Polyelectrolyte-Assisted Removal of Metal Ions with Ultrafiltration

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ABSTRACT: The water-soluble polymers poly(styrene sulfonic acid-*co*-maleic acid) and poly(acrylic acid-*co*-maleic acid) were investigated with respect to their metal-ion-binding ability with ultrafiltration. The studied metal ions included Ag(I), Cu(II), Ni(II), Co(II), Ca(II), Mg(II), Pb(II), Cd(II), Zn(II), Al(III), and Cr(III) ions. The retention properties of the polyelectrolytes for the metal ions depended strongly on the ligand type. As for the carboxylate ligands, with increasing concentration and pH, the metal-binding affinity increased. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 95: 1091–1099, 2005

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

INTRODUCTION

Polyelectrolytes (PEs), polymers with a high concentration of ionic groups or ionogens, have the ability to chelate or exchange metal ions.[1–4] This property facilitates their use in the recovery and separation of metal ions from aqueous solutions. In this context, PEs are employed in water treatment and in hydrometallurgy on both industrial and laboratory scales for quantitative analytical and recovery procedures.[5,6]

The PE/metal-ion interaction can be only electrostatic in nature or can include the formation of coordinative bonds. The type of interaction depends on the chemical nature (ionization potential and electronic affinity) of the functional groups. The variables that affect the polyion/metal-ion interaction are classified into two groups: intrinsic to the polymer and extrinsic to the polymer. The former includes the polymer structure in terms of the composition and geometry, which affect the flexibility of the chains in solution, the branches of the chain, the chemical nature of the functional groups, their distribution at the polymer chain, and so forth. The second group includes the charge and type of the metal ion, the pH of the solution, the ionic strength, the temperature, and the dielectric constant of the medium.[7]
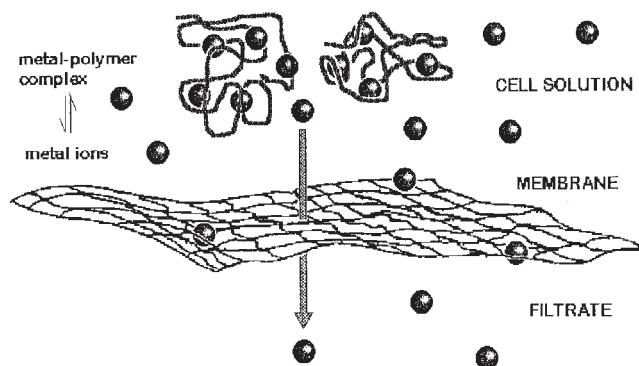
Thus, a number of soluble and hydrophilic polymers have been prepared through addition polymerization and through the functionalization of various polymers and have been found to be suitable for the separation and enrichment of metal ions in conjunction with membrane filtration. Membrane filtration allows the easy separation of metal ions bound to soluble polymers from nonbound metal ions. This method is known as liquid-phase polymer-based retention (LPR).[2,8,9] Different applications of water-soluble polymers to the homogeneous enrichment or selective separation of various metal ions from dilute solutions have been reported. Ultrafiltration has been found to be the most suitable technique for LPR studies, and a vast amount of data has been collected in different journals.[8–26]

Carboxylic and sulfonic acid groups are among the most interesting and studied functional groups. The interactions between series of PEs such as poly(carboxylic acid)s, poly(acrylic acid) (PAA), and poly(methacrylic acid), poly(vinyl sulfonic acid) (PVSA), poly(2-acrylamido-2-methyl-1-propane sulfonic acid), and several cations have been studied by potentiometric and spectroscopic techniques as well as LPR.[27–38] Polymers containing sulfonic acid moieties, such as PVSA, do not act as ligands, but the functional-group/metal-ion interaction is predominantly of the electrostatic type.

Membrane filtration processes can be successfully used for the separation of inorganic species and for their enrichment from dilute solutions with the aid of water-soluble polymers. This technique is called the LPR technique. Ultrafiltration is a fast emerging, new,

Figure 1 Schematic representation of the PE-assisted removal of metal ions with ultrafiltration.

and versatile technique in concentration, purification, and separation processes. The ultrafiltration of water-soluble, high-molecular-weight polymers in the presence of low-molecular-weight electrolytes or molecules allows the assessment of interactions between the macromolecules and low-molecular-weight species such as metal ions (Fig. 1). The polymers, before their use in the LPR technique, are fractionated by the same method with different membranes of known molecular weight exclusion limits. Thus purified, they are then lyophilized and characterized. For LPR experiments, the highest molecular weight fractions are normally used in combination with low-molecular-weight-exclusion-limit membranes to ensure that no macromolecules pass through membrane of the ultrafiltration system. Metal ions featuring high interaction rates with polymers are retained by the polymers, which are eluted through the membrane.

Some variables that may affect the polymer/metal-ion interactions are intrinsic to the polymer: the nature of the atoms in the backbone chain, the nature of the functional groups attached to the backbone, the structure and copolymer composition, the molecular weight and polydispersity, the distance between the functional groups and backbone, the degree of branching, and so forth. Other variables may be extrinsic to the polymer: the pH, the ionic strength, the nature and charge of the metal ion, the temperature, and the nature of the counterion of the metal ion.

The aim of this article is to compare the behavior of the interactions between weak and strong acid moieties as ligands and metal ions with the LPR technique.

EXPERIMENTAL

Reagents

The commercial polymers poly(styrene sulfonic acid-*co*-maleic acid) [P(SSA-*co*-MA); sodium salt, 3:1 or 1:1 styrene sulfonic acid/maleic acid; Aldrich, Milwau-

kee, WI] and poly(acrylic acid-*co*-maleic acid) [P(AA-*co*-MA); sodium salt, 1:1; Aldrich] were purified and fractionated with ultrafiltration membranes.

Fractions between 3000 and 10,000 g/mol as well as fractions greater than 100,000 g/mol were used to investigate the metal-ion-retention properties. The metal nitrates of Ag(I), Cu(II), Ni(II), Co(II), Ca(II), Mg(II), Pb(II), Cd(II), Zn(II), Al(III), and Cr(III) (Merck, Stuttgart, Germany; analytical-grade) were used as received. The solutions were prepared with twice distilled water, the conductivity of which was lower than 1 μS cm^{-1}.

Equipment

The ultrafiltration equipment consisted of a filtration cell with a membrane with a defined molar mass cutoff (MMCO) of 3000, 10,000, or 100,000 g/mol (Filtron, Pal Gelman), a reservoir for the washing solution, a selector, and a pressure source.

Procedure (Washing Method)

A 20.0-mL solution containing 5.0×10^{-3} mol/L of a water-soluble polymer, 0.010 or 0.10M NaNO$_3$, and $1.0 \times 10^{-4}M$ metal ions was placed in a solution cell provided with an ultrafiltration membrane with an MMCO of 10,000 g/mol (Filtron, Pal Gelman, Ann Arbor, MI). The pH was adjusted to 5.0 with dilute HNO$_3$. A washing solution (0.010 or 0.10M NaNO$_3$ in water at pH 3.0, 5.0, or 7.0, depending on the metal ion) was passed under pressure (3 kPa of N$_2$) from the reservoir through the cell solution. All the experiments were carried out at a constant ionic strength. As the influx and outflux were rapidly equaled, the initial volume (20.0 mL) was kept constant during the experiment. Ten fractions of 10 mL each were collected, and then 10 more of 20.0 mL each were collected. Each fraction was collected in graduated tubes, and the corresponding metal-ion concentration was determined.

Measurements

The thermal stability was studied under a nitrogen atmosphere with a Polymer Laboratories (UK) STA 625 thermal analyzer. The heating rate was 10°C/min.

The pH was determined with a Jenco Electronics (CA) 1671 pH meter. For the LPR technique, a membrane filtration system was employed to test the coordinating properties of the polychelatogen. A Unicam Solaar M5 atomic absorption spectrometer (UK) was used for the determination of the metal-ion concentrations in the filtrate.

RESULTS AND DISCUSSION

Different PEs, P(SSA-*co*-MA) (sodium salt, 3:1 or 1:1 styrene sulfonic acid/maleic acid; Aldrich) and P(AA-*co*-MA) (sodium salt, 1:1), were purified and fractionated with ultrafiltration membranes. These water-soluble polymers contained strong and weak acid groups as salient features of their structures. P(AA-*co*-MA) contained only carboxylic acid groups, but P(SSA-*co*-MA) featured sulfonic acid and carboxylic acid groups.

The most important properties of these polymers were as follows:

1. They had good chemical and physical stability.
2. They were linear polymers with high flexibility and functional groups linked directly to the backbone.
3. They had very good solubility in water.
4. They had a high capacity to incorporate metal ions because of the high local concentration of functional groups.

Metal-ion-retention properties

The metal-ion-binding properties of the water-soluble polymers P(SSA-*co*-MA) and P(AA-*co*-MA) were investigated with the LPR method. The binding properties are documented as retention profiles, which are plots of the retention (*R*) versus the filtration factor (*Z*). *Z* is defined as the ratio of the filtrate volume (V_f) to the volume in the cell (V_0), that is, $Z = V_f/V_0$. The metal ion remaining in the cell during filtration consists of the sum of the metal ion bound to the polymer chain and the metal ion free in the solution. *R* of metal ions in a cell solution by a polymeric reagent can be conveniently calculated as follows:

$$R \ (\%) = C_r \times C_0^{-1} \times 100$$

where C_r is the metal-ion concentration in the retentate (the cell solution after V_f has been passed) and C_0 is the initial metal-ion concentration in the cell. Typical retention profiles are shown in Figures 2–5.

The polymer fractions greater than 100,000 g/mol were used to investigate the metal-ion-binding properties at different pH and *Z* values. The ions were Ag(I), Cu(II), Co(II), Ni(II), Cd(II), Zn(II), Pb(II), Ca(II), Mg(II), Cr(III), and Al(III).

In general, an effect of the pH on the retention properties could be observed. As the pH increased, the metal-binding affinity also increased.

Figure 2 shows the metal-ion-binding properties of P(SSA-*co*-MA) (fraction > 100,000 g/mol) at pH 5. Here no specific behavior in the metal-ion-retention profile can be observed, as all the metal ions interacted strongly with the ligands. Figure 3 shows the effect of

the pH on the metal-ion retention of P(SSA-*co*-MA). At pH 3, the retention of Cr(III) and Al(III) ions was practically quantitative. For all the other metal ions, it was over 80%, and at pHs 5 and 7, it was practically 100%. Cr(III) and Al(III) ions were not investigated at pHs greater than 3 to avoid precipitation. It is necessary to consider that at this pH, chromium exists basically as Cr^{3+}, which coexists with basic species such as $Cr(OH)_2^+$ and $CrOH^{2+}$. Copper(II) was not studied above pH 5 to avoid the precipitation of $Cu(OH)_2$.

When the content of styrene sulfonic counits was increased, the retention of all metal ions decreased significantly (see Figs. 2 and 4). The metal-ion/ligand interaction could be considered very weak, as it decreased and was kept constant from $Z = 2$. The maximum retention found at such *Z* values was close to 40%. That meant that the carboxylate groups were the most relevant groups for the formation of complexes, particularly at higher pHs.

On the contrary, for P(AA-*co*-MA), which contained only carboxylic acid groups, an effect of the pH on the metal-ion retention was observed. This effect was shown clearly for the retention of Ag(I) ions; the retention at pH 3 was very low and at pH 7 was 100%.

Z can be interpreted as measure of the stability of the polymer-ligand/metal-ion interactions. Figure 6 shows the metal-ion-retention properties of the three hydrophilic polymers at $Z = 10$ and different pHs.

For P(AA-*co*-MA), the highest retention (ca. 60%) was observed for Al(III) ions at pH 3, but with an increase in the pH, the carboxylate groups formed very stable complexes with all the metal ions studied, except for silver ions. This behavior was maintained at pH 7.

For P(SSA-*co*-MA), no essential effect of the pH on the metal-ion retention was observed, and this showed that the retention mechanism would be different with respect to P(AA-*co*-MA).

Polymer/metal-ion interactions

In terms of Pearson's concept of hard and soft acids and bases, carboxylate groups are soft bases, whereas sulfonate groups are relatively hard bases.

On the other hand, Cu(II) is a soft acid. As a general rule, hard acids coordinate better with hard bases, and soft acids coordinate better with soft bases. The hard-base/hard-acid interaction is a charge-controlled one, resulting mostly from a favorable electrostatic interaction between a donor and an acceptor, respectively, with high and low orbital electronegativity. However, the interaction between a soft acid and a soft base normally leads to the covalent coordination of a donor with low orbital electronegativity and an acceptor with high orbital electronegativity. Therefore, a strong interaction between Cu^{2+} and P(AA-*co*-MA) was expected to be found in the ultrafiltration experiments

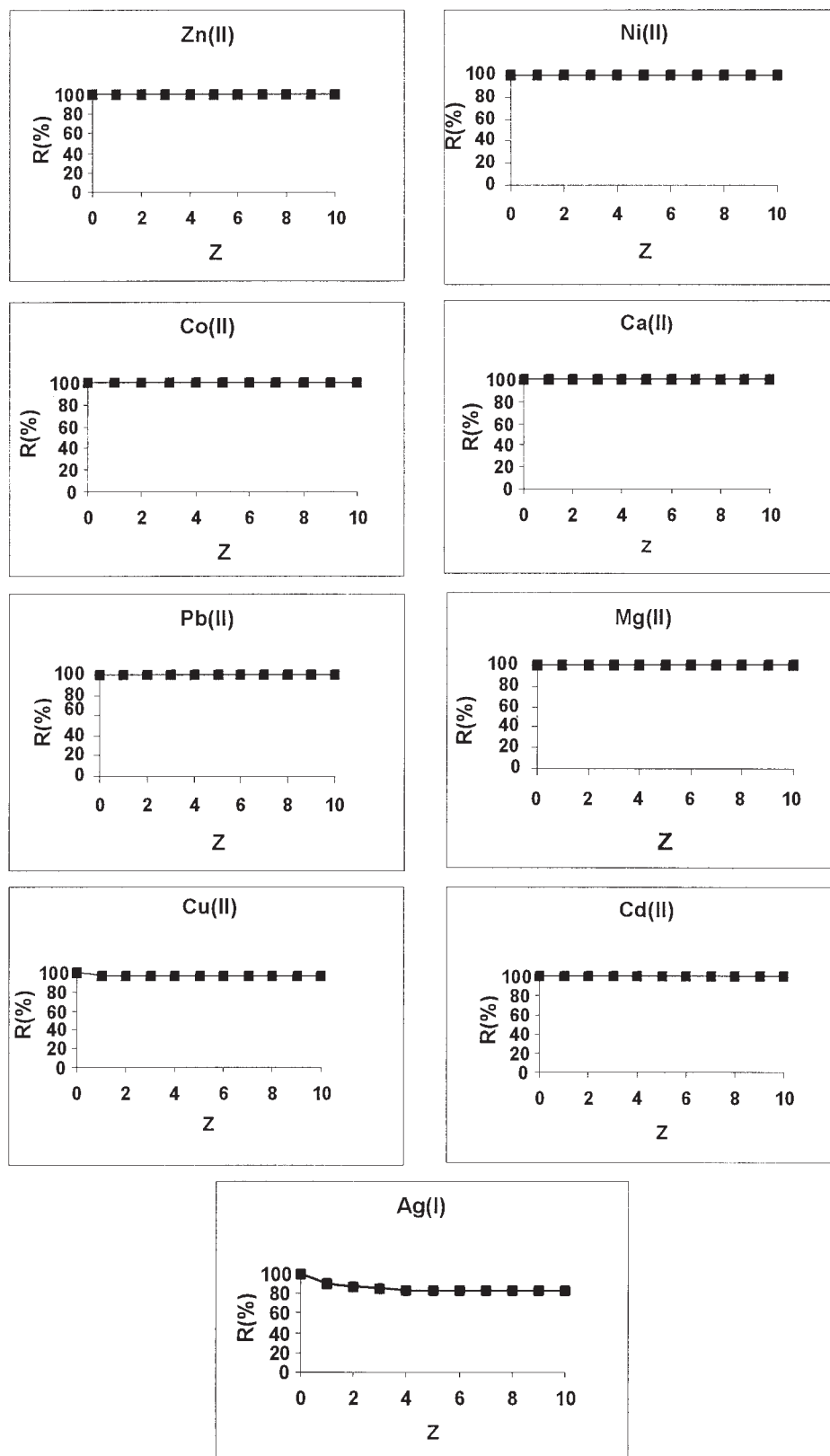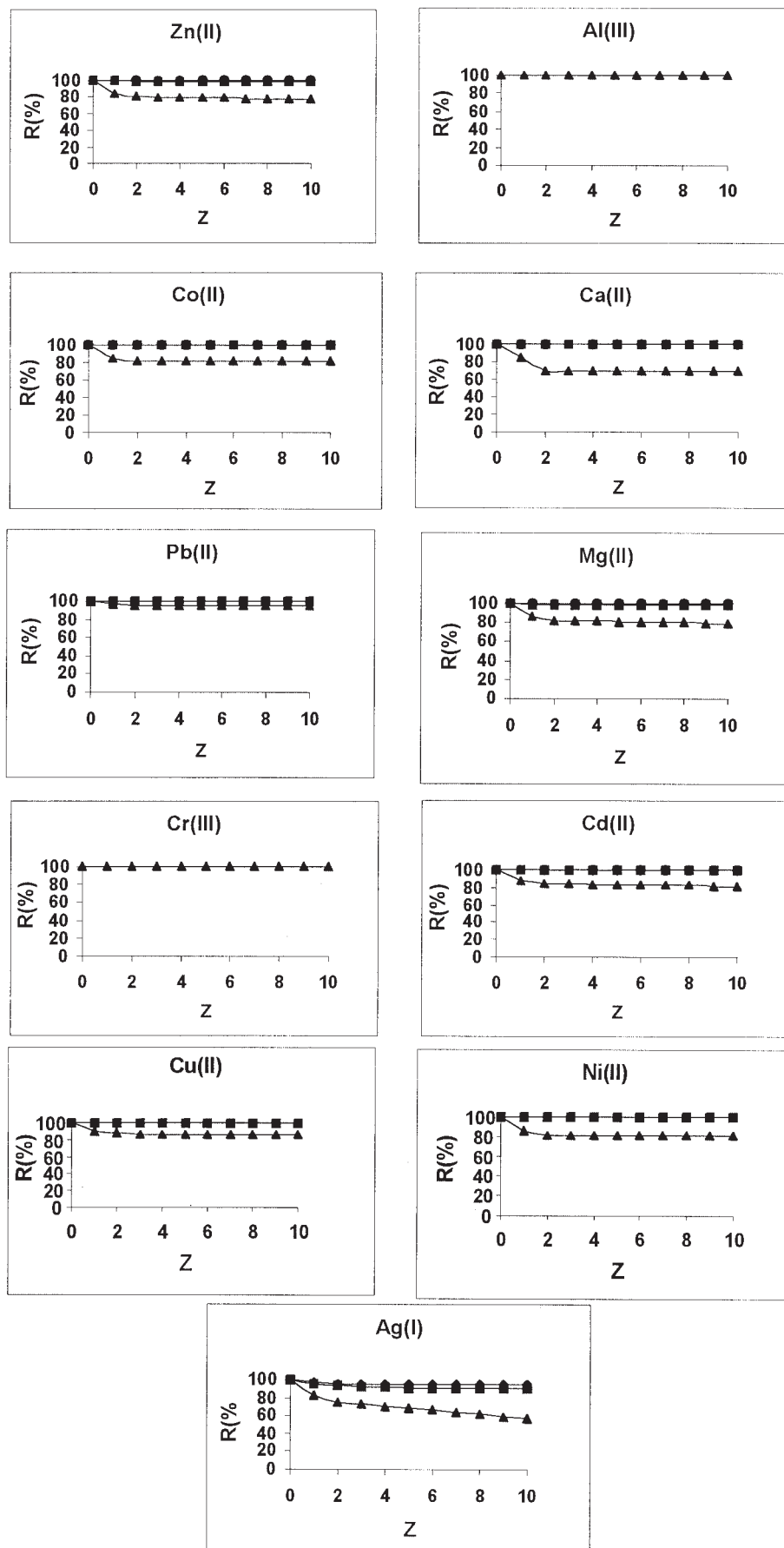**Figure 2** Retention profiles for 3:1 P(SSA-*co*-MA) fractions greater than 100,000 g/mol at pH 5.

Figure 3 Retention profiles for 1:1 P(SSA-*co*-MA) fractions greater than 100,000 g/mol at the following pHs: (▲) 3, (■) 5, and (♦) 7.
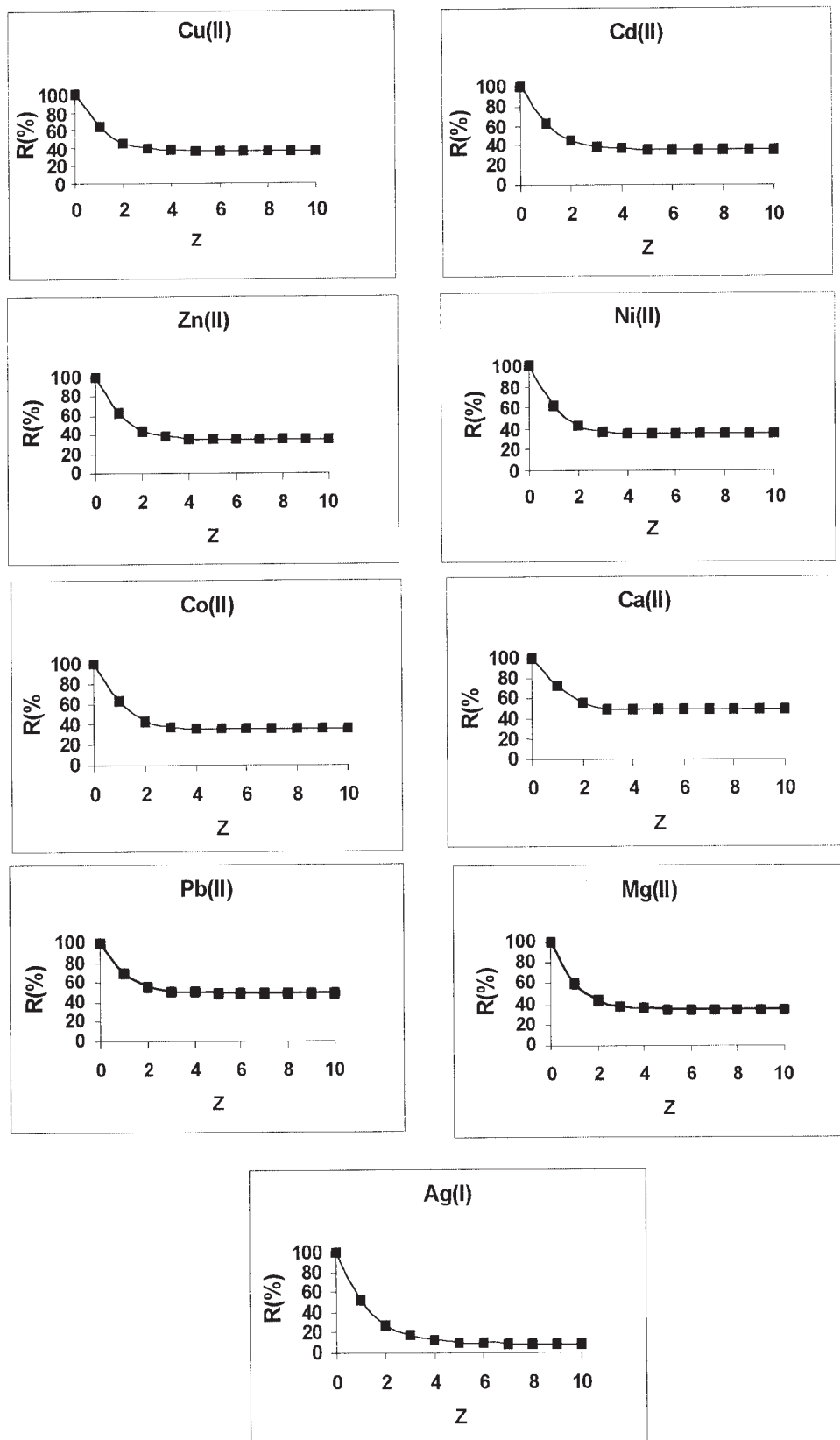
Figure 4 Retention profiles for 1:1 P(SSA-*co*-MA) fractions greater than 100,000 g/mol at pH 5.
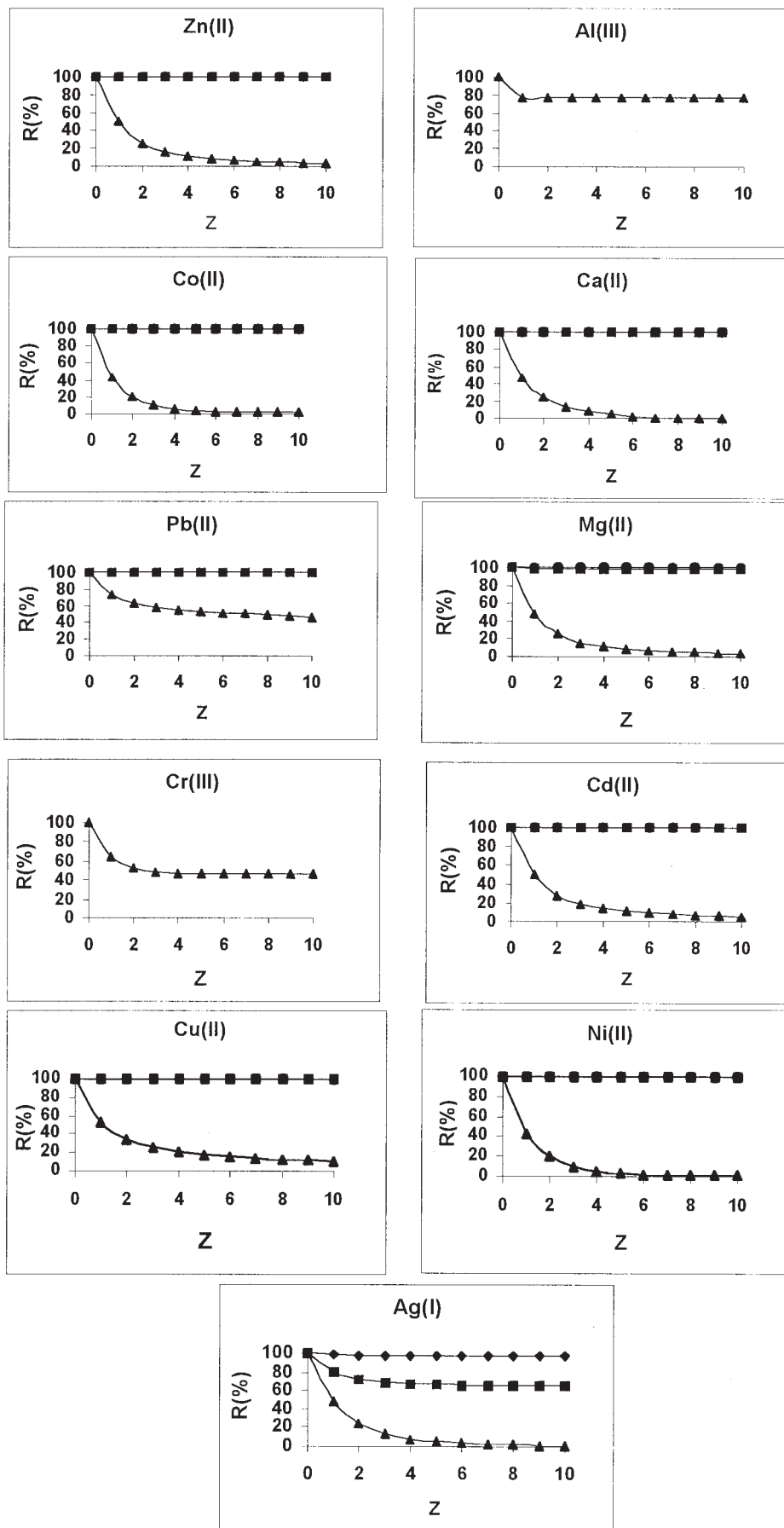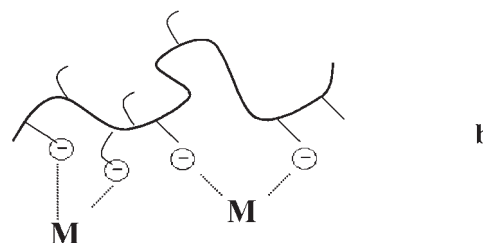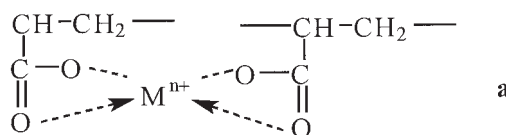
Figure 5 Retention profiles for 1:1 P(AA-*co*-MA) fractions greater than 100,000 g/mol at the following pHs: (▲) 3, (■) 5, and (♦) 7.
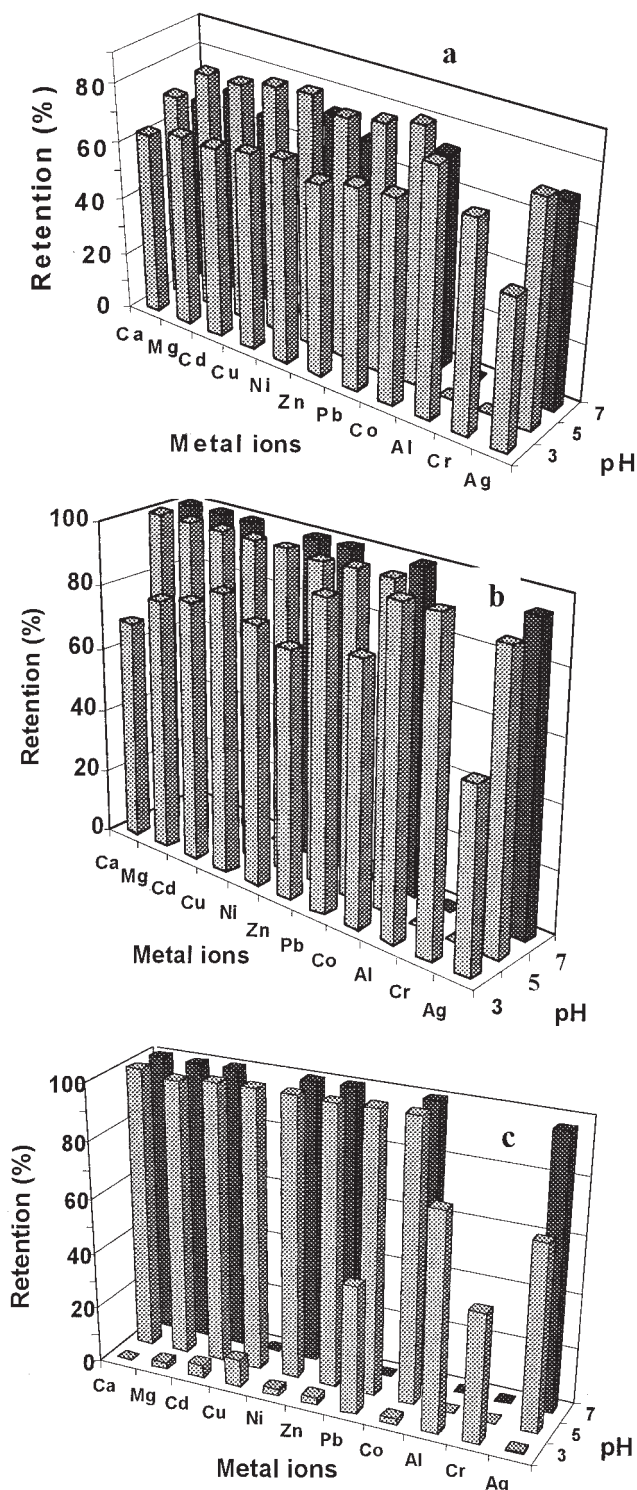
because of their high ability to form coordination bonds.

The complexing process of metal ions with polymers may be preceded by long-range attracting electrostatic interactions, and once the metal ion is con-

Scheme 1   Possible polymer/metal-ion interaction mechanism for (a) carboxylate groups (complex formation) and (b) sulfonate groups (electrostatic interaction).

densed on the polymer surface, its site is fixed by the polymer ligands.

Scheme 1 shows the most accepted mechanisms for these polymer/metal-ion interactions. The carboxylic groups can act as monodentate and bidentate ligands. According to the pH value, ionized PAA may form complexes with D_{2h} or D_{4h} (dimer) symmetry. At high pH values, the PAA chain has a drawn shape because of the electrostatic repulsion of charged carboxylate groups. Metal ions are then binding with either one or two neighboring groups. At pH 4.5, the macromolecular globules contract, and the metal ions are able to coordinate two to four carboxylic groups. The interaction of metal ions with polyacids is an isothermal process. Therefore, the formed complexes have to be stabilized because of high changes in the entropy factor. On the contrary, water-soluble polymers with sulfonic acid/sulfonate groups favor electrostatic polymer/metal-ion interactions [see Scheme 1(b)].

The polymer/metal-ion interaction may be intramolecular, intermolecular, or both. The first is the most common for numerous groups of polymer–metal complexes showing comparatively high chemical and thermal stability. Another specific feature of these compounds is the total saturation of the coordination sphere of the transition-metal ion. The interchain polymer/metal-ion interaction may proceed via the binding of functional groups of two different macromolecules; usually one of them provides acidic functional groups, and the second provides basic groups. This type of metal-ion binding with mixed biopolymers is a process of great importance for biological reactions.

Figure 6   Metal-ion retention for (a) 3:1 P(SSA-co-MA), (b) 1:1 P(SSA-co-MA), and (c) 1:1 P(AA-co-MA) at Z = 10 and different pHs.

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