Water-Soluble Amine and Imine Polymers with the Ability To Bind Metal Ions in Conjunction with Membrane Filtration

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ABSTRACT: The commercial polymers poly(ethylene imine) (PEI), poly(ethylene imine epichlorohydrin), and poly(dimethylamine-*co*-epichlorohydrin) were purified and fractionated by ultrafiltration. Their metal-ion-binding properties with respect to different ligand groups and the effect of the concentration on the retention properties were investigated. The amine ligands of the polymers formed the most stable complexes with the metal ions. In general, there was an effect of the pH and polymer fraction size on the retention properties. As the pH and polymer fraction size increased, the affinity to bind metal ions also increased. PEI had the highest metal-retention values, particularly at higher pHs, at which the amine groups were nonprotonated and could coordinate easily with the metal ions. Only Pb(II) was poorly retained. The affinity for all the metal ions, except Pb(II), increased significantly at pH 5. The metal-ion retention decreased quickly as the filtration factor increased, except for Cu(II), Co(II), Ni(II), Cd(II), and Zn(II) ions, which were retained by over 40% at a filtration factor of 4. For other metal ions such as Pb(II), Ca(II), and Mg(II), only 10% remained bound to the polymer. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 222–231, 2005

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

INTRODUCTION

Polymers containing metals have emerged as new-generation materials with tremendous potential in applications such as superconducting materials, ultra-high-strength materials, liquid crystals, catalysts, and biocompatible polymers.[1–7] The structures of some polymer/metal-ion complexes have been reported in the literature.[1,7–12]

Insoluble polymeric supports have been widely investigated and are applied to metal recovery from dilute solutions.[13–23] There are different natural and synthetic products that show ion-exchange properties. The organic resins are by far the most important ion exchangers. Their main advantages are their high chemical and mechanical stability and high ion-exchange capacity and ion-exchange rate. Another advantage is the possibility of selecting the fixed ligand groups and the degree of crosslinking.

Heterogeneous two-phase systems, which include an aqueous metal-ion solution and a water-insoluble polymer (resin), can be avoided with separation methods based on membrane processes, which are among the most promising techniques for the enrichment of various species from solutions.[24–26] Thus, a number of soluble and hydrophilic polymers have been prepared through addition polymerization and through the functionalization of various polymers, and they have been found to be suitable for the separation and enrichment of metal ions in conjunction with membrane filtration.

Ultrafiltration is fast emerging as a new 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 detection of interactions between the macromolecules and low-molecular-weight species such as metal ions. The polymers, before being used for liquid-phase polymer-based retention (LPR), are fractionated by the same method with different membranes of known molecular mass exclusion limits. Thus purified, they are then lyophilized and characterized. For LPR experiments, the highest molecular weight fractions are normally used in combination
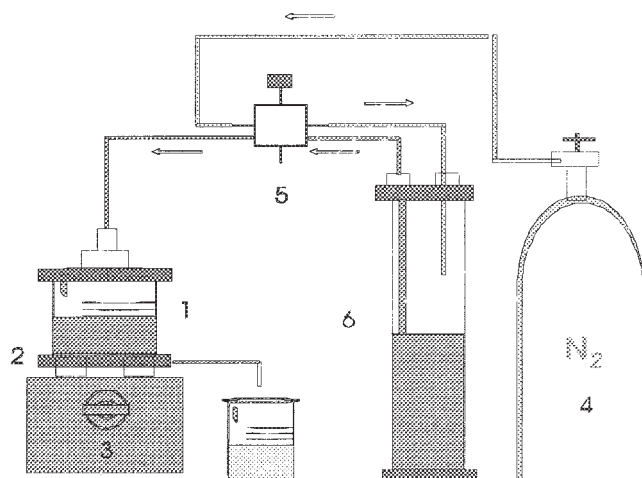
Figure 1 Instrumental arrangement: (1) filtration cell with polymeric and metal-ion solution, (2) membrane filtrate, (3) magnetic stirrer, (4) pressure trap, (5) selector, and (6) reservoir with water.

with low-molecular-mass-exclusion-limit membranes to ensure that no macromolecule passes through the membrane.

Membrane filtration allows the easy separation of metal ions bound to soluble polymers from nonbound metals. This method is known as the LPR technique.[27,28] Applications of water-soluble polymers to the homogeneous enrichment or selective separation of various metal ions from dilute solutions have been reported. Metal ions with high interaction rates with the polymer are retained by the polymer, which is not able to pass through the ultrafiltration membrane, whereas other ions are eluted through the membrane (see Fig. 1). Ultrafiltration is the most suitable technique for LPR studies, and a vast amount of data is being published in different journals.[29–45]

Water-soluble polymers are commercially available or can be synthesized via different routes. Among the most important requirements for the technological applications of these polymers are high solubility in water, easy and cheap synthesis, an adequate molecular weight and molecular weight distribution, chemical stability, a high affinity for one or more metal ions, and selectivity for the metal ion of interest.

The ability of the molecules to form complexes with metal ions depends on several variables, such as the charge/radius ratio, charge distribution, polarization of both ligands and the central atom, and possibility of chelate formation. The ionic radius of Cu(II) (0.71 Å) is smaller than that of Cd(II) (0.92 Å) or Pb(II) (1.33 Å) but does not differ much from that of Co(II) (0.72 Å), Zn(II) (0.74 Å), or Ni(II) (0.69 Å; see Table I).

The aim of this article is to investigate the metal-ion-binding properties of different polymers containing amine and hydroxyl ligand groups as well as the effect of the concentration of the molecular size on the

retention properties. The metal ions were selected because of their interest from environmental and biological points of view.

EXPERIMENTAL

Reagents

The commercial polymers poly(ethylene imine) (PEI; Aldrich, Milwaukee, WI), poly(ethylene imine epichlorohydrin) (PEIE; Aldrich), and poly(dimethyl-amine-*co*-epichlorohydrin) (PDMA-*co*-E; Aldrich) were purified and fractionated with ultrafiltration membranes.

The water-soluble polymers were characterized by Fourier transform infrared (FTIR) and ^{1}H-NMR spectroscopy.

PEI

FTIR (cm^{-1}): 3280.57, 1593.31 (N—H), 2814.82–2938.12 (C=C), 1296.19–1348.12 (—CH$_2$—), 1050.92–1118.43 (C—N). ^{1}H-NMR (ppm): 2.6 (CH_2—N).

PEIE

FTIR (cm^{-1}): 3436.93 (OH, N—H), 1629.61 (N—H). ^{1}H-NMR (ppm): 3.1 (CH_2—N), 3.6 (CH_2 of the side chain), 4.2 (CH—OH).

PDMA-*co*-E

FTIR (cm^{-1}): 3416.85 (OH), 1477.04, 1103.36 (C—O of alcohol). ^{1}H-NMR (ppm): 3.2 (CH_3), 3.6 (CH_2), 4.9 (CH).

Fractions between 3000 and 10,000 g/mol and 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),

TABLE I
Ionic Radii and Valence Electronic Configurations of the Metal Ions

Metal ion	Ionic radii (Å)[a]	Electronic configuration
Ag$^+$	0.81	d^{10}
Cu^{2+}	0.71	d^9
Ni^{2+}	0.69	d^8
Co^{2+}	0.72	d^7
Cd^{2+}	0.92	d^{10}
Zn^{2+}	0.74	d^{10}
Ca^{2+}	1.14	[Ar]
Mg^{2+}	0.71	[Ne]
Pb^{2+}	1.33	s^2
Al^{3+}	0.53	[Ne]
Cr^{3+}	0.76	d^3

[a] Taken from ref. 47.

TABLE II
Thermal Behavior of the Polychelatogens

Polychelatogen	Residual weight (%) at different temperatures (°C)					
	100	200	300	400	500	550
PEI	94.3	81.4	79.1	2.1	1.0	1.0
PEIE	98.8	91.5	75.7	15.6	8.5	7.2
PDMA-*co*-E	99.5	94.7	47.1	12.8	8.3	7.4

Heating rate = 10°C/min. Nitrogen atmosphere.

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}.

Table I lists the ionic radii and electronic configurations of all these metal ions.

Equipment

The ultrafiltration equipment was previously described.[26,27] It had 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, USA), a reservoir for the washing solution, a selector, and a pressure source (see Fig. 1).

Procedure (Washing Method)

A solution (20.0 mL) containing 5.0×10^{-3} equiv/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). 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 were collected, and then 10 more of 20.0 mL were collected. Each fraction was collected in graduated tubes, and the corresponding metal-ion concentration was determined.

Measurements

The molecular weight and molecular weight distributions of the polychelatogens were analyzed by gel permeation chromatography with a PerkinElmer Series 200 (USA) with a differential-refractive-index detector and PL Aquagel OH columns. The water and polystyrene were the solvent and standard, respec-

tively. The FTIR spectra were recorded on a Magna Nicolet 550 spectrophotometer (Nicolet Analytical Instruments, Madison, WI). The ^{1}H-NMR spectra were recorded in D$_2$O with a Bruker Multinuclear AM 250 spectrophotometer (Bruker Instruments, Billerica, MA). The thermal stability was studied under a nitrogen atmosphere with a Polymer Laboratories STA 625 thermal analyzer (Polymer Laboratories, Amherst, UK). The heating rate was 10°C/min.

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

RESULTS AND DISCUSSION

It is well known that polyamines are suitable macromolecular ligands for coordination with metal ions. One of the most representative polymers containing amine groups is PEI, which possesses a number of advantages as a polymer chelating reagent, such as good water solubility, a high concentration of functional groups, good physical and chemical stability, and a suitable molecular weight.

The commercial polymers were characterized with FTIR and ^{1}H-NMR spectroscopy (see the Experimental section) and thermogravimetric analysis (see Table II). PEIE showed thermal behavior similar to that of PEI, with a slightly higher residual weight. PDMA-

TABLE III
Molecular Weights (M_w and M_n) of the Water-Soluble Polymers with Water as the Solvent and Polydispersity (M_w/M_n)

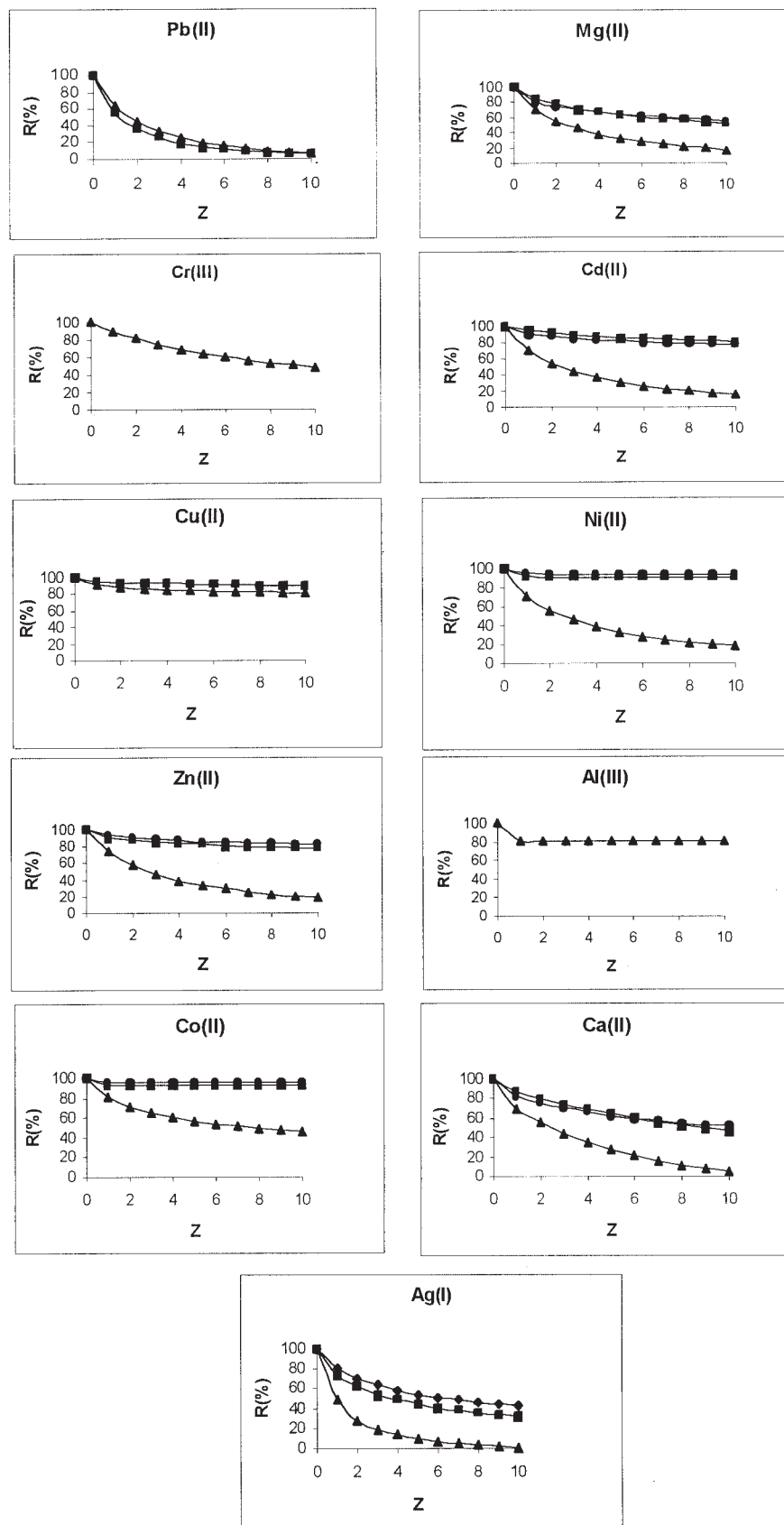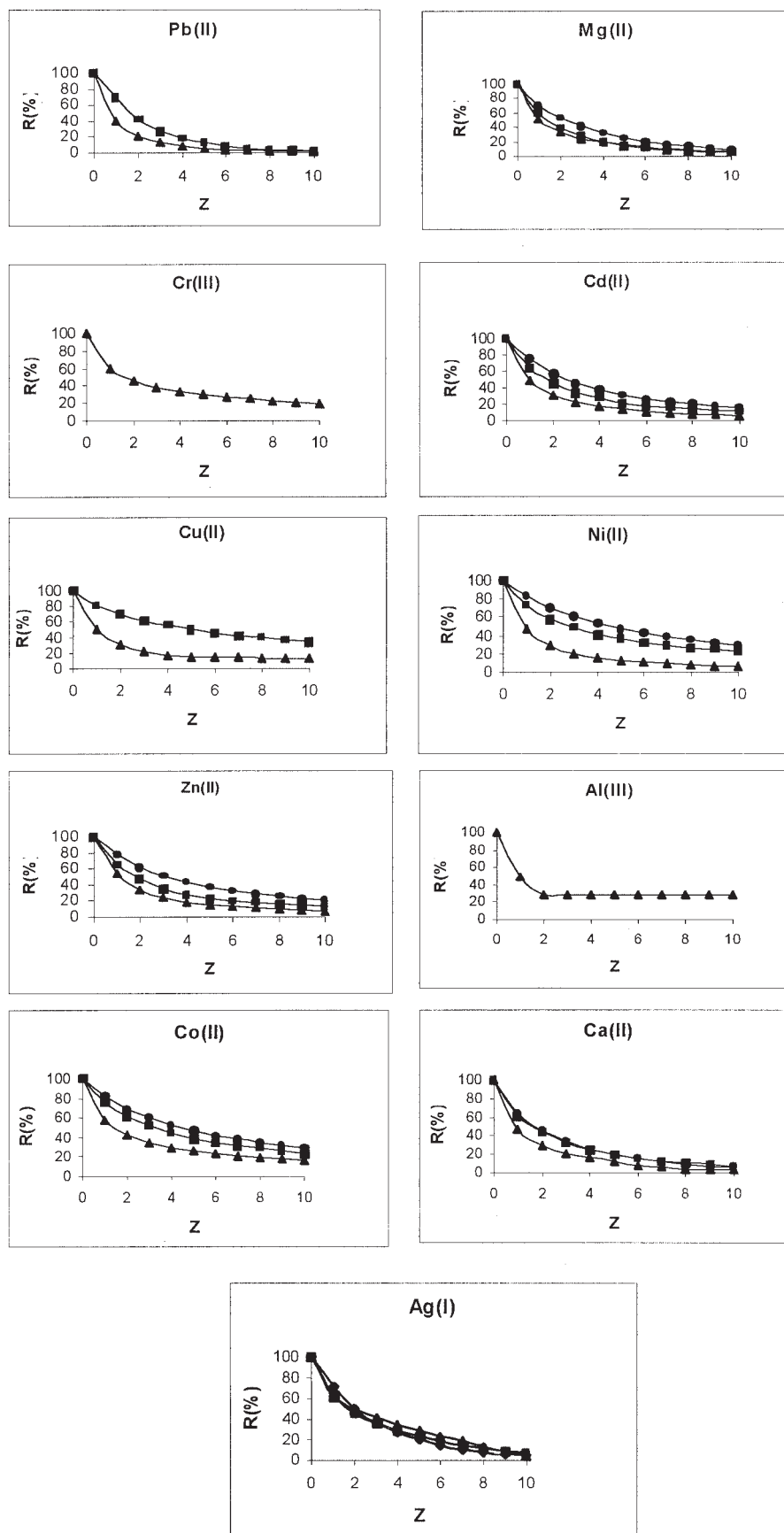| Fraction of water-soluble polymer	Area (%)	M_w	M_n	M_w/M_n
PEI	2.4	209,490	197,830	1.06
>100,000	5.9	21,480	21,030	1.02
	91.7	41,500	27,500	1.51
PEIE 3,000–10,000	82.2	145,000	6,000	1.67
PDMA-*co*-E 3,000–10,000	96.9	9,600	6,150	1.58

Figure 2 Retention profiles of PEI fractions greater than 100,000 D at the following pHs: (▲) 3, (■) 5, and (●) 7.

Figure 3 Retention profiles of PEI fractions greater than 3000 but less than 10,000 D at the following pHs: (▲) 3, (■) 5, and (●) 7.
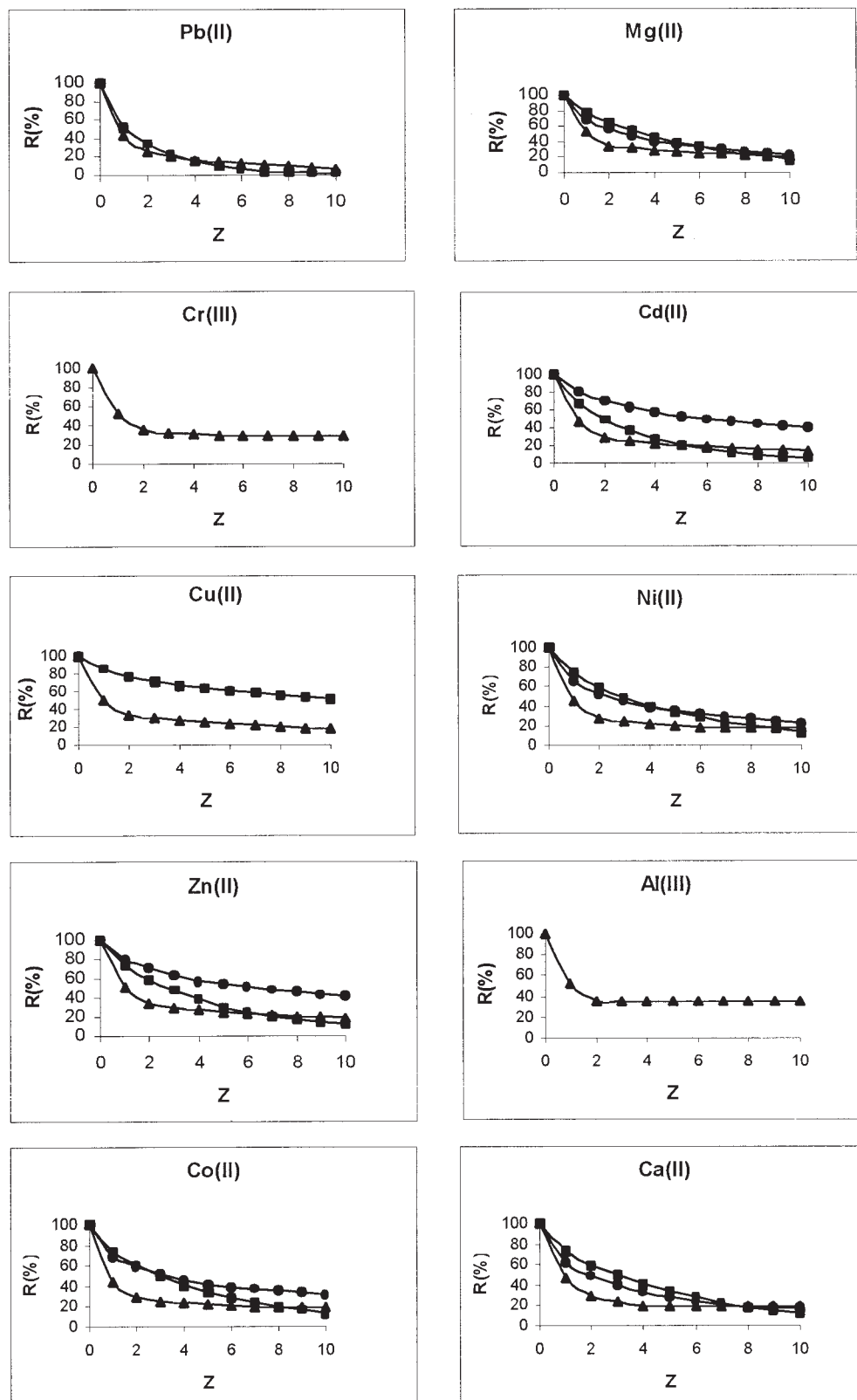
Figure 4 Retention profiles of PEIE fractions greater than 100,000 D at the following pHs: (▲) 3, (■) 5, and (●) 7.

co-E showed a strong weight loss between 200 and 300°C, probably because of the evolution of ammonium.

Table III shows the molecular weight, molecular weight distribution, and polydispersity of the different fractions, especially those greater than 3000 and
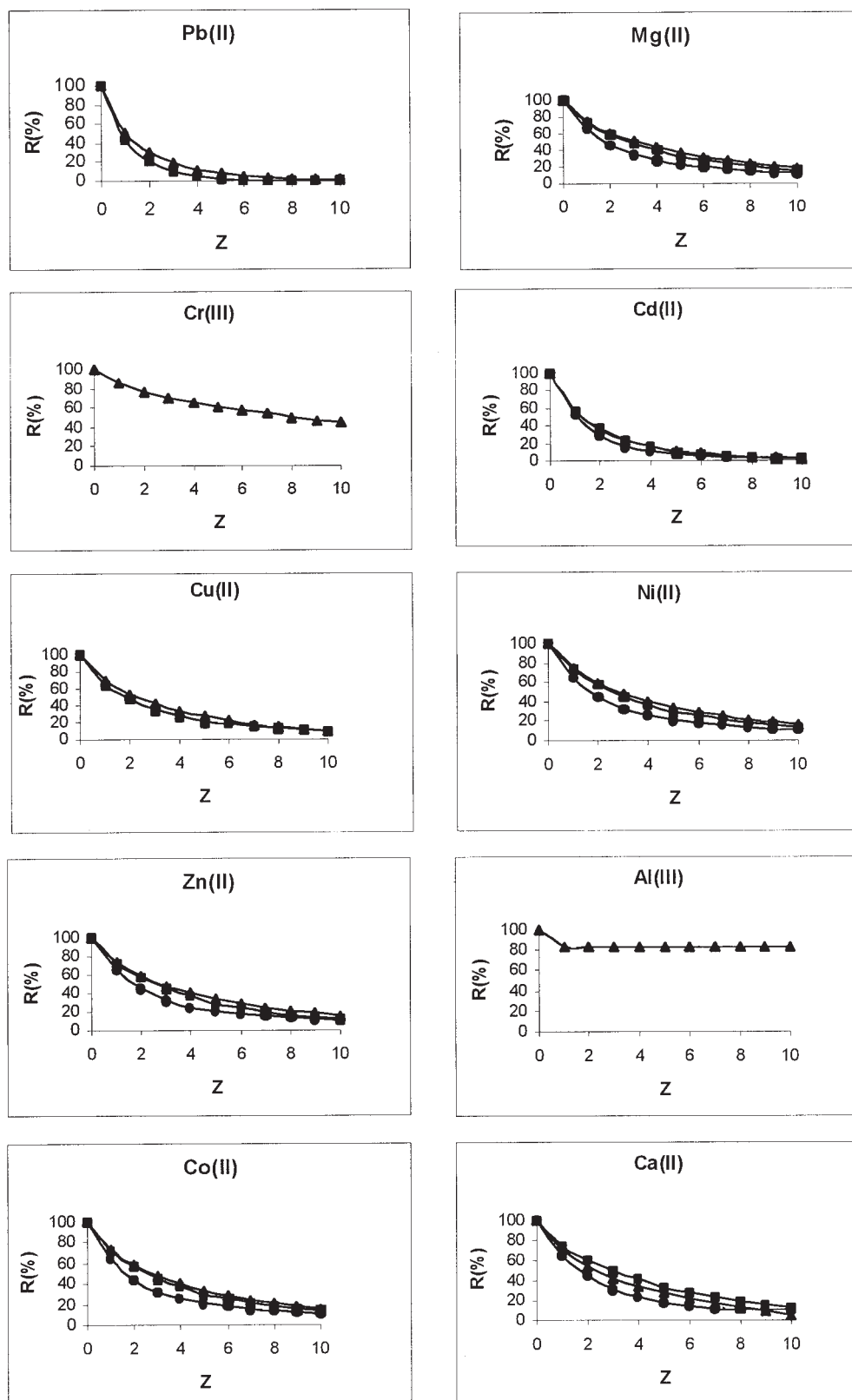
Figure 5   Retention profiles of PDMA-*co*-E fractions greater than 100,000 D at the following pHs: (▲) 3, (■) 5, and (●) 7.
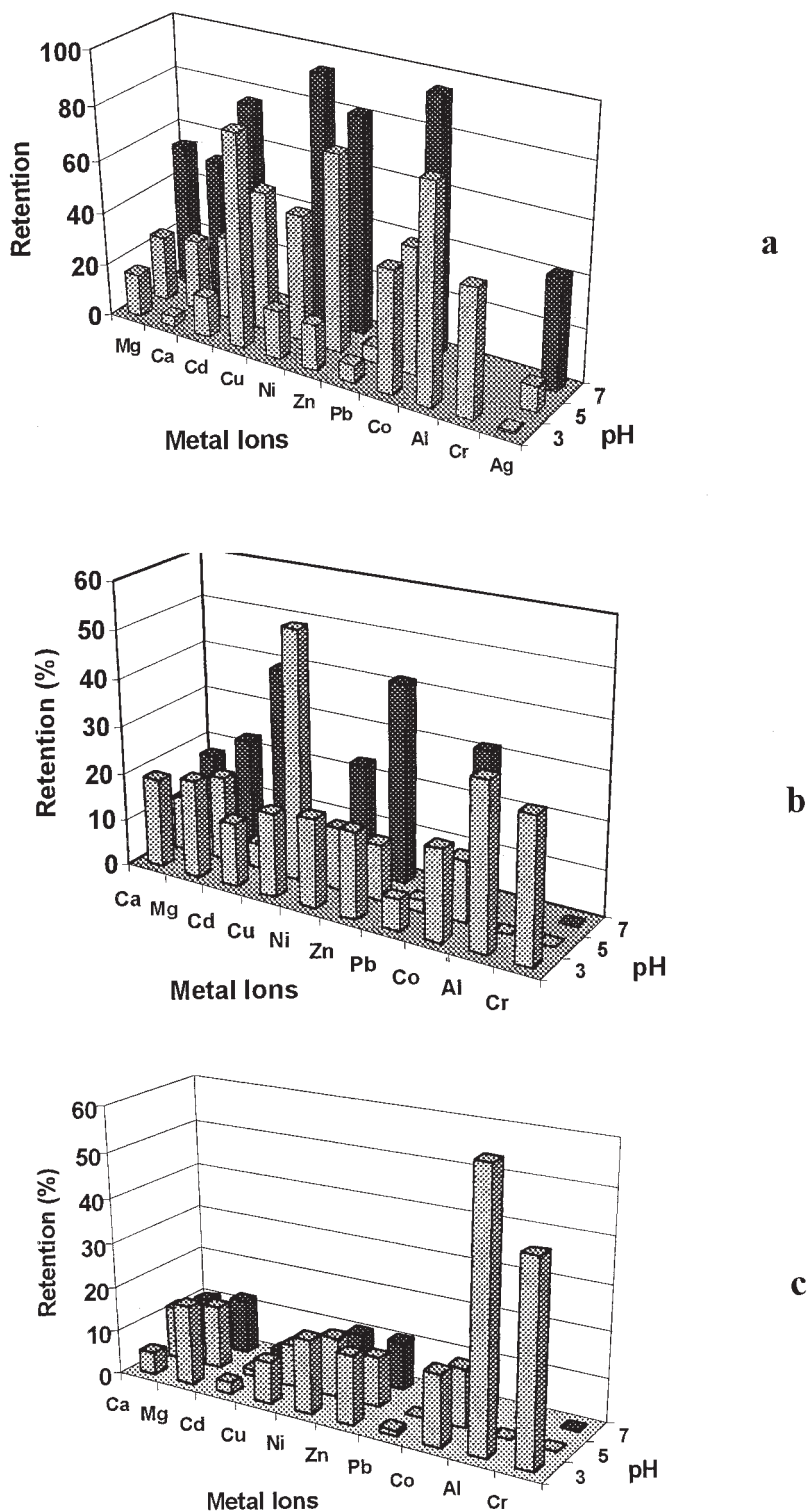
Figure 6   Metal-ion retention at $Z = 10$ and different pH values of (a) PEI, (b) PEIE, and (c) PDMA-*co*-E.

less than 10,000 g/mol, that were used for the LPR runs. The polydispersity values varied between 1.01 and 1.67, demonstrating a relatively homogeneous length of the polymer chains.

The metal-ion-binding properties of the water-soluble polymers (PEI, PEIE, and PDMA-*co*-E) were investigated with the LPR method. The binding properties are documented in retention profiles, which are plots of the retention (R) versus the filtration factor (Z). Z is defined as the ratio of the volume of the filtrate (V_f) and the volume of the cell solution. R of metal ions in the 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 a filtrate volume of 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 and greater than 3000 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, there was an effect of the pH on the retention properties. As the pH increased, the affinity to bind metal ions also increased.

Figure 2 shows the metal-ion-binding properties of PEI. The polymer fractions were greater than 3000 and less than 10,000 g/mol. The metal-ion retention decreased quickly as Z increased, except for Cu(II), Co(II), Ni(II), Cd(II), and Zn(II) ions, which were retained by over 40% at $Z = 4$. For other metal ions such as Pb(II), Ca(II), and Mg(II), only 10% remained bound to the polymer. The first five metal ions had similar ionic radii (see Table I) and were ions with uncompleted d-orbitals. The last one was a fundamental condition for the formation of coordinated bonds with the electron pair of the amine groups in the polymers, yielding polymer–metal complexes. On the contrary, the last three metal ions had larger ionic radii and had more stable electronic structures, and this prevented complex formation. This behavior was similar to that of the other polymers. Therefore, a higher polymeric fraction greater than 100,000 g/mol was investigated (see Figs. 3–6) to increase the density of the polymer ligand sites.

PEI showed the highest metal-retention values, particularly at higher pHs, at which the amine groups were more available and could coordinate more easily with the metal ions. Although the amine groups in PEI were protonated even at pH 7, they formed polymer–metal complexes with several metal ions at pHs 3, 5, and 7. In effect, because pK_a was 10 for the amine groups in the polymer, we determined that only 0.00001% of these groups were deprotonated at pH 3, whereas at pH 5, the value reached 0.001%, and at pH 7, it was 0.1%. This meant that there was strong competition between the metal ions and protons for the electron pairs in the amine groups from PEI. This competition was favored for the metal ions at higher pH values. The proposed structure for this kind of complex is presented in Scheme 1. Only Pb(II) was poorly retained. The affinity for all the metal ions, except Pb(II),
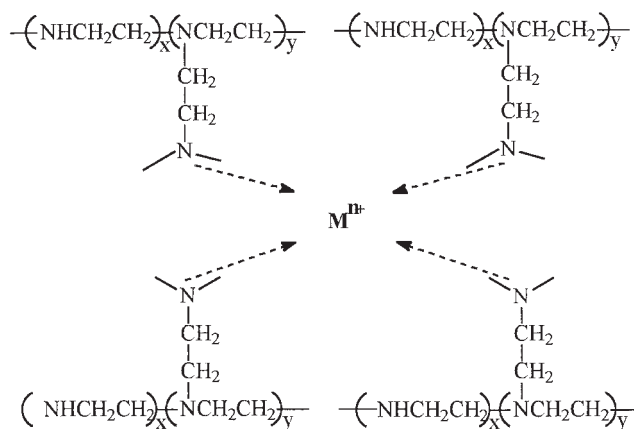
Scheme 1 Proposed structure of the PEI–metal complex.

increased significantly at pH 5. Cr(III) ions were not investigated at pHs greater than 3 to avoid precipitation. At pH 3, Cr(III) was retained to nearly 50%. It is necessary to consider that at this pH, chromium exists basically as Cr^{3+}, coexisting with basic species such as $Cr(OH)_2^+$ and $CrOH^{2+}$. Copper(II) was not studied above pH 5 to avoid the precipitation of $Cu(OH)_2$. Ni(II), Co(II), Cd(II), and Zn(II) ions interacted relatively strongly with the amine groups during the filtration, and this was in agreement with the literature data.[46]

By the inclusion of hydroxyl groups, which were weak ligand groups, it was possible to change the metal-ion-binding capabilities (see Figs. 4 and 5).

PEIE showed a lower metal-ion affinity than PEI, fundamentally because PEIE contained hydroxyl groups, which were weaker ligands than amine groups. In addition, the presence of hydroxyl groups reduced the number of amine ligands per mass unit and increased the steric hindrance for the complex formation. At pH 5 and $Z = 5$, it retained only Cu(II) and Zn(II) ions by over 50%.

PDMA-co-E showed the lowest metal-ion-binding capacity, but it exhibited a high retention and selectivity for the trivalent cations Al(III) (>80%) and Cr(III) (>60%) at $Z = 5$.

Z is a measurement of the stability of the polymer ligand/metal-ion interaction. Figure 6 shows the metal-ion-retention properties of the three hydrophilic polymers at $Z = 10$ and different pHs.

At pH 3, the retention values of Cu(II) and Al(III) for PEI were very similar (ca. 60%). For PEIE, it decreased. The highest retention (ca. 25%) was observed for Al(III) ions. PDMA-co-E showed metal-ion-retention values lower than 10% at pHs 3, 5, and 7 for all metal ions, except for Al(III) (52%) and Cr(III) (34%). It showed a higher selectivity for the trivalent cations, particularly for Al(III) ions.

CONCLUSIONS

The metal-ion-retention properties of water-soluble polymers containing amine ligand groups depended on the pH. As the pH increased, the affinity to bind metal ions also increased.

PEI showed the highest metal-retention values, particularly at higher pHs, at which the amine groups were more available and could coordinate more easily with the metal ions. Only Pb(II) was poorly retained. The affinity for all the metal ions, except Pb(II), increased significantly at pH 5.

The copolymer structure of the polychelatogen may diminish the possibility of complex formation because of the higher distance between the ligand groups and could also change the affinity for the metal ions by increasing the selectivity.

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