 5). The results indicate that at about equal proportions of the two ions, Pb^{2+} gets adsorbed nine times as much as Ca^{2+} ions.

Acknowledgement

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