

# Metal Ion Binding Capability of the Water-Soluble Poly(Vinyl Phosphonic Acid) for Mono-, Di-, and Trivalent Cations

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**ABSTRACT:** A water-soluble polymer containing phosphonic acid groups was investigated as a polychelator by using the liquid-phase polymer-based retention technique (LPR) under different experimental conditions. The maximum retention capacity of this polymer was determined at different pHs and polymer–metal ion ratios. The metal ions investigated were Ag(I), Cu(II), Co(II), Ni(II), and Cr(III). The maximum retention capacity values of the divalent

metal ions were very similar and higher than those for the trivalent cations, indicating that the polymer–metal ion interaction was basically through electrostatic type. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2917–2922, 2004

**Key words:** water-soluble polymers; metal-polymer complexes; membranes

## INTRODUCTION

Polymeric supports with complexing groups are widely investigated and applied for the metal recovery from dilute solutions, such as industrial fluids and waste waters. Water-soluble functional polymers containing ligands at the main or side chains were investigated for the removal of metal ions in the homogeneous phase.<sup>1–6</sup> These chelating polymers, termed polychelators, were prepared by functionalizing various functional polymers. Hydrophilic polymers with complexing groups were tested to show the applicability of the method for the separation of various metal cations for analytical and technological purposes. This method, the liquid-phase polymer-based retention (LPR) method, is based on the retention of certain ions by a membrane that separates low molecular mass compounds from macromolecular complexes of the ions. Thus, uncomplexed inorganic ions can be removed by the filtrate, whereas the water-soluble polymer complexes are retained. Water-soluble polymers are commercially available or can be synthesized by different routes. Among the most im-

portant requirements for technological applications of these polymers are their high solubility in water, their easy and cheap route of synthesis, an adequate molecular weight and molecular weight distribution, chemical stability, high affinity for one or more metal ions, and selectivity for the metal ion of interest. These ligands are attached at the backbone or at the side chain, either directly or through spacer groups. By using these polychelators in combination with membrane filtration, higher efficiency and selectivity of membrane separations can be achieved.

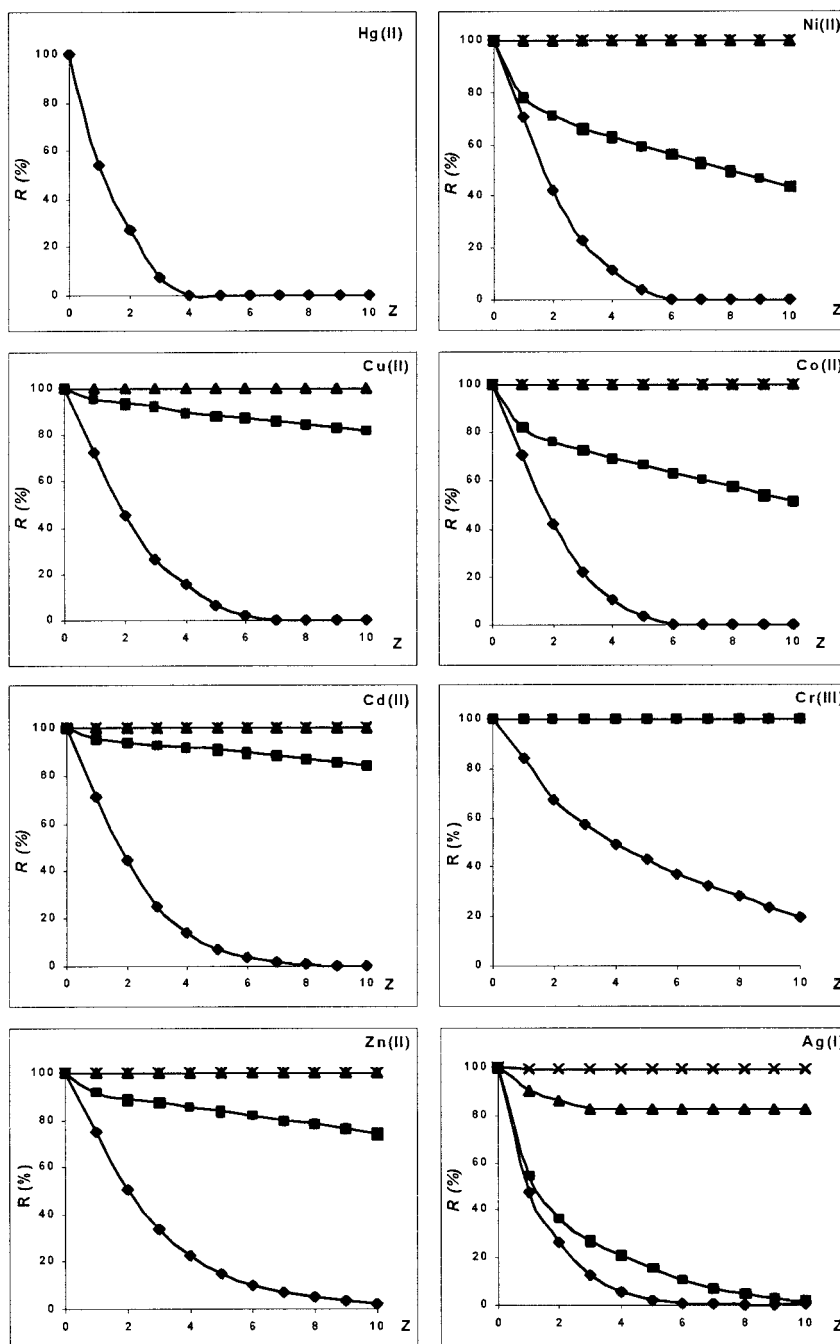
A series of polymers were designed and investigated with respect to the analytical determination of metal ions.<sup>4,5,7–12</sup> Among these, poly(ethyleneimine)-methyl phosphoric acid was tested as a macromolecular reagent to the isolation and analysis of plutonium in contaminated waters from the area near to the Chernobyl nuclear power plant.<sup>10</sup> Poly(acrylic acid) and copolymers with acrylamides,<sup>13–14</sup> *N*-maleyl glycine,<sup>15</sup> *N*-vinyl-2-pyrrolidone,<sup>14</sup> poly(2-acrylamido-2-methyl-1-propane sulfonic acid),<sup>16</sup> poly(*N*-acryloyl-*N*-methyl piperazine),<sup>17</sup> as well as mixtures of two polychelators<sup>18</sup> were investigated for their ability to bind di- and trivalent cations.

To achieve enrichment of the metal ions, their solution can be passed from a reservoir to a smaller volume filtration unit in the presence of a complexing polymer. This concentration method (enrichment method) is designed for metal recovery from dilute technological solutions and for absolute preconcentra-

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**Figure 1** Retention profiles for poly(vinyl phosphonic acid) (PVPH) at a pH ( $\blacklozenge$ ), 1; ( $\blacksquare$ ), 3; ( $\blacktriangle$ ), 5; AND ( $\ast$ ), 7.

tion of elements in analytical chemistry. However, interfering components of the test solution remain partly in the cell after the filtration run, even though they do not interact with the reagent. This can cause difficulties (e.g., in trace analysis of highly mineralized waters). To avoid this, a combined procedure is applied to both absolute and relative preconcentrations.

The ability of the phosphonic acid group to bind metal ions is well known, particularly when bound to the side chain of water-insoluble polymers.<sup>18–23</sup>

Therefore, the aim of this article was to study the metal ion retention properties of water-soluble poly-

mer containing phosphonic acid moieties directly bound to the backbone through the LPR technique under different experimental conditions.

## EXPERIMENTAL

### Reagents

Poly(vinyl phosphonic acid) (PVPH, Polysciences, Warrington, PA), was purified prior to use by membrane filtration as described previously.<sup>4,11</sup> The metal nitrates, Ag(I), Cu(II), Ni(II), and Co(II) (Merck, Stutt-

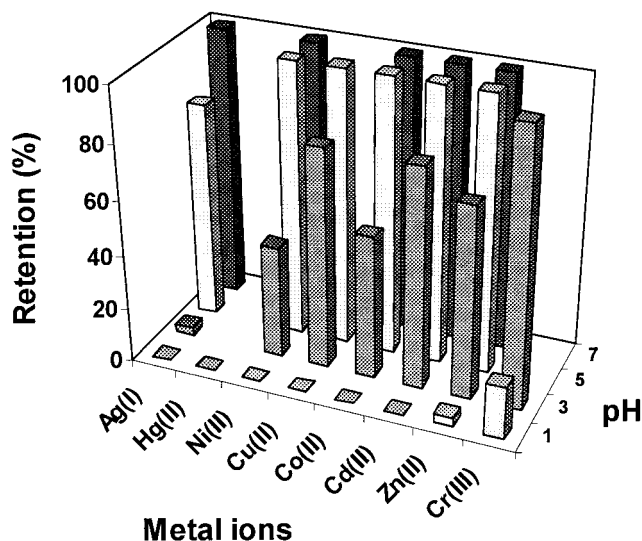


Figure 2 Retention of metal ions at different pH and  $Z = 10$ .

gart, Germany; analytical grade), were used as received.

#### Procedure

The maximum retention capacity (MRC) was determined by the enrichment method according to the LPR technique. In this method, a metal ion solution of known concentration passed through the polymer solution PVPH (20 mL). The volume of the polymer solution was kept constant and the metal ion content was determined in the different filtrate volume. With these data, the plots of metal ion concentration in the filtrate, as a function of filtrate volume, were obtained. For this study, 0.8 mmol of repeat units of PVPH was

dissolved in 20.0 mL of bidistilled water and adjusted at the respective pH. According to the solubility properties of the metal ions, three pHs were studied, 3, 5, and 7.

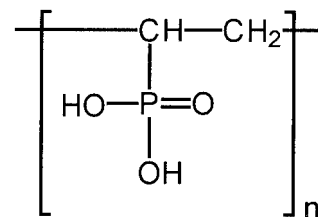
The retention profiles at  $Z = 10$  were carried out considering a metal ion concentration of 0.005 mmol in 20 mL. The polymer concentration was 0.2 mmol of repeat unit in 20 mL.

#### Measurements

The pH was determined with a Jenco Electronics 1671 pH meter. For the LPR technique, a membrane filtration system was employed to test the coordinating properties of the polychelator.<sup>4,5,11</sup> A Unicam So-laar M5 Atomic Absorption Spectrometer was used for the determination of the metal ion concentrations in the filtrate.

## RESULTS AND DISCUSSION

PVPH (see structure below):



was studied as polychelator to determine the MRC by the LPR technique through the enrichment method. The metal ion retention profiles were also determined (see Fig. 1).

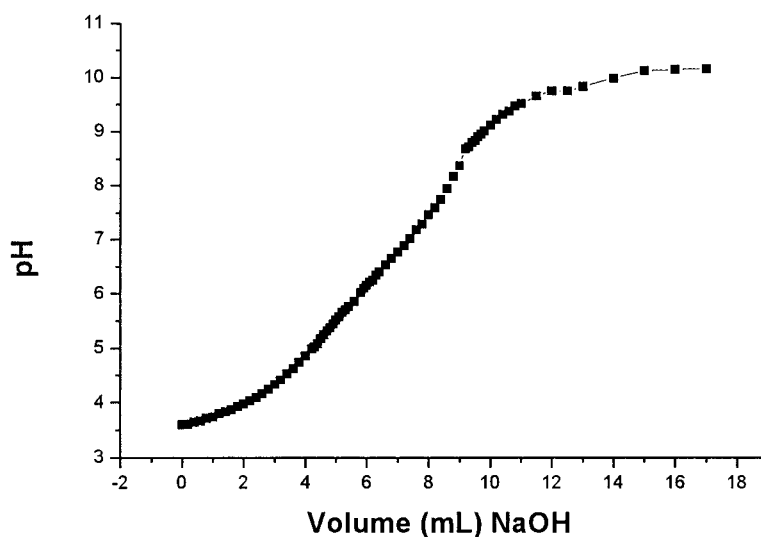
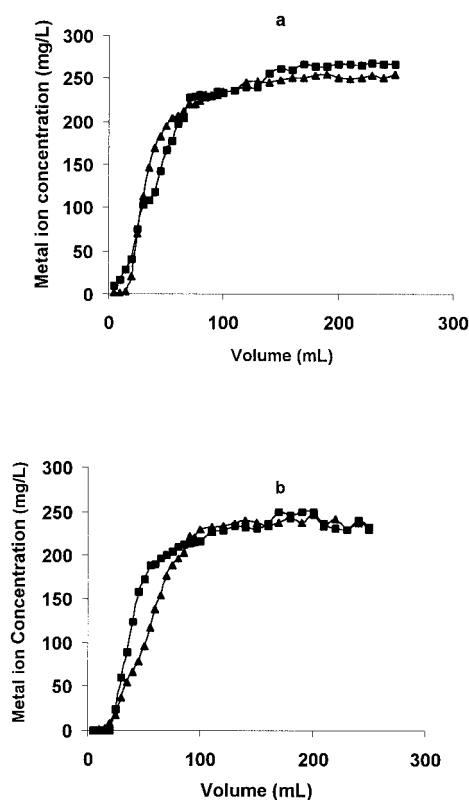


Figure 3 Potentiometric titration of poly(vinyl phosphonic acid) (PVPH) with 5.0 mM NaOH.



**Figure 4** Maximum retention capacity, MRC, for Ni(II), at pH 3 (a) and pH 5 (b). (■), blank; (▲), PVPH.

It is possible to observe a high retention value for all the metal ions studied. This retention is a function of the pH. At pH 1, the retention was practically zero. At pH 3, the retention increased deeply for all metal ions. However, this increase was higher for trivalent ions, such as  $\text{Cr}^{3+}$ , with a retention of 100%, than for the divalent ions with a retention between 50 and 80%, and for monovalent ions, such as  $\text{Ag}^+$ , whose retention was only 5%. This should indicate that besides the complex formation, there is an electrostatic interaction between the phosphonate groups and the metal ions.

This type of interaction normally shows the following pH dependence: at very acid pH, the PVPH is protonated and immersed in a high ionic strength environment. This prevents the electrostatic interactions. With increasing pH, the acid groups of PVPH increased their dissociation.

The filtration factor,  $Z$ , is a measurement of the strength of the interaction between the ligand group and the metal ion. Figure 2 shows that at pH = 7 and  $Z = 10$  the interactions between the phosphonic ligand groups and the metal ions are very strong. It increased as the pH increased.

To determine the major species of PVPH at different pH values, the apparent ionization constant,  $pK_{\text{app}}$ , was determined by potentiometric titration (see Fig. 3) and by using the Henderson–Hasselbach equation. The  $pK_{\text{app}}$  changes with the ionization degree  $\alpha$  of PVPH. Then, the intrinsic ionization constant  $pKa_1 = 3.02$  was obtained from the plot  $pK_{\text{app}}$  versus  $\alpha$ . Here, the intercept in the  $y$ -axis is the value of  $pKa_1$ . This way, it is possible to consider that, at pH = 3, the first ionization is practically completed; then, the negative charges on the polymer are able to interact with the metal ions, also increasing the metal ion retention. It is in agreement with the results shown in Figures 1 and 2. Moreover, at pH = 5 and pH = 7, the acid groups will be more dissociated and the polychelator–metal ion interaction increases, yielding the highest retention values at these pHs. The metal ion retention mechanism is not the only one and it can coexist with the complexes formation.

With this information on metal ion retention, the maximum retention capacity under different experimental conditions was studied.

Comparing the profiles of the metal ion concentration in the filtrate versus filtrate volume for the polymer with the corresponding control experience, it is possible to obtain the necessary filtrate volume to achieve the MRC for each metal ion (see Fig. 4).

With this volume and by the relationship,

**TABLE I**  
MRC Values for Mono- and Divalent Metal Ions under Different Experimental Conditions

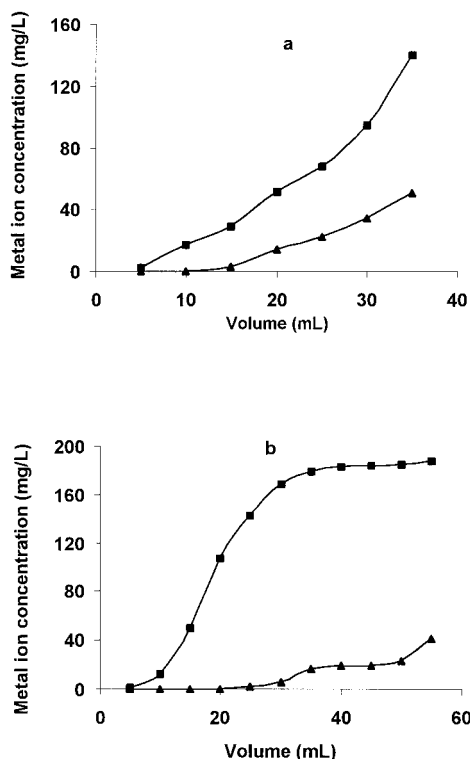
Metal ion	Initial concentration (mg/L)	pH	MRC	
			(mg metal/g polymer)	(mol metal ion/mol repeat unit)
Cu(II)	170.0	3	60.6	0.10
	170.0	5	73.4	0.13
Ni(II)	220.0	3	0.0	0.0
	220.0	5	0.0	0.0
Co(II)	190.0	3	69.7	0.12
	190.0	5	113.7	0.21
Ag(I)	428.0	3	0.0	0.0
	428.0	5	0.0	0.0

$$\text{MRC} = (M \times V) / P_m$$

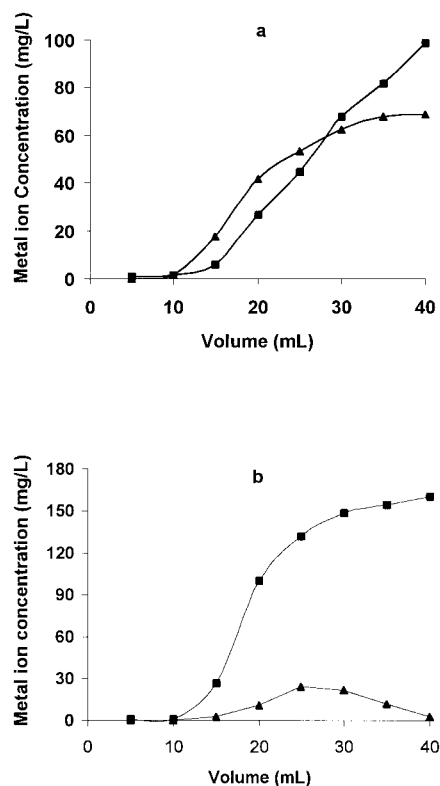
where MRC is mg of metal ion retained per g of polymer;  $M$  is the metal ion concentration of metal ion (mg/L);  $V$  is the filtrate volume through the membrane free of metal ion (L); and  $P_m$  is the mass of polymer (g), the MRC was calculated and the results for the metal ions at different pHs and concentrations are summarized in Table I. The highest value corresponds to  $\text{Co}^{2+}$  at pH 5 (0.21 mol metal ion/mol repeat unit).

For Ni(II) and Ag(I) at pH = 3 and pH = 5, the MRC values are zero (see Fig. 4), indicating that for this metal ion concentration the retention is negligible. On the other hand, the MRC values for Cr(III), Cu(II), and Ni(II) are difficult to obtain, because the polymer-metal complexes precipitate when the volume of the metal ion solution added is near to 50 mL. This can be observed in Figures 5 and 6. For this reason, it is only possible to obtain the MRC values just before precipitation. The values obtained for Co(II) at pH 3 and pH 5 are 0.12 and 0.21 mol of metal ion per mole of repeat unit, respectively. From these values, the polymer-metal complexes formed were insoluble. For the Cu(II), these values were smaller, 0.10 and 0.13 mol, of metal ion for mole of repeat unit at pH = 3 and pH = 5, respectively.

Different from the retention profile results, the MRC assays showed a selectivity in the polymer-metal ion



**Figure 5** Maximum retention capacity, MRC, for Co(II), at pH 3 (a) and pH 5 (b). (■), blank; (▲), PVPH.



**Figure 6** Maximum retention capacity, MRC, for Cu(II), at pH 3 (a) and pH 5 (b). (■), blank; (▲), PVPH.

interaction, indicating a possible polymer-metal complex formation in this case only with Cr(III), Co(II), and Cu(II).

However, it is possible to see the effect of the pH on the MRC values that is in agreement with the retention profile. With increasing pH, the MRC values increased, because the concentration of phosphonate ligand groups also increased.

## CONCLUSION

The water-soluble PVPH was studied under the conditions of the LPR method for the metal ions Hg(II), Ag(I), Cu(II), Co(II), Ni(II), Zn(II), Cd(II), and Cr(III). From pH = 3, at which the first ionization is practically complete, the metal ion retention increased. An important difference in the binding behavior of these metal ions as a function of pH and time could not be determined under these conditions. The maximum retention capacity values were found to be in the range of 60–113 mg metal/g polymer, depending on pH.

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