

# Poly(sodium 4-styrenesulfonate)–Metal Ion Interactions

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**ABSTRACT:** The metal ion-binding properties of poly(sodium 4-styrenesulfonate) in conjunction with membrane filtration were investigated for Cu(II), Cd(II), Co(II), Cr(III), Hg(II), Ni(II), Pb(II), Zn(II), and Fe(II). Different experiments were carried out at different pH's, metal ion concentrations, polymer concentrations, and molecular weight fractions. Only Fe(II) and Cr(III) were retained at pH 1, which allows a selective separation of these metals from all the other metal ions. At pH 3 the retention ability of this polymer increased for all the metal ions. On the other hand, the metal ion-retention properties are dependent on the polymer/metal ratio. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 219–225, 1998

**Key words:** water soluble polymers; metal ions; ultrafiltration membranes; polymer metal ion interactions

## INTRODUCTION

Research on functional polymers is of great interest in polymer science. These polymers have been widely used in recent years as supports for solid-phase synthesis<sup>1</sup> and chromatography,<sup>2</sup> and as carriers of organic reagents,<sup>3</sup> catalysts,<sup>4</sup> enzymes,<sup>5</sup> and pharmacologically active compounds,<sup>6</sup> in addition to their classical use as ion exchangers.<sup>7</sup> Crosslinked insoluble resins are the most-developed polymers for these applications, showing some advantages in simulation of high dilution or pseudodilution conditions, the fish-hook and concentration principle, the facilitation of selective intrapolymeric reactions, the stabilization of reactive species, the elimination of volatile malodorous reagents, and the easy separation of the by-products of the reaction.<sup>8</sup> In this context, polymers with chelating groups have been employed for the removal of metal ions from

diluted solutions, and they imply potential technical applications.<sup>9–11</sup> However, a two-phase process involves disadvantages such as reactions in heterogenous phase and long contact-times.

Efficient and selective separation of inorganic ions can also be achieved by water-soluble polymeric reagents. A number of techniques to recover metals from water using water-soluble polymers have been described.<sup>11–13</sup> The liquid-phase polymer based retention technique<sup>11,14–18</sup> is based on the separation by membrane filtration of ions bound to water-soluble polymers with chelating or ion-exchanging groups from nonbound ions. Application in the recovery of metals from diluted solutions both in analytical and technical scale has been reported.<sup>17</sup> However, no study of the influence of different variables in the retention properties has yet been done.

Water-soluble polymers with sulfonate functionality have commercial utility in a number of applications.<sup>19–21</sup> Other uses and chemical properties have been widely described in the literature.<sup>22–25</sup> The sulfonate groups have been extensively employed in ion-exchange resins, but their use in water-soluble polymers with ability to bind metal ions has been less studied.

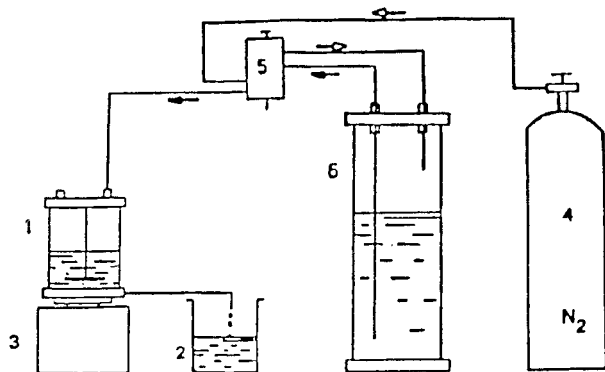
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**Figure 1** Instrumental arrangement: (1) filtration cell with polymeric and metal ion solution; (2) membrane filtrate; (3) magnetic stirrer; (4) pressure trap; (5) selector; (6) reservoir with water.

In this paper the metal ion-binding properties of poly(sodium 4-styrenesulfonate) (PSS) in conjunction with a membrane filtration were investigated for Cu(II), Cd(II), Co(II), Cr(III), Hg(II), Ni(II), Pb(II), Zn(II), and Fe(II), as a function of the pH, filtration factor, polymer concentration, metal ion concentration, and polymer size.

## EXPERIMENTAL

### Reagents

Commercially available PSS, 20 wt % solution in water (Aldrich, USA, synthesized from the *para*-substituted monomer), was fractionated by ultra-filtration over three membranes with exclusion ratings of 3,000, 10,000, or 100,000 g/mol (Filtron, Germany); and the fractions were washed with water and lyophilized. Three fractions were obtained corresponding to the following molecular weight ranges: 3,000–10,000; 10,000–100,000; and over 100,000 g/mol.

Metal standard solutions of 1,000 ppm (Merck, Germany) were used to prepare the metal ion solutions.

### Equipment

The unit used for retention studies consisted of a filtration cell with a magnetic stirrer; a membrane with an exclusion rating of 3,000, 10,000, or 100,000 g/mol (Filtron); a reservoir; a selector; and a pressure source (see Fig. 1).

Metal ion concentrations were measured by atomic absorption on a Perkin-Elmer 3100 spec-

trometer. The pH was controlled on a pH meter from H. Jürgens & Co.

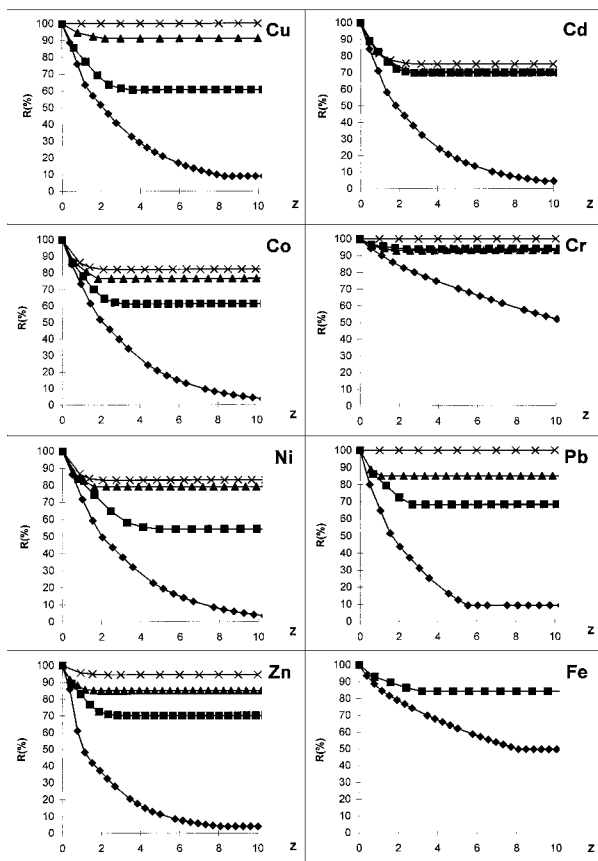
### Procedure

Polymer (molecular weight fraction over 100,000 g/mol) and NaNO<sub>3</sub> (255 mg) were dissolved in bidistilled water, and metal solutions were added. The solution was brought to 20 mL of total volume and the pH was adjusted. The solution was left overnight. The pH of the cell and the reservoir solutions were adjusted to the same value. The filtration runs were carried out over a membrane with an exclusion rating of 10,000 g/mol under a total pressure of 3 bar, keeping the total volume in the cell constant at 20 mL. A membrane with an exclusion rating of 3,000 g/mol was used when fractions ranging from 3,000 to 10,000 g/mol were studied. Filtration fractions were collected and the metal concentrations analyzed. The metal ions studied were Cu(II), Cd(II), Co(II), Cr(III), Hg(II), Ni(II), Pb(II), Zn(II), and Fe(II). Fe(II) was not used at pH over 3 because it is susceptible to precipitate. No results on Hg(II) retention values are shown due to the high detection limit of the atomic absorption spectrometer.

## RESULTS AND DISCUSSION

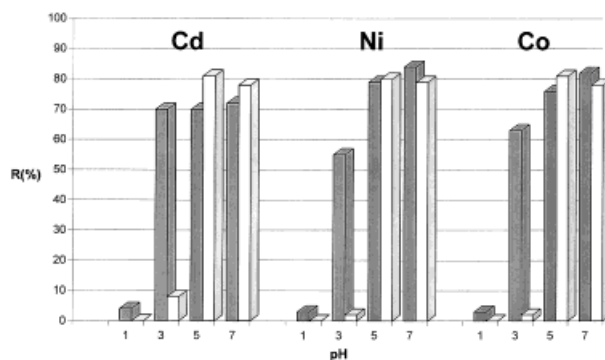
In order to study the retention properties of PSS, different assays were carried out, changing some of the variables which may influence these properties.

A typical retention profile shows the metal ion retention ( $R$ ) versus filtration factor ( $Z$ ).  $Z$  is defined as the ratio volume of the filtrate ( $V_f$ ) versus volume in the cell ( $V_0$ ) and  $R$  is the fraction per unit of metal ions remaining in the cell.  $R$  is normally expressed as a percentage [ $R(\%)$ ]. At  $Z$  values high enough a remaining residue of metal ions is frequently found which cannot be eluted by filtration at the same pH conditions. This remaining percentage is called "the retention capacity of a polymer." In Figure 2 the profiles of the retention for the different metal ions studied are shown as a function of the pH. In general, only Cr(III) and Fe(II) are retained at pH 1, which allows a selective separation of these metals from all the other metal ions. Because it is a strong acid, the retention ability of the polymer is important yet at pH 3. The comparison of the behavior of this polymer with a weaker acid such as poly(acrylic acid)<sup>26</sup> shows that the latter polymer is able to

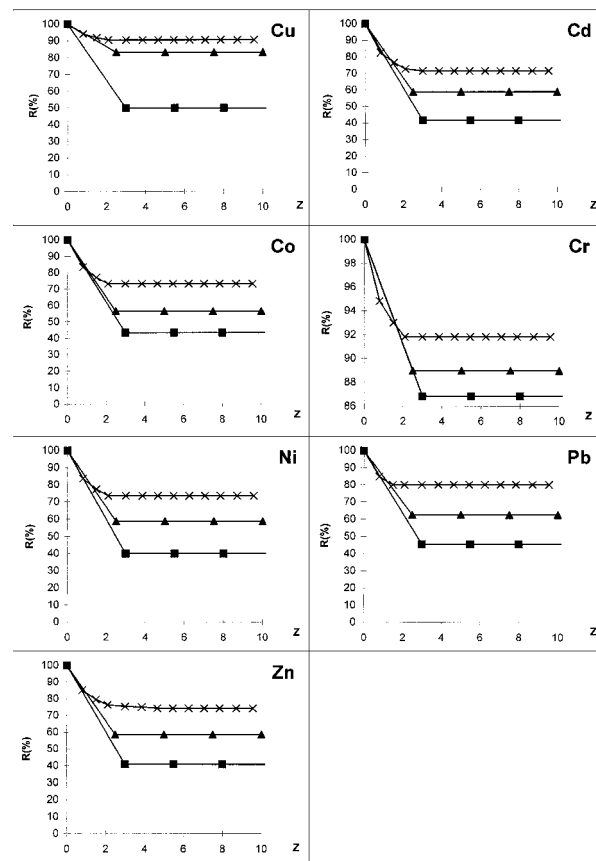


**Figure 2** Retention profiles of Cu(II), Cd(II), Co(II), Cr(III), Ni(II), Pb(II), Zn(II), and Fe(II) using PSS. Absolute polymer amount: 1.6 mmol. Absolute metal ion amounts: 400  $\mu\text{g}$  of each metal species. (—◆—) pH 1; (—■—) pH 3; (—▲—) pH 5; (—×—) pH 7.

retain metal ions only from higher values of pH (see Fig. 3), where all the carboxylic groups are dissociated as carboxylate.

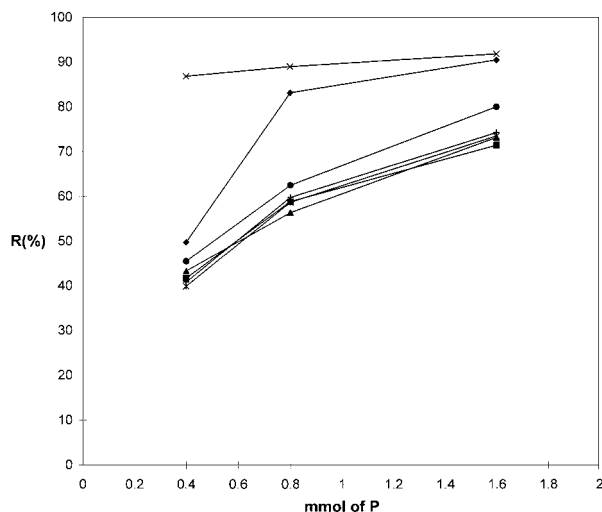


**Figure 3** Retention values of Cd(II), Ni(II), and Co(II) at four different pH values and  $Z = 10$ . Polymers: white, poly(acrylic acid); grey, PSS.



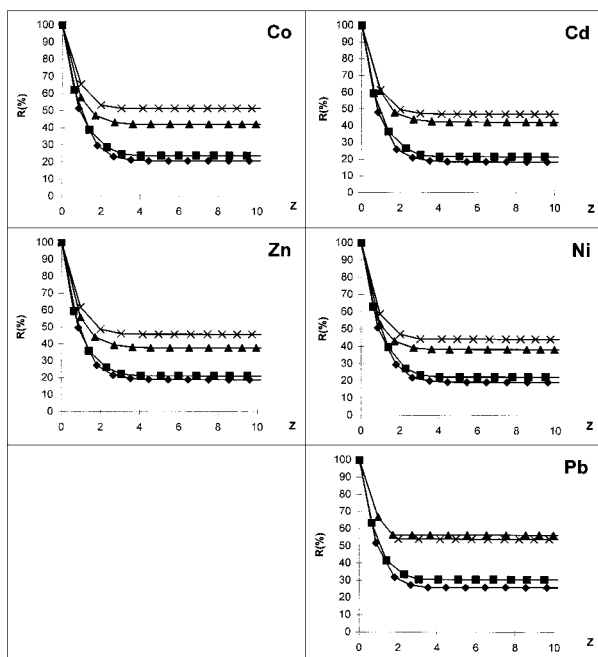
**Figure 4** Effect of the polymer concentration on the retention profiles of Cu(II), Cd(II), Co(II), Cr(III), Ni(II), Pb(II), and Zn(II), at pH 5. Absolute metal ion amounts: 400  $\mu\text{g}$  of each metal species. Absolute polymer amounts: (—■—) 0.4 mmol; (—▲—) 0.8 mmol; (—×—) 1.6 mmol.

The effect of the polymer concentration is shown in Figure 4. By increasing the polymer concentration from 0.02 to 0.08M, the retention increases. This dependence is less important in the case of Cr(III), whose high values of retention stay in the range of 85 to 90% at these polymer concentrations. The increase of the polymer concentration implies that the number of functional groups in solution and then the polymer/metal ratio increases. Despite the fact that in all cases the functional groups in the polymer are in large excess over the metal ions (at least 50 : 1), the influence of the polymer concentration is accused. Figure 5 shows the effect of the polymer concentration on the retention value at a constant filtration factor,  $Z = 10$ . For most of the metal ions studied, the increase of the amounts of polymer does not induce an exact proportional increase in



**Figure 5** Effect of the polymer concentration on the retention values at  $Z = 10$  and pH 5. P = PSS. (—x—) Cr(III); (—◆—) Cu(II); (—●—) Pb(II); (—■—) Cd(II); (—▲—) Co(II); (—+—) Zn(II); (—\*—) Ni(II).

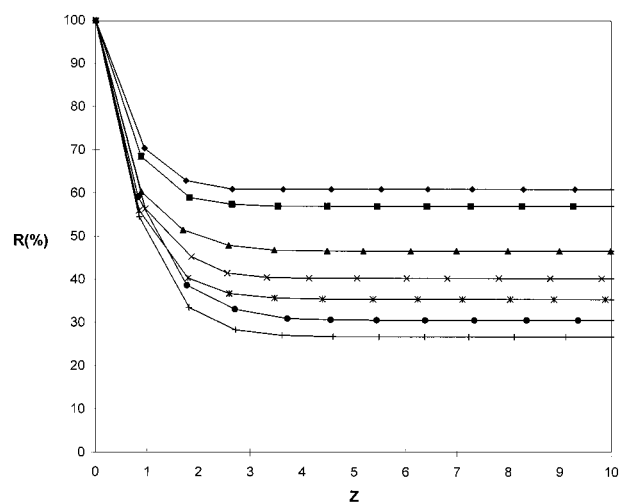
the retention. The influence of the polymer concentration is less accused at higher values of polymer concentration. This pattern is very clear in



**Figure 6** Effect of the metal ion concentration on the retention profiles of Cd(II), Co(II), Ni(II), Pb(II), and Zn(II) at pH 5. Absolute polymer amount: 0.4 mmol. Absolute metal ion amounts; (—x—) 400  $\mu\text{g}$  of each metal ion; (—▲—) 800  $\mu\text{g}$  of each metal ion; (—■—) 2,000  $\mu\text{g}$  of each metal ion; (—◆—) 3,000  $\mu\text{g}$  of each metal ion.

the case of Cu(II), whose retention increases sharply from 50 to 83% when the polymer concentration is increased from 0.02 to 0.04M, and stays near this value for higher polymer concentrations. From these data it can be concluded that, for technical applications, selective enrichment of Cr(III) solutions at pH 5 may be more effective at low concentrations of PSS.

The effect of the metal concentration is shown in Figure 6. The study is done only for the five metal ions that are not susceptible to precipitate at these concentrations and pH 5. The general tendency is that the retention capacity percentage decreases when the metal concentration is increased, but it is noted that the absolute amounts of metal retained do increase. Because of its relative independence of the pH around pH 5 and its moderate high retention value, several experiments considering only Cd(II) as the metal ion were carried out. Figure 7 shows the retention profiles of seven runs with different initial concentrations of Cd(II) varying from 3.56  $\mu\text{mol}/20$  mL to 88.96  $\mu\text{mol}/20$  mL. The figure clearly shows a dependence of the retention profile on the initial metal-ion concentration. Although the retention capacity percentage decreases with the increase of the metal concentration, the absolute amounts of metal retained increase, as seen in Table I. For example, the polymer is able to retain 22.0  $\mu\text{mol}$  when the initial metal amounts are 71.2  $\mu\text{mol}$ ,



**Figure 7** Retention profiles of Cd(II). Absolute polymer amount: 0.4 mmol; pH 5. Absolute Cd(II) amounts: (—◆—) 400  $\mu\text{g}$  (3.56  $\mu\text{mol}$ ); (—■—) 800  $\mu\text{g}$  (7.12  $\mu\text{mol}$ ); (—▲—) 2,000  $\mu\text{g}$  (17.79  $\mu\text{mol}$ ); (—x—) 3,000  $\mu\text{g}$  (26.68  $\mu\text{mol}$ ); (—\*—) 5,000  $\mu\text{g}$  (44.48  $\mu\text{mol}$ ); (—●—) 8,000  $\mu\text{g}$  (71.17  $\mu\text{mol}$ ); (—+—) 10,000  $\mu\text{g}$  (88.959  $\mu\text{mol}$ ).

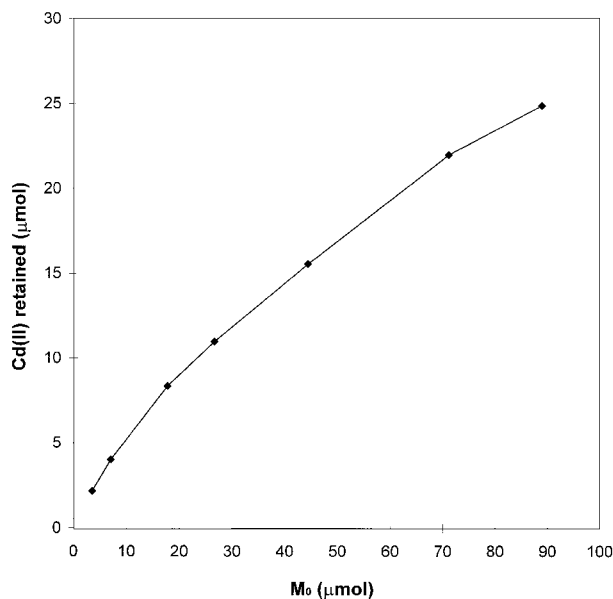
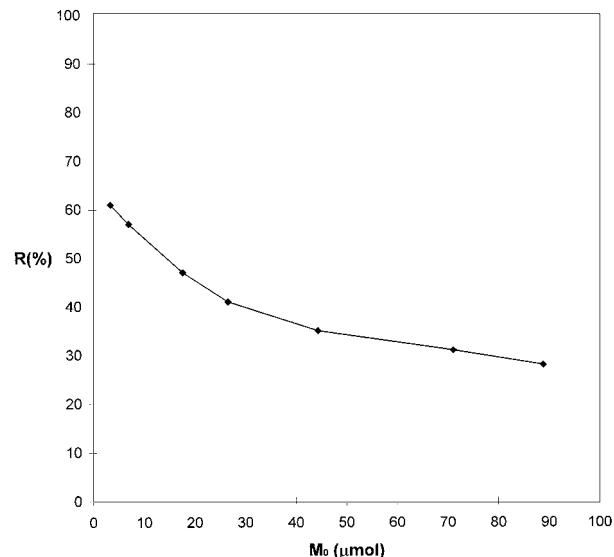
**Table I Absolute Amounts of Cd(II) Retained as a Function of the Initial Metal Amounts**

Run	Initial ( $\mu\text{mol}$ )	Retained ( $\mu\text{mol}$ )	$R$ (%)
1	3.56	2.17	61
2	7.12	4.04	57
3	17.8	8.36	47
4	26.7	11.0	41
5	44.5	15.6	35
6	71.2	22.0	31
7	89.0	24.9	28

but retains only 8.36  $\mu\text{mol}$  when the initial metal amounts are 17.8  $\mu\text{mol}$ . On the other hand, the analysis of the absolute retention at  $Z = 10$  versus the initial amounts of Cd(II) ( $M_0$ ) is shown in Figure 8. There is no linearity, but a general tendency to increase sharply at low values of  $M_0$ , smoothly at higher values, is found. A straight line should indicate a constant value of the retention, since

$$R = \text{metal retained}/M_0 \quad (1)$$

The retention value for this  $Z$  then corresponds to the slope of the curve in each point. A constant variation of  $R$  versus  $M_0$  would indicate a second-order dependency on the absolute amounts of

**Figure 8** Absolute retention of Cd(II) versus Cd(II) initial absolute amounts ( $M_0$ ) at  $Z = 10$ .**Figure 9** Retention [ $R(\%)$ ] versus Cd(II) initial absolute amounts ( $M_0$ ) at  $Z = 10$ .

metal retained versus the initial metal amounts, which may give important information for technical applications. This variation is not constant, as can be seen in Figure 9.

The retention properties associated to each metal ion are not independent of each other. The influence of the presence of other metal species on the retention profile of a metal ion was also studied. These results are summarized in Table II and Figure 10. Figure 10 shows the influence on the retention of the initial 3.56  $\mu\text{mol}$  of Cd(II) when some other ions are present. The presence of other species diminishes the retention capacity of Cd(II). In fact, comparing the different experiments, it is con-

**Table II Effect of the Nature of the Divalent Metal Ions on the Overall Absolute Retention**

Run	Metal Ion	Initial ( $\mu\text{mol}$ )	Retained ( $\mu\text{mol}$ )	$R$ (%)
1	Cd <sup>2+</sup>	3.56	1.67	47
	Co <sup>2+</sup>	6.79	3.46	51
	Ni <sup>2+</sup>	6.82	3.00	44
	Zn <sup>2+</sup>	6.12	2.81	46
	Pb <sup>2+</sup>	1.93	1.04	54
		25.22 <sup>a</sup>	11.98 <sup>a</sup>	
2	Cd <sup>2+</sup>	26.7	11.0	41
3	Cd <sup>2+</sup>	3.56	2.17	61

<sup>a</sup> Total amount of metal ions.

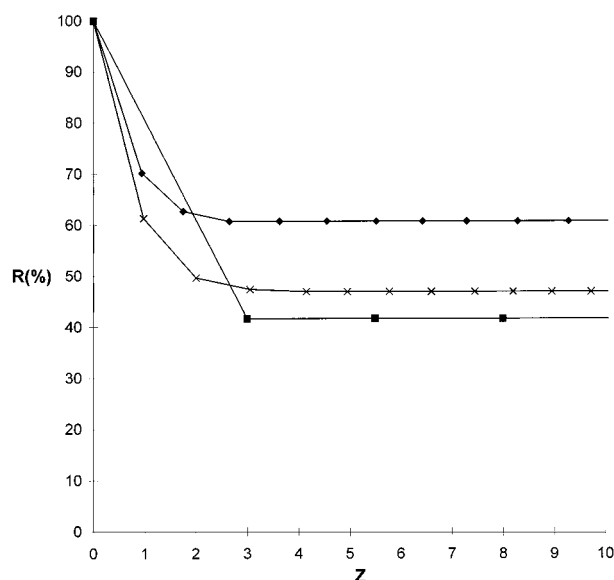
cluded that at pH 5 the polymer has a retention capacity that depends slightly on the nature of the divalent metal ions studied, with the exception of Cu(II). It can even be considered an additional effect of the divalent species because similar amounts of mixed divalent ions are likewise retained (see Table II).

The polymer size also influences the retention properties of the polymer. Figure 11 shows that the lowest molecular-weight fractions lose their retention capacity, whereas a slight difference is found in comparing the two other fractions.

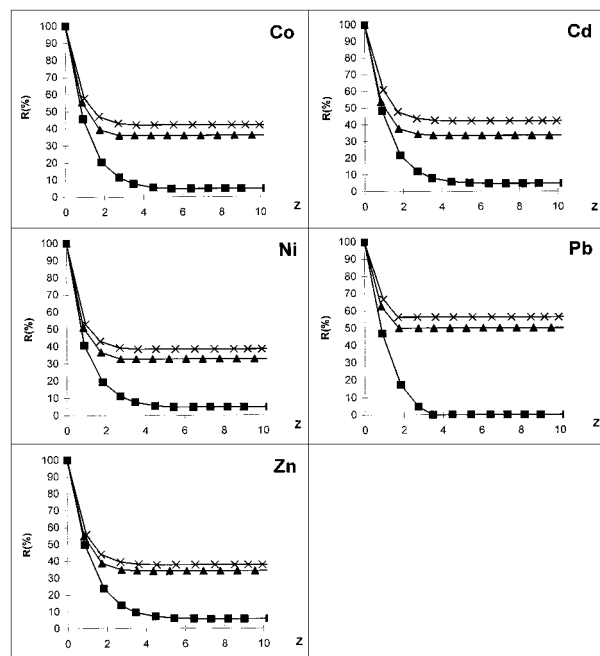
## CONCLUSIONS

The polymer with all the interacting groups as sulfonate showed an important retention ability for all the metal ions studied. This ability increased by increasing the molecular weight or the polymer/metal ratio.

The retention behavior of the metal ions depended on the pH, polymer concentration, and metal ion concentration, as well as the polymer size. At low pH the selective separation of Cr(III) and Fe(II) from all the other divalent metal ions investigated was possible. At pH 5 and 7 all the



**Figure 10** Retention profiles of Cd(II) when other metal ions are present in the solution. Absolute polymer amount: 0.4 mmol; pH 5. Absolute amount of Cd(II): 400  $\mu\text{g}$ . (—◆—) Cd(II) alone; (—×—) Cd(II) with 400  $\mu\text{g}$  each of Co(II), Ni(II), Zn(II), and Pb(II); (—■—) Cd(II) with 400  $\mu\text{g}$  each of Cu(II), Co(II), Cr(III), Hg(II), Ni(II), Zn(II), and Pb(II).



**Figure 11** Effect of polymer size on the retention profiles of Cd(II), Co(II), Ni(II), Pb(II), and Zn(II) at pH 5. Absolute polymer amount: 0.4 mmol. Absolute metal ion amounts: 400  $\mu\text{g}$  of each metal ion. Polymer fractions: (—■—) 3,000 to 10,000; (—▲—) 10,000 to 100,000; (—×—) over 100,000 g/mol.

metal ions were retained above 70%, the retention being higher at pH 7 than pH 5. Only Cd(II) did not show a dependence on the pH between pH 3 and 7, remaining around 75%. Higher selectivities were found for Cr(III) at low polymer concentrations. Cu(II) showed a strong increase in retention on increasing the polymer concentration from 0.02M [ $R(\%) = 50$ ] to 0.04M [ $R(\%) = 85$ ]. This behavior was not observed for all the other metal ions.

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