

Preparation and Adsorption Properties of the Chelating Resins Containing Carboxylic, Sulfonic, and Imidazole Groups

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ABSTRACT: The crosslinked poly(1-vinylimidazole-co-acrylic acid), P(VIm-co-AA), and poly(1-vinylimidazole-co-2-acrylamido-2-methyl-1-propane sulfonic acid) P(VIm-co-APSA) were synthesized by radical polymerization and tested as adsorbents under competitive and noncompetitive conditions for Cu(II), Cd(II), Hg(II), Zn(II), Pb(II), and Cr(III) by batch equilibrium procedure. The resin-metal ion equilibrium was achieved before 1 h. The resin P(VIm-co-AA) showed a maximum retention capacity (MRC) value for Pb(II) at pH 3 and Hg(II) at pH 1 of 1.1 and 1.2 mEq/g,

respectively, and the resin P(VIm-co-AA) showed at pH 3 the following MRC values: Hg(II) (1.5 mEq/g), Cd(II) (1.9 mEq/g), Zn(II) (2.7 mEq/g), and Cr(III) (2.8 mEq/g). The recovery of the resin was investigated at 25°C with 1 M and 4 M HNO₃ and 1 M and 4 M HClO₄. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2852–2856, 2003

Key words: resins; metal polymer-complexes; ion exchangers

INTRODUCTION

Reactive polymeric materials for wastewater treatment and metal recovery have received much attention. Metal ions are nonbiodegradable in nature; their intake at a certain level is toxic.¹ Attempts have therefore been made to incorporate a vast number of chelating groups into a polymer network.^{2–8} Of various common methods to prepare such chelating resins, by far the most common technique is the chemical modification of crosslinked polymers. Ion-exchange resins are very important to metal ion complexation reactions due to their hydrophilicity, accessibility, and high capacity. However, due to a wide range of materials and methods of synthesis, it is not surprising that the chelating exchanger's physical form may vary from rock-hard material to soft gel. One of the most important challenges is to achieve a selective resin. The idea of hard and soft acid base (HSAB) concept⁹ and stability of the metal complexes are the valuable guidelines for the active site selection. Anchoring the active site to a solid support in a polymer matrix provides an immobilized active surface capable of selective and quantitative separation of cations from aqueous solutions. This solid-phase extraction system

can be operated indefinitely without loss of the expensive ligand groups.^{10–12}

In recent studies on complexing polymers in our laboratory, we reported on the synthesis of structures bearing amide, amine, ammonium, and carboxylic groups obtained by radical polymerization.^{13–18} Complexing properties of these structures have been investigated by the batch equilibrium procedure to study their behavior in respect to different metal ions. We have now extended these investigations to the synthesis of insoluble polymers containing carboxylic, sulfonic, and imidazole groups.

EXPERIMENTAL

Reagents

Acrylic acid (AA), Merck, and 1-vinylimidazole (VIm) 99%, Aldrich, were purified by distillation. 2-acrylamido-2-methyl-1-propanesulfonic acid (APSA), Aldrich, *N,N'*-methylene-bis-acrylamide (MBA) 99%, Aldrich, ammonium persulfate (AP), Aldrich, were used without further purification.

The metal salts used were: cadmium(II) nitrate tetrahydrated, Merck, copper(II) nitrate 2.5 hydrated, T.J. Baker, chromium(III) nitrate nonahydrated, Merck, mercury(II) nitrate monohydrated, Merck, lead(II) nitrate, Merck, and zinc(II) nitrate hexahydrated, Merck. The analytical grade, nitric acid, perchloric acid, and sodium hydroxide were purchased from Merck.

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Synthesis of the resins

The synthesis of poly(1-vinylimidazole-*co*-acrylic acid) P(VIm-*co*-AA) was carried out in a polymerization flask at which 0.03 mol (2.7 mL) of VIm, 0.03 mol (2.5 mL) of AA, 2.0 mol % of MBA as the crosslinking reagent, and 1.0 mol % of AP as the initiator were added. The reaction was kept under nitrogen at 70°C for 24 h. The resin was filtered and washed with abundant water, and dried up to constant weight. Yield: 79%.

The resin poly(1-vinylimidazole-*co*-2-acrylamido-2-methyl-1-propanesulfonic acid) P(VIm-*co*-APSA) was synthesized in a polymerization flask at which 0.016 mol (1.44 mL) of VIm, 0.016 mol (3.4 g) of APSA, 0.00064 mol (2.0 mol %) of MBA as the crosslinking reagent, and 0.00032 mol (1.0 mol %) of AP as the initiator were added. The reaction was kept under nitrogen at 70°C for 24 h. The resin was filtered and washed with abundant water, and dried up to constant weight. Yield: 99%.

Afterwards, both resins were sized by screening, and the fraction with mesh size in the range of 180–250 μm (0.16–0.125 mm) was chosen.

Resin-metal ion uptake

The batch metal uptake experiments were performed using standard metal salt $\text{Cu}(\text{NO}_3)_2$, CdCl_2 , HgCl_2 , $\text{Zn}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$, and $\text{Cr}(\text{NO}_3)_3$ at pH range 1–5 depending of the metal ion. All experiments were performed in flasks mounted on a shaker at 25°C. The capacities for Cu(II), Cd(II), Zn(II), Hg(II), Pb(II), and Cr(III), under noncompetitive and competitive conditions were determined as a function of the pH. Batches of 0.1 g resin were used, together with a mixture of 10 mL of metal ion solution. After a shaking time of 1 h, the samples were filtered, washed with water, and dried under vacuum at 50°C. Batch metal-uptake experiments under competitive conditions were performed with the following metal ion mixtures: batches of 0.1 g resin were used together with a mixture of 10 mL of each metal solution (0.5 g/L). After a shaking time of 1 h, the samples were further handled as described for the noncompetitive experiments.

To obtain the maximum adsorption capacity for the metal ions, 50 mL of an aqueous solution 1 g/L were shaken with 0.1 g of the resin for 1 h at 25°C. The mixture in the flask was filtered and washed with water, and the filtered solution was transferred into a calibrated flask. The process was repeated three times, the volume was made up to 250 mL and then the metal ion was determined colorimetrically by atomic absorption spectrometry.

In the regeneration experiments (1 M and 4 M) HNO_3 and HClO_4 were tested for their stripping potential. Batches of 1.0 g resin were loaded with metal

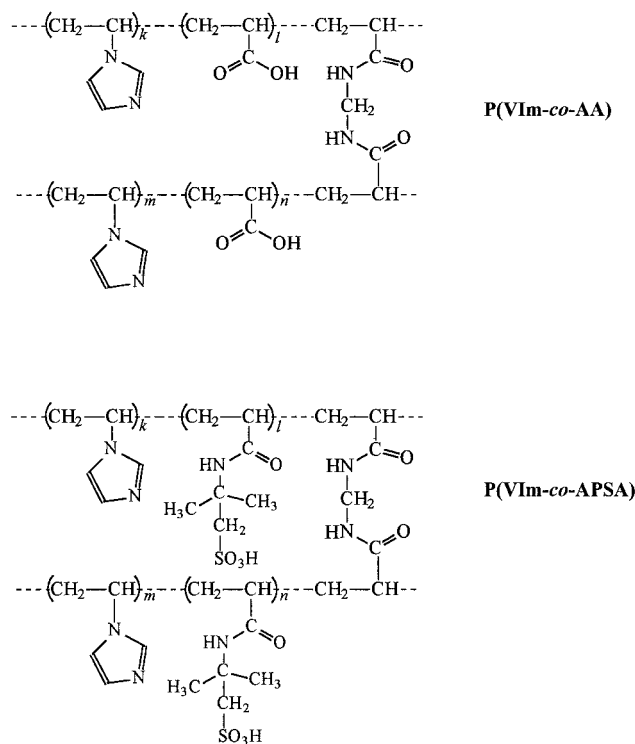
ion solution (50 mL of the metal solution 1.0 g/L) at pH 5 by shaking for a period of 1 h. The loaded resin was washed with water and the filtrates collected. This procedure was repeated three times.

Measurements

A Julabo air-batch shaker was used for shaking the solution at a desired temperature. The pH was measured with a digital H. Jurgens & Co. pH meter. A Unicam Solaar 5M series atomic absorption spectrometer was used for the determination of single and mixed metal ions. The FTIR spectra of the sample were recorded with a Magna Nicolet 550 spectrophotometer. The thermograms of the loaded and unloaded resins were recorded on a STA-625 thermoanalyzer (Polymer Laboratories). Approximately 5 mg of the dry sample were heated at 10°C/min heating rate under dynamic nitrogen atmosphere.

RESULTS AND DISCUSSION

Crosslinked poly(1-vinylimidazole-*co*-acrylic acid), P(VIm-*co*-AA) and poly(1-vinylimidazole-*co*-2-acrylamido-2-methyl-1-propane sulfonic acid) P(VIm-*co*-APSA) were synthesized by radical polymerization. Both resins contained an imidazole group. The structures are shown below.



The FTIR spectrum of the resin P(VIm-*co*-AA) showed absorption bands (in cm^{-1}) at 3449 (OH, carboxylic acid), 3143 ($-\text{C}=\text{C}-\text{H}$, imidazole), 1721 ($\text{C}=\text{O}$), 1567 ($\text{C}=\text{N}$), and 1224 ($\text{C}-\text{N}$) (see Fig. 1).

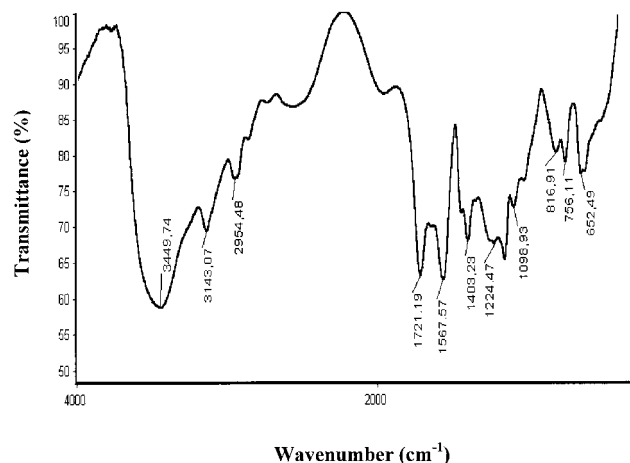


Figure 1 FTIR of the resin poly(1-vinylimidazole-co-acrylic acid), P(VIm-co-AA).

The FTIR spectrum of the resin P(VIm-co-APSA) showed the following characteristic absorption bands (in cm^{-1}): 3457 (OH, carboxylic acid and NH, secondary amide), 1664 (C=O) 1547 (C=N, imidazole), and 1296 (S—O, sulfonic acid) (see Fig. 2).

The copolymer P(VIm-co-APSA) was very close to equimol composition because the yield was about 100%, indicating the total incorporation of the comonomers in an equimol ratio.

The thermogravimetric analysis showed that both resins are stable up to 200°C with a weight loss lower than 5%. At 300°C, the resins P(VIm-co-APSA) and P(VIm-co-AA) showed a weight loss of 14 and 30%, respectively (see Table I).

Uptake of Cu(II), Cd(II), Zn(II), Pb(II), Hg(II), and Cr(III)

The metal ion uptake behavior of the resins P(VIm-co-AA) and P(VIm-co-APSA) was tested under both competitive and noncompetitive conditions as a function of the pH according to the water solubility of the metal

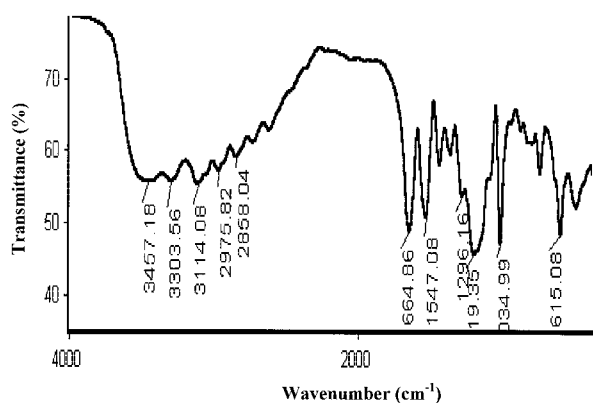


Figure 2 FTIR of the resin poly(1-vinylimidazole-co-2-acrylamido-2-methyl-1-propane sulfonic acid) P(VIm-co-APSA).

TABLE I
Thermal Stability of the Resins Expressed in Weight Loss Percentage at Different Temperatures

Resin	Temperature (°C)				
	100	200	300	400	500
P(VIm-co-AA)	0	2	30	48	70
P(VIm-co-APSA)	1	4	14	62	66

salt. Thus, Hg(II) ions were studied only up to pH 2 to avoid precipitation.

The uptake results under noncompetitive conditions are given in Figure 3. Metal nitrate solutions were used. As pH was increased, the metal ions retention was also increased for both resins. For P(VIm-co-AA), at pH 1 only H(II) was significantly retained (64%, 0.201 mmol/g resin). The retention of all other metal ions was lower than 30%. At pH 0 the retention of all other metal ions was higher than 60% and particularly Pb(II) (90%, 0.280 mmol/g), Cd(II) (75%, 0.237 mmol/g), and Zn(II) (79%, 0.237 mmol/g). This retention behavior was very similar at pH 5 with the highest retention value for Cd(II) (95%, 0.314 mmol/g). In addition, the dependence on the pH value for the adsorption of the metal ions with P(VIm-co-APSA)

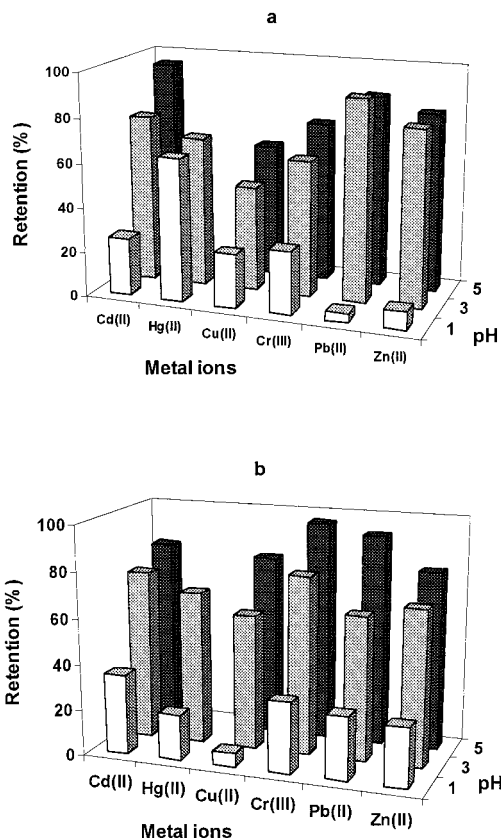
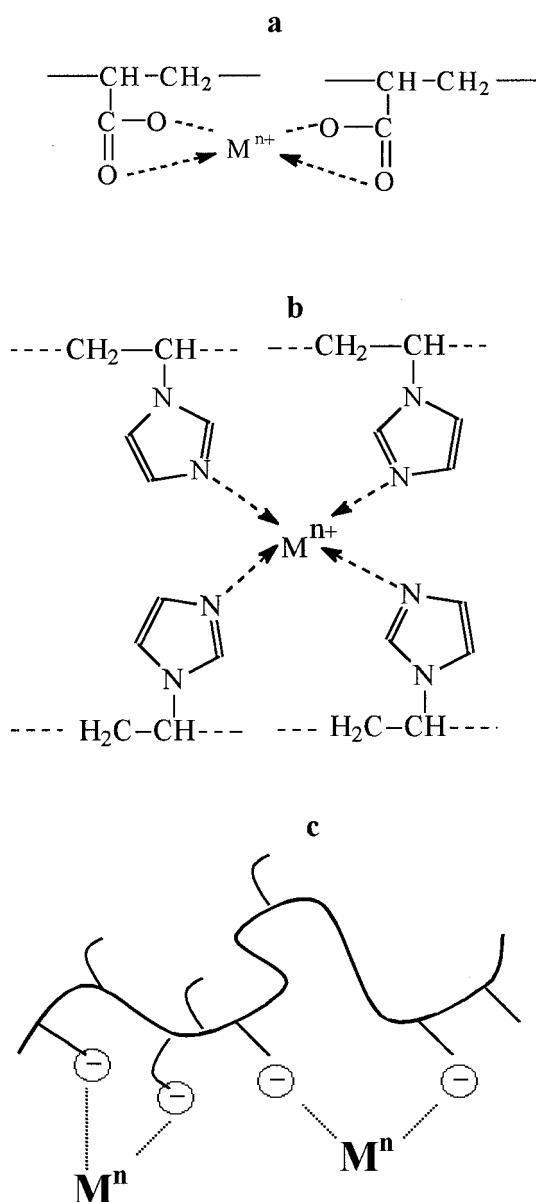


Figure 3 Metal ions sorption in noncompetitive conditions for (a) P(VIm-co-AA) resin and (b) P(VIm-co-APSA) resin, at different pH.

resin was also investigated. At pH 1 the retention of the metal ion was lower than 40%, but at higher pH, the metal ion retention increased significantly. Thus, at pH 3, the highest retention values were observed for Cd(II) (74%, 0.126 mmol/g), and Cr(III) 78%, 0.136 mmol/g). By increasing the pH up to 5, the retention values were higher than 78%. Thus, Pb(II) (92%, 0.160 mmol/g) and Cr(III) (96%, 0.158 mmol/g).

This behavior may be explained taking into account the different interaction mechanisms between the ligand groups of the resin and the metal ions. In this sense, Scheme 1 shows these possibilities.

There exists basically two different mechanisms; the complex formation between carboxylic and/or imida-



Scheme 1 Resin-metal ion interaction mechanism: (a) carboxylic-type complexes, (b) imidazole-type complexes, and (c) electrostatic interaction with sulfonate groups.

TABLE II
Selectivity Sorption of Hg(II) from a Tertiary Mixture with Cd(II) and Zn(II) at pH 1 and pH 3

Resin	pH	Selectivity (S)
P(VIm-co-AA)	1	0.80
	3	0.05
P(VIm-co-APSA)	1	0.19
	3	0.17

zole groups with the metal ions, and the electrostatic interaction between the sulfonate or carboxylate groups with the metal ions. All these possibilities are not excluded, and may coexist simultaneously. On the other hand, these mechanisms are favored at pH values higher than 3 because under these conditions the ligand groups (carboxylic, sulfonic, and imidazole) are partly deprotonated.

The adsorption kinetic properties of the metal ions by the resins are important for the assessment of the suitability of this material to serve as a packed bed ion exchanger or chelating integrated through a flow column. In cases where the exchange reaction seems to be slow for an application of the resin in combination with a dynamic flow system, the batch technique might be a reasonable alternative. The time required to achieve the equilibrium conditions was approximately 1 h, which can be considered relatively fast considering that the reaction occurs in a heterogeneous phase.

To determine the effectiveness of the chelating resins for heavy metal ions removal, the adsorbents must be evaluated in several ways. Table II shows the removal of the mixed heavy metal ions using an amount of the resins P(VIm-co-AA) and P(VIm-co-AA).

To explore the applications of the sorbent, it is relevant to obtain knowledge on the sorption capacity of the resin toward different metal ions. A maximum amount of metal ion can be removed from the solution when the exchange or chelating sites of the resin are occupied in high magnitude for the metal ion. This corresponds to the maximum retention capacity (MRC) value. According to the anterior results, not all the metal ions were investigated. The resin P(VIm-co-AA) showed a MRC value for Pb(II) at pH 3 and Hg(II) at pH 1 of 1.1 and 1.2 mEq/g, respectively. The resin P(VIm-co-AA) at pH 3 showed the following MRC values: Hg(II) (1.5 mEq/g), Cd(II) (1.9 mEq/g), Zn(II) (2.7 mEq/g), and Cr(III) (2.8 mEq/g).

The selectivity sorption of Hg(II) in a tertiary mixture was carried out at pH 1 and 3. Selectivity is given by:

$$S = \log K_{d_{\text{Hg(II)}}} - \log \sum_{i=1}^2 K_{d_{(\text{ion})i}}$$

where K_d is the distribution coefficient of the respective metal ions. K_d is defined as:

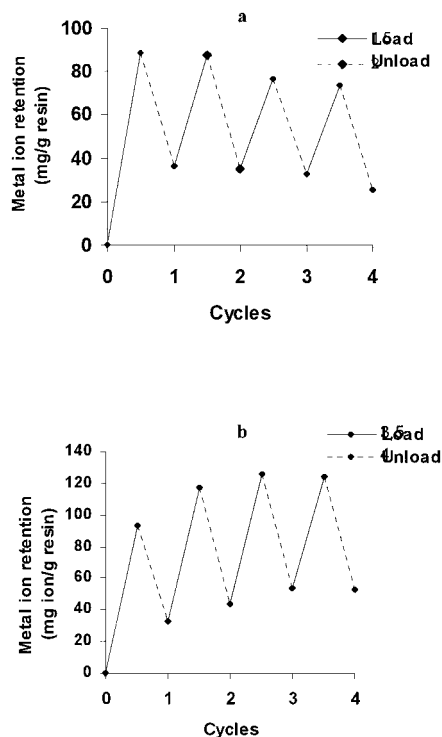


Figure 4 Loading-elution cycles of mercury ions on (a) P(VIm-co-AA) resin and (b) P(VIm-co-APSA) resin, at pH 3.

$$K_d = \frac{\text{mg of metal ion sorbed per gram of}}{\text{mg of free metal ions per mL of}}$$

The selectivity values (see Table II) at pH 1 were higher for the P(VIm-co-AA) resin than that P(VIm-co-APSA) resin. This fact is in agreement with the proposal mechanism of resin-metal ion interaction, because this resin preferentially forms complexes compounds with Hg(II). This mechanism was more specific for some metal ions and then the selectivity was higher. At pH 3, the selectivity decreased because the electrostatic interaction increased and this mechanism was less specific for metal ions of the same charge.

Desorption of metal ions from the loaded resins was studied with 1 M and 4 M HClO₄ and 1 M and 4 M HNO₃ solutions at 25°C for 1 h under stirring. The final amount of the metal ion was determined by AAS and calculated by using the following expression:

Desorption rate

$$= \frac{\text{amount of metal ion desorbed to the elution medium}}{\text{amount of metal ion adsorbed on the resin}}$$

These media cannot efficiently destroy the ligand-metal ion complex as being independent on the concentration; the recovery was not higher than 90 mg/g dry resin obtained for Hg(II).

The retention-elution cycles (see Fig. 4) showed that after four cycles, the retention of mercury ions decreased from 88.4 (mg metal ion/g resin) to 41.3 (mg metal ion/g resin) for P(VIm-co-AA) and from 93.3 (mg metal ion/g resin) to 70.5 (mg metal ion/resin g) for P(VIm-co-APSA). Moreover, in the first cycles the elution was near 60% for both resins, but in the next cycles the elution reached values near 90%.

CONCLUSIONS

Crosslinked resins completely insoluble in water were synthesized by radical polymerization in high yields. The resins contained imidazole, carboxylic acid, and sulfonic acid groups. The metal ion retention behavior investigated by the batch equilibrium procedure demonstrated that the retention depended strongly on the pH, and that the sulfonic acid group showed a higher affinity than that the carboxylic acid group for the metal ions, particularly for Cr(III). The electrostatic interactions between the sulfonate groups and the metal ions would be favored.

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