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NOVEL ION-EXCHANGE/COORDINATION RESIN WITH CARBOXYETHYL PHOSPHONATE LIGANDS

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Abstract—A novel ion-exchange/coordination resin containing carboxyethyl phosphonate ligands was obtained from vinylbenzyl chloride/styrene/divinylbenzene copolymer. Its properties (acid capacity, phosphorus content, water regain) and sorption of di- and trivalent cations were determined. The efficiency of metal cation removal was compared to that displayed by ethylenediphosphonate resins. It was found that carboxyethyl phosphonate based resin, being less acidic, displayed higher selectivity. The obtained log *D* for Cd(II), Zn(II), Ni(II) and Fe(III) were 2.81, 2.77, 1.05 and 2.43, respectively. The hydrophilicity of resins was increased by introducing sulfonic groups into their structure which had a negligible effect on kinetics of ion removal under studied conditions. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Many studies have been done in the field of synthesis and characterization of polymer-bound complexing agents. This area is of particular importance in polymer chemistry since such materials are being used as very convenient and selective ion-exchange/coordination resins [1, 2]. Resins with metal ions attached to them, either by ion-exchange or coordination bonds, are used as catalysts in organic chemistry and separation media in biotechnology.

The list of specific low molecular substances which have been attached to various polymer matrices is very long and includes multiketones [3, 4], oxine [5], heterocyclic formazanes [6] and pyrazole [7] to name a few. However, most of them are either weak acids or weak bases and the useful pH range is limited as was pointed out in [8]. To overcome this problem, new polymers with more acidic ligands have been synthesized [9, 10]. Both resin with diphosphonate ligands as part of the polymer backbone [9] and diphosphonate as the pendant group on vinylbenzylchloride mers [10] are active and retain ion-exchange/coordinating properties under acidic conditions. Further investigation was devoted to the role of adjacent groups in the selectivity of metal ion removal [11]. A polymer with diphosphonate groups obtained by polymerization of the functional monomer was also used as an effective catalyst [12]. The synthesis of such resins required either obtaining starting monomers or in the case of modification obtaining tetraalkyl phosphonates which are contaminated with trialkyl phosphonates $RP(O)(OR)_2$ and need purification.

Recently, other resins with phosphorus containing ligands attached to various matrices were studied in Mo(VI) removal [13].

The aim of this work is to obtain an ion-exchange/coordination resin using ethoxycarbonylethyl phosphonate which can be easily obtained from acrylic acid and triethyl phosphite [14] in a fast and efficient addition reaction with a negligible amount of side products. The properties of the obtained resin are to be determined and compared to properties of resins bearing ethylenediphosphonate and methylenediphosphonate ligands.

EXPERIMENTAL

A copolymer of vinylbenzylchloride (VBC), styrene (St) and technical divinylbenzene (DVB) was prepared by a suspension polymerization technique. 0.5 wt.% of benzoyl peroxide was used as initiator. The nominal crosslinking degree was 2 wt.%. Polymerization was carried out in the presence of dodecane equal to the amount of monomers. The obtained polymer was washed with hot water and acetone, dried and extracted with toluene in Soxhlet apparatus.

Diethyl ethoxycarbonylethyl phosphonate was obtained as described in [14]. The tetraethyl ester of methylenediphosphonic acid was prepared as described earlier [10]. The tetraisopropyl ester of 1,2-ethylenediphosphonic acid was prepared by reacting 18.7 g of 1,2-dibromoethane (0.1 mole) with 124.95 g of triisopropyl phosphite (0.6 mole, 3 times excess with respect to dibromide), and refluxing in round bottom flask for 24 hr. Vacuum distillation afforded the tetraisopropyl ester of 1,2-ethylenediphosphonic acid collected at 140–141°C/0.1 mm Hg yield 23.7 g (66%).

Ion-exchange resins were prepared by reacting the sodium derivative of diethyl ethoxycarbonylethyl phosphonate with VBC/St/DVB copolymer. Thus, 10 g of the above copolymer containing 46.8 mmol of Cl was reacted with 117 mmol of the sodium derivative of diethyl ethoxycarbonylethyl phosphonate in 150 mL of dry toluene at reflux for 20 hr. After such time, the resin was separated by filtration, washed with dioxane, dioxane/water and acetone. In similar reactions two other resins were obtained using the sodium derivative of the tetraisopropyl ester of 1,2-ethylenediphosphonate and the tetraisopropyl ester of methylenediphosphonate, respectively. They were coded 1, 2, and 3.

Such obtained resins were subsequently hydrolysed using concentrated hydrochloric acid. The polymers were refluxed in HCl for 20 hr. The only exception was the resin obtained from diethyl ethoxycarbonylethyl phosphonate (Resin 1), which was treated with bromotrimethylsilane, hydrolysed with water and subsequently with sodium hydroxide as described in [15]. All resins after hydrolysis were conditioned using 1 M sodium hydroxide, distilled water and 1 M hydrochloric acid.

Part of each resin was chlorosulfonated using 10 wt.% of chlorosulfonic acid in ethylene dichloride at RT. Thus, 5 g of the resin was swollen in 25 mL of the above solvent for 24 hr and then 25 mL of chlorosulfonic acid solution was added and the entire mixture kept in flask for 2 hr with occasional stirring. Next, the resin was separated on a glass filter, washed with ethylene dichloride, dioxane, dioxane/water and finally kept in 2 M sodium hydroxide solution overnight. Conditioning was done as in the case of hydrolysed resins. They were coded 1 S, 2 S, and 3 S.

In order to determine the sorption capacity of resins towards Zn(II), Cd(II), Ni(II), and Fe(III) they were contacted with 1×10^{-4} N metal salt solution in 0.01 M nitric acid. Resin equivalent to 0.1 meq of acid capacity was shaken with 10 mL of the appropiate solution for the desired time and the metal ion concentration was determined by atomic absorption on Varian 250+ spectrophotometer with the wavelength set at 213.9, 228.8, 232.0 and 248.3 nm, respectively.

In some experiments, resins were contacted with 1×10^{-4} N metal salt solutions in 0.1 M nitric acid and with the solutions of 1×10^{-4} N metal salt formulated with an excess of sodium cations (1×10^{-2} M $NaNO_3$).

The phosphorus content was measured by digesting a sample of resin in a perchloric acid solution and subsequent reaction with amidol and ammonium molybdate.

Water regain was determined by centrifuging off an excess of water from the swollen resin, drying the resin at 100°C for 24 hr and calculating as:

$$W = (m_w - m_d)/m_d$$

where m_w is the weight of swollen resin after centrifugation and m_d is the weight of resin after drying.

The acid capacity was determined by contacting approx. 1 g of water swollen resin in acid form with 100 mL of 0.1 M sodium hydroxide solution for 24 hr, then titrating an 50 mL aliquot with 0.05 M sulfuric acid solution.

RESULTS AND DISCUSSION

Modification of the VBC/St/DVB copolymer with the sodium salt of ethoxycarbonylethyl phosphonate and the sodium salt of 1,2-ethylenediphosphonate proceeded to almost same extent as was observed in the case of methylenediphosphonate [10]. After modification with the above compounds and before hydrolysis, precursors of resins 1 and 2 displayed phosphorus contents of 1.79 and 2.51 mmol/g, respectively. This corresponds to 77 and 60% yields, respectively. See Fig. 1 for the resin structures.

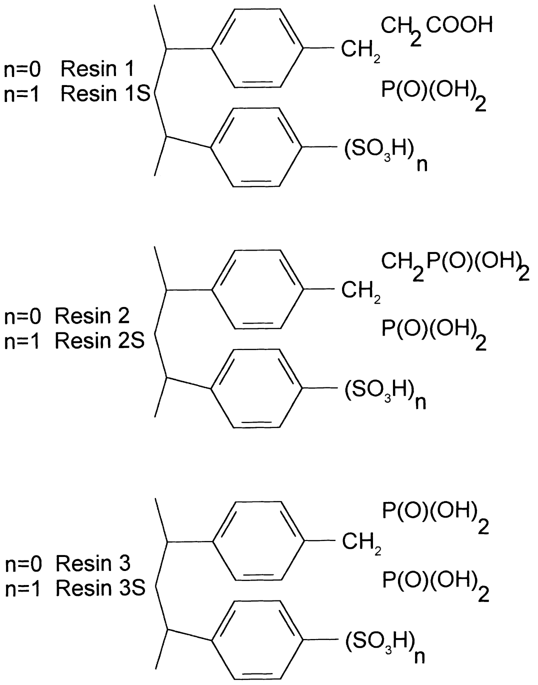

Fig. 1. Structure of resins.

The obtained resins with ligands in ester form were subjected to hydrolysis using concentrated hydrochloric acid. Only ethoxycarbonylethyl phosphonate was hydrolysed using a two-step procedure—reaction of phosphonate ester with bromotrimethylsilane and subsequent treatment with water in order to hydrolyse trimethylsilyl ester [16] followed by alkaline hydrolysis of carboxylate ester. Thus, the polymer with ethoxycarbonylethyl phosphonate was first reacted with an excess of bromotrimethylsilane in chloroform for 5 days at room temperature. The resulting trimethylsilyl ester of phosphonic acid was hydrolysed with water and subsequently the ester of carboxylic acid was hydrolysed with 3 M sodium hydroxide for 8 hr. Such a method caused no decarboxylation. As can be seen in Table 1, the acid capacity of the above resin (Resin 1) is almost (93% of theoretical value) three times higher than the phosphorus content.

Resins 2 and 3 (with ethylenediphosphonate and methylenediphosphonate, respectively) also display good agreement between acid and phosphorus capacities. In both cases they are almost theoretical. Resin 2 has a phosphorus content of 2.98 mmol/g and acid capacity two times higher—6.10 mmol/g. For Resin 3, the figures are 3.16 mmol/g and

Table 1. Characteristics of obtained ion-exchange resins

Resin	P capacity (mmol/g)	Acid capacity (mmol/g)	Water regain (g/g)
1	2.01	5.61	1.29
1S	1.49	8.21	2.42
2	2.98	6.10	1.42
2S	2.14	7.82	3.36
3	3.16	6.00	1.35
3S	2.35	7.68	2.87

6.00 mmol/g, respectively (see Table 1). This agrees with the results obtained in the case of lightly crosslinked polymer hydrolysis in [10]. The hydrophilicity of these resins, (measured as water regain) is moderate (1.29–1.42 g/g) and apparently depends on the number of acid groups. In order to increase the hydrophilicity and hence facilitate ion transport in beads, Resins 1–3 were subjected to chlorosulfonation in a solution of chlorosulfonic acid in ethylene dichloride giving Resins 1 S–3S. This reaction resulted in a sharp increase in the amount of water imbibed by the resins and a simultaneous increase of the acid capacity. For example, water regain of Resin 1 S is double that of Resin 1. The same trend is seen in the case of two other resins (2 and 2 S, 3 and 3 S). The phosphorus content decreases as a result of polymer net weight gain during reaction (Resins 1 S–3S).

All six resins were used in ion removal experiments. In order to determine the effect of water regain on the kinetics of ion-exchange/coordination, samples of solution were taken after 10, 20, 40, 60, 120 and 240 min contact time. As can be seen in Fig.2 there is no significant difference in the shape of log *D* vs. time curves for hydrolysed resins (Resins 1, 2 and 3) and for sulfonated resins (Resins 1 S, 2 S and 3 S). It means that under experimental conditions all resins have sufficient hydrophilicity and swelling. Ion uptake reaches equillibrium fast, in most cases in 40 min.

The distribution coefficients of Cd(II) and Zn(II) are approximately ten times higher for Resins 1 S–3S than for their counterparts 1–3. Even greater difference is seen for Ni(II) and Fe(III) where sulfonated polymers are 100 times more efficient. This effect is due to the presence of sulfonic groups

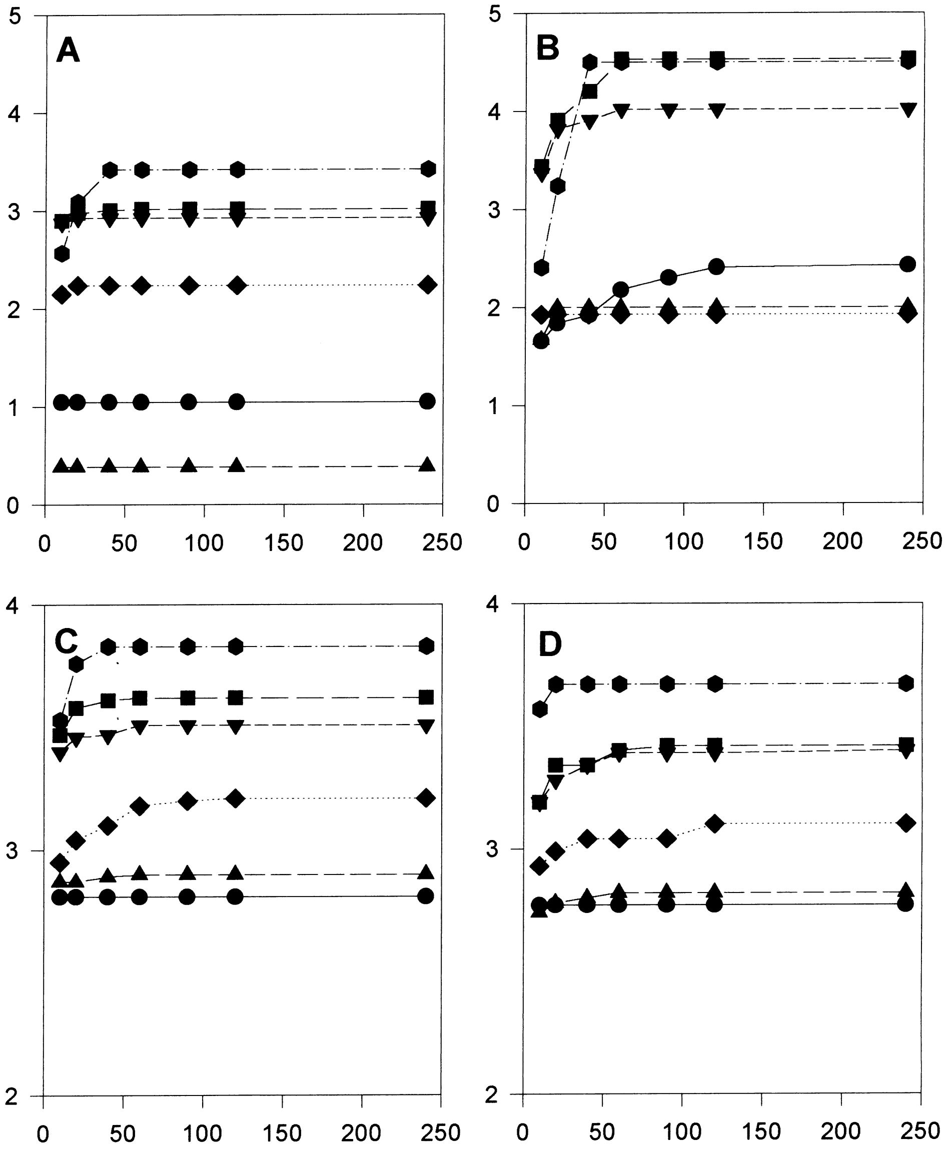

Fig. 2. Metal ion uptake by investigated resins: (a) Ni(II), (b) Fe(III), (c) Cd(II), (d) Zn(II).

Table 2. Zn(II) uptake as log *D* from various solutions

	1×10^{-4} N Zn (II) solution in:		
Resin	0.01 M nitric acid	0.1 M nitric acid	0.01 M nitric acid/0.01 M $NaNO_3$
1	2.77	0.88	2.54
1S	3.42	2.97	2.68
2	2.82	1.09	2.70
2S	3.40	2.91	2.72
3	3.10	2.33	3.04
3S	3.67	3.19	3.00

which are not only hydrophilic but also active in the ion-exchange process in 0.01 M nitric acid solution. When ion-exchange experiments are performed in 0.1 M nitric acid, increased acidity causes protonation of carboxylic and phosphonic groups in ligands resulting in a rapid decrease of log *D*. Values of log *D* obtained when 1×10^{-4} N Zn(II) in 0.1 M nitric acid was contacted with investigated resins are presented in Table 2.

It can be noted that the less acidic the ligand, the more significant the log *D* decrease drop for the hydrolysed resins. Resin 1 loses most of its capacity towards Zn(II)—log *D* drops to 0.88, whereas resins with more acidic diphosphonate ligands retain it to some extent. The resin with methylenediphosphonate (Resin 3) stays active towards Zn(II) ions in 0.1 M nitric acid; log *D* in this case decreases to 2.33. In the case of sulfonated resins, the decrease is only slight and probably a result of suppressed ion exchange on phosphonate ligands present in these resins. The decrease is similar in all cases and equal to about half a log unit. It is possible, however, to prove the potential usefulness of such sulfonated resins when solutions used for ion-exchange experiments are formulated with an excess of sodium cations. Thus, when 1×10^{-4} N Zn(II) in 0.01 M nitric acid is also 1×10^{-2} M Na(I), log *D* for hydrolysed resins is almost identical to log *D* obtained for Zn(II) in a solution free from Na(I), whereas for sulfonated resins log *D* decreases (Table 2). This decrease can be explained by the lack of selectivity of sulfonic groups, which are exchanging protons for cations present in high concentration—Na(I). Log *D* for Zn(II) under competitive conditions drops in the case of Resins 1 S, 2 S and 3 S. It can be expected that this effect will be even stronger when a higher concentration of balast metal ions is used.

Under competitive conditions, Resins 1, 2 and 3 show almost no decrease of log *D* for Zn(II). This means that carboxyethylphosphonate and diphosphonate ligands are selective towards the above cation. Thus, it can be concluded that the only purpose of the presence of sulfonate groups in the structure of Resins 1 S, 2 S and 3 S is to increase the hydrophilicity of the resins and by doing this providing better conditions for exchanging targeted ions by selective carboxyethyl and diphosphonate ligands.

It also should be noted that in Ni(II) removal (see Fig. 2(a)), interactions between the above cation and ligands of Resins 1,2 and 3 are different in each case. The resin with carboxyethyl phosphonate is not able to remove Ni(II) from a solution of 0.01 M nitric acid. When the carboxyl group in this ligand is replaced with a phosphonate group (Resin 2), the acidity of the ligand gets higher and so does log *D*. Both resins can be used to separate Fe(III), Zn(II), Cd(II) and Cu(II) from Ni(II) in 0.01 M nitric acid solutions. Resin 3 with geminal phosphonic groups displays high acidity with a $pK_a < 1.4$ and cannot be used for this purpose. It can be concluded that not only the type of donor atom in neighbouring group and the distance between groups but also the effect of that neighbouring group on the acidity of the entire ligand plays an important role in metal ion recognition.

Further experiments in this field include EPR studies of Cu(II) complexes with ligands derived from ethoxycarbonylethyl phosphonate and are presented in other paper [15].

CONCLUSIONS

In the case of ion removal from less concentrated acid solutions (less than 0.1 M), sulfonation of resins in order to increase the kinetics of ion uptake is not necessary.

The presence of strongly acidic sulfonic groups does not adversely affect the selectivity of ion uptake if the solution contains an excess of balast ions such as Na(I).

Under the conditions used in this work only resins with less acidic ligands (for example, carboxyethyl phosphonate) display sufficient selectivity to separate some di- and trivalent cations from Ni(II).

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