DOI: 10.1002/masy.200851017

Water-soluble Polyelectrolytes Contaning Sulfonic Acid Groups with Metal Ion Binding Ability by Using the Liquid Phase Polymer Based Retention Technique

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Summary: Water-soluble polyelectrolytes from 2-acrylamido-2-methyl-1-propane sulfonic acid (APSA) were obtained by radical polymerization with different comonomers which contain weak acid and neutral groups. These copolymers were investigated as polyelectrolytes and polychelatogens, in view of their metal ion binding properties using the *liquid-phase polymer-based retention* (LPR) technique under different experimental conditions. The metal ions investigated were: Ag(I), Co(II), Cu(II), Zn(II), Cd(II), and Pb(II). APSA allowed increase metal ion interaction of weak acid, meanwhile did not improve the metal ion interaction of neutral monomers at these experimental conditions. Results indicated that retention capability depended strongly on the structure of the polyelectrolyte, arrangement of comonomers at main chain, pH, and the filtration factor, Z.

Keywords: membranes; polyelectrolytes; polymer-metal ion interactions

Introduction

Polyelectrolytes (PEs), polymers with a high concentration of ionic groups have the ability to chelate or exchange metal ions. This property facilitates their use to recover and/or separate metal ions from aqueous solution. In this context, the PEs are used in water treatment and in hydrometallurgy at both industrial and laboratory scales, for quantitative analytical and recovery procedures. The continuous increase of world needs for most of the known metals, the decrease in grade of the available ores, and strict environmental regulations make it interesting to find effective and efficient methods for processing waste solutions containing metal ions, even at very low concentrations.

The removal and separation of metal ions are a technological challenge with respect to industrial and environmental applications. Conventional methods include the use of water-insoluble polymers that allow the quantitative and partially selective enrichment of ions. However, these heterogeneous methods require additional steps, for example, back extraction, elution, etc., and show less favorable kinetics.[1–2]

On the other hand, many commercial separation problems are being solved by membrane processes, which can be successfully used to treat industrial effluents. By far, the most important membrane separation processes, that is, for water treatment purposes are ultrafiltration (UF) and reverse osmosis, and to a lesser-degree, electrodialysis.

The liquid-phase polymer-based retention ultrafiltration technique has been efficiently used to evaluate the interactions of water-soluble polymers with metal ions. This technique uses water-soluble polymers containing functional groups with ability to bind metal ions, in combination with membrane filtration.[3–6] These polymers are termed *polychelatogens*. It is based on the separation of ions bound to the polymers with chelating or ion-exchange groups from non-bound ions. The ultrafiltration cell is equipped with a ultrafiltration membrane with a known exclusion rating. Non-bound

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low molecular weight species as metal ions pass through the membrane during filtration into permeate because of their small size. In contrast, the high molecular weight species, precursor polymer, and polymer-metal ion adducts, with a substantial larger size than that the membrane pores are retained in the cell solution. The filtrate solution is collected in small and volume-equivalent fractions, and the concentration of metal ions in every fraction is analyzed.

Water-soluble polymers containing sulfonic acid groups, as poly(vinylsulfonic acid) (PVSA), poly(styrenesulfonic acid) (PSSA) or poly(2-acrylamido-2-methyl-1-propane sulfonic acid) (PAPSA) do not act as ligands, but the functional group–metal ion interaction is only of the electrostatic type.[7–16] This was also demonstrated previously by application of the cyclic voltammetric technique.

Polyelectrolytes derived from 2-acrylamido-2-methyl-1-propane sulfonic acid (APSA) have a broad application spectrum, these are used in acrylic fiber industry, in pharmaceutical industry as surfactants, in mining as flocculant, water purification and others. Recent studies reveal new application of APSA as fuel cell membrane,[17] nanofiber production[18] or in light emmiting devices,[19] in medicine are studied as antitumoral,[20] inhibitors of angiogenesis agents[21] or antibacterial agent.[22]

Polyelectrolytes may be distinguished from chelating polymers (polychelatogens). The former have charged groups, or easily ionizable groups in aqueous solution, while the latter bear functional groups with the ability to form coordination bonds.

The aim of this paper is to investigate the retention properties of different polyelectrolytes containing sulfonic acid groups through the *liquid phase polymer based retention* technique.

Experimental Part

Reagents

The monomers 2-acrylamido-2-methyl-1-propane sulfonic acid, APSA, (Aldrich), methacrylic acid, MA, (Merck), 2-acrylamido glycolic acid, AGA, (Aldrich), 4-acryloylmorpholine, AMo, (Aldrich), polyethyleneglycol methyl ether methacrylate, PEGMEM, (Aldrich) were purified before the polymerization reaction. The following metal salts were used without further treatment: $Co(NO_3)_2 \cdot 6\ H_2O$, 99%, p.a. Merck; $Ni(NO_3)_2 \cdot 6H_2O$, 99%, p.a., Merck, $Cu(NO_3)_2 \cdot 3\ H_2O$, 99%, p.a. Merck; $Zn(NO_3)_2 \cdot 6\ H_2O$, extra pure, Merck; $Cd(NO_3)_2 \cdot 4\ H_2O$, 99%, p.a., Merck, $Pb(NO_3)_2$, >99%, extra pure, Merck, $AgNO_3$, p.a., Merck. Sodium hydroxide (NaOH, Merck), nitric acid 70% (HNO_3, Caledon) were used to adjust the solution pH.

Polymerization

Poly(2-acrylamido-2-methyl-1-propane sulfonic acid), P(APSA), poly(2-acrylamido-2-methyl-1-propane sulfonic acid-*co*-methacrylic acid), P(APSA-*co*-MA), poly (2-acrylamido-2-methyl-1-propane sulfonic acid-*co*-2-acrylamido glycolic acid), P(APSA-*co*-AGA), poly(2-acrylamido-2-methyl-1-propane sulfonic acid-*co*-4-acryloylmorpholine, P(APSA-*co*-AMo), poly (2-acrylamido-2-methyl-1-propane sulfonic acid-*co*-*N*-acryloyl-*N*-methylpiperazine), P (APSA-*co*-APz), and poly(2-acrylamido-2-methyl-1-propane sulfonic acid-*co*-polyethylene glycol methyl ether methacrylate), P(APSA-*co*-PEGMEM) were obtained by radical polymerization. Polymerization reactions were carried out using an equimol feed ratio of monomers, ammonium persulfate (APS) was used as initiator (1 mol-%), the reaction was kept in a polymerization flask for 24 hours in oil bath at 60 °C.

Purification

All the polymers were purified by passing them through a ultrafiltration membrane with a molar mass cut off (MMCO) of 3,000 Daltons (Da). Then, the polymers were fractionated by membranes with different MMCO and the fraction >100,000 or >50,000 Da were used for LPR runs. Polymers were lyophilized at low temperature for characterization and LPR experiences.

Characterization

The FT-IR and NMR spectra were recorded on a a Magna Nicolet 550 spectrophotometer and multinucleous Brucker AC 250P spectrometer, respectively.

Procedure of LPR Technique, Washing Method

The LPR system consist on a filtration cell with a magnetic stirrer containing a membrane filter with a known exclusion rating, a reservoir and a pressure source, *e.g.* a nitrogen bottle (see Figure 1). In ideal cases, this system may be considered a steady-state mixed flow reactor. Conventional stirred filtration cells or a specially designed tangential-flow cell equipped with a pump can be used. Essential parameters are the molar mass exclusion rate in a wide pH range (1–12), an appropriate permeate flow rate (0.5–12 mL min^{-1}), retentate volume (2–50 mL) and gas pressure, where 300 kPa is a suitable pressure in most cases. The most usual molar mass cut-offs range between 1,000 and 300,000 Da. A nominal exclusion rate of 10,000 Da proved to be convenient for polymers having a molecular mass between 30 and 50 kg mol^{-1}.

20.0 mL of a solution containing $5.0 \cdot 10^{-3}$ meq/L of a water-soluble copolymer and $1.0 \cdot 10^{-4}$ M of metal ions are placed into the solution cell provided with a ultrafiltration membrane with a MMCO of 10,000 Da (Millipore, Amicon).

The pH was adjusted with dilute HNO_3, or NaOH. A washing solution (water at pH = 3.0, 5.0, and 7.0, depending on the metal ion) was passed through under pressure (3.5 bar of N_2) from the reservoir through the cell solution. As the in- and out flux are rapidly equaled, the initial volume (20.0 mL) is kept constant during the experiment. Ten fractions of 20 mL were collected. Each fraction was collected in graduated tubes, and the corresponding metal ion concentration was determined.

Measurements

For the LPR technique, a membrane filtration system was employed to test the coordinating or ion exchange properties of the polychelatogen. The pH was determined with a Jenco Electronics 1671 pH-meter. A Unicam Solaar M5 series Atomic Absorption Spectrometer was used for the determination of the metal ion concentrations in the filtrate.

Results and Discussion

Water-soluble polyelectrolytes containing the sulfonic acid groups as one the most important functional groups were

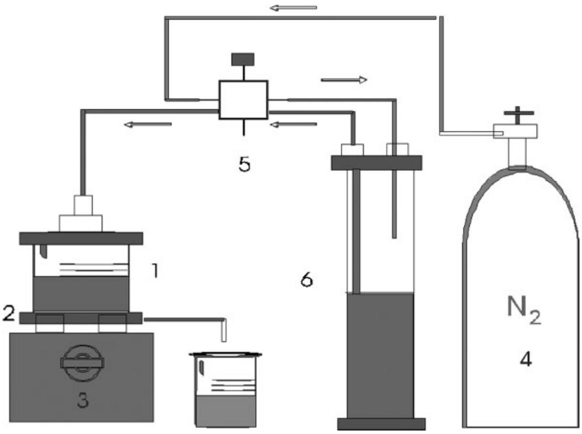


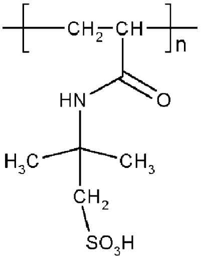
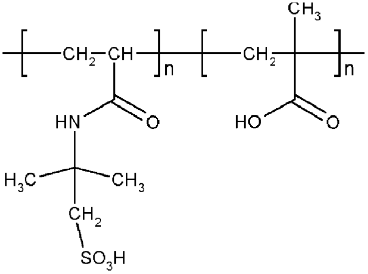
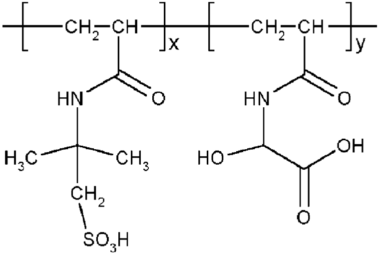
Figure 1.
Instrumental arrangement: (1) filtration cell with polymeric and metal ion solution; (2) membrane filtrate; (3) magnetic stirrer; (4) pressure trap; (5) selector; (6) reservoir with water.[3]

synthesized by radical polymerization and studied as a polychelatogen using the LPR technique. The P(APSA) contain amide and sulfonic acid (strong acid) groups as possible metal ion interaction sites, for P(APSA-*co*-AM) and P(APSA-*co*-AGA) the comonomer incorporates basically carboxylic acid groups (weak acids) at the structure, P(APSA-*co*-AMo), P(APSA-*co*-APz), and P(APSA-*co*-PEGMEM) the comonomers incorporate neutral groups as ether, tertiary amine, and glycol groups respectively for chelating processes (see Table 1).

According to the yield, these polymers would have a copolymers composition very close to 1:1, with a random distribution on polymer chain due to radical polymerization in aqueous media (see Table 2).

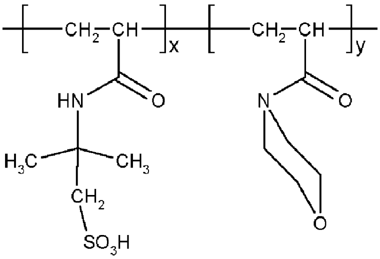
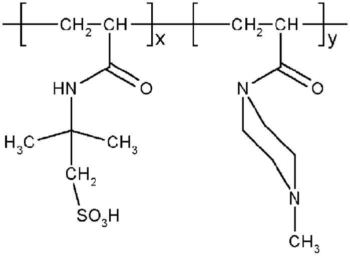
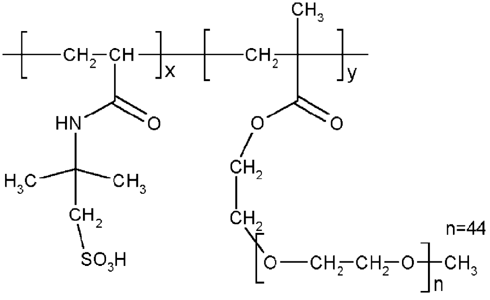
The metal ions were selected by their impact on the environment and human health: Cu(II), Co(II), Ni(II), Zn(II), Cd(II), Pb(II), and Ag(I). They are also important for their potential applications as metal ion-polymer complexes, particularly those with Cu(II) and Ag(I). The high solubility of APSA in aqueous media has been used to increase the solubility of other

Table 1.
Structure of the polychelatogens, functional groups, and possible interaction mechanism type.

Polymer	Functional groups	Interaction mechanism
 P(APSA)	Amide, sulfonic acid	Electrostatic (sulfonate)
 P(APSA-*co*-AM)	Amide, sulfonic acid, carboxylic acid	Electrostatic (sulfonate) and chelate (carboxylate)
 P(APSA-*co*-AGA)	Amide, sulfonic acid, hydroxy, carboxylic acid	Electrostatic (sulfonate) and chelate (carboxylate and hydroxy)

(*Continues*)

Table 1. (Continued)

Polymer	Functional groups	Interaction mechanism
 P(APSA-*co*-AMo)	Amide, sulfonic acid, ether	Electrostatic (sulfonate)
 P(APSA-*co*-APz)	Amide, tertiary amine, sulfonic acid	Electrostatic (sulfonate), intramolecular formation of chelates (APz)
 P(APSA-*co*-PEGMEM)	Amide, sulfonic acid, ethylene glycol	Electrostatic (sulfonate), bidentade chelate (ethylene glycol)

^{1}H-NMR characterization indicates the following signals (in ppm) for P(APSA-*co*-AM) –C**H**$_3$ (AM) at 0.9–1.2, –C**H**$_3$ (APSA) at 1.3–1.7, –C**H** and –C**H**$_2$ at 1.8–2.3, –C**H**$_2$–SO$_3$H at 3.2–3.7; for P(APSA-*co*-AMo) –C**H**$_3$ at 1.4–1.5, –C**H** at 3.0–3.2, NH–C**H**$_2$–, –C**H**$_2$–N–C**H**$_2$ and C**H**$_2$–O–C**H**$_2$ at 3.4–3.7, C**H**$_2$–SO$_3$H at 3.8–4.1; for P(APSA-*co*-AGA) –C**H**$_3$ at 1.3–1.7, –C**H** and –C**H**$_2$ at 1.9–2.6, –C**H**$_2$–SO$_3$H at 3.1–3.7, –NH–C**H**–OH at 5.1–5.3, –O**H**, –COO**H** and –SO$_3$**H** at 6.9–7.3; for P(APSA-*co*-APz) –C**H**$_3$ at 1.2–1.7, –C**H** and –C**H**$_2$ 1.7–2.3, N–C**H**$_3$ at 2.8–3.2, C**H**$_2$–SO$_3$H at 3.2–3.6, 7.3; for P(APSA-*co*-PEGMEM) –C**H**$_3$ at 1.2, –C**H** and –C**H**$_2$ at 1.7, –C**H**$_2$–SO$_3$H at 3.2, O–C**H**$_2$–C**H**$_2$ at 3.3–3.7. FT-IR spectra show the following absorption signals: for P(APSA-*co*-AM) νN–H 3430 cm^{-1}, νC–H 2930 cm^{-1}, νC=O(carboxylic acid) 1720 cm^{-1}, νC=O(amide) 1630 cm^{-1}, νC–N 1400-1450 cm^{-1}; for P(APSA-*co*-AGA) νN–H 3423 cm^{-1}, νO–H 3083 cm^{-1}, νC–H 2994 cm^{-1}, νC–O(carboxylic acid) 1739 cm^{-1}, νO=C(amide) 1655 cm^{-1}, νC–OH and νC–N 1455 cm^{-1}, νS=O 1343 cm^{-1}, νC–O 1220 cm^{-1}, CH$_2$–COO$^-$ δ 805 cm^{-1}; for P(APSA-*co*-APz) νN–H 3448 cm^{-1}, νC–H 2934–2744 cm^{-1}, νC=O(amide) 1652 cm^{-1}, νC–N 1218 cm^{-1}, νC–S 622 cm^{-1}, for P(APSA-*co*-AMo) νC–H 2931 cm^{-1}, νO–CH$_2$ 2859 cm^{-1}, νC=O(amide) 1629 cm^{-1}, CH$_2$–O–CH$_2$ 1110 cm^{-1}, νS=O 1167 cm^{-1}, C–S 620 cm^{-1}; for P(APSA-*co*-PEGMEM) νN–H 3400 cm^{-1}, νC–H 2887 cm^{-1}, νC=O(ester) 1720 cm^{-1}, νC=O(amide) 1665 cm^{-1}, CH$_2$–O–CH$_2$ 1110 cm^{-1}.

polymers, as could be obtained for P(APSA-*co*-AMo) and P(APSA-*co*-AGA). In order to quantify the separation process, metal species retention versus the filtration factor is plotted. The binding and elution processes may be formulated as a chemical reaction, where reversible reaction in combination with an irreversible transfer of metal ions across the membrane is responsible for metal retention (see

Table 2.
Monomer feed, copolymer composition, and yield for the copolymers.

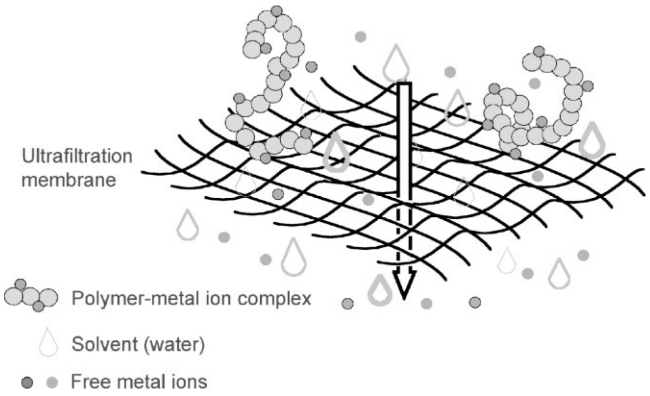
Polymer	Monomer feed		Polymer composition		Yield (%)
	APSA	Comonomer	APSA	Comonomer	
P(APSA-*co*-MA)	1.0	1.0	1.60	1.00	96
P(APSA-*co*-AGA)	1.0	1.0	*	*	99
P(APSA-*co*-AMo)	1.0	1.0	*	*	98
P(APSA-*co*-APz)**	1.0	1.0	1.04	1.00	98
P(APSA-*co*-PEGMEM)**	1.0	1.0	1.95	1.00	95

*According to the yield, this polymer could be a copolymer composition very close to 1:1.
**Composition obtained by elemental analysis.

Scheme 1). Retention (R) is defined for any species as the fraction per unit of the species under study remaining in the cell during filtration. The filtration factor (Z) is defined as the volume ratio of the filtrate (Vf) versus volume in the cell (Vo). The metal ion (M) remaining in the cell during filtration is equal to the sum of the metal ion bound to the polymer chain and the metal ion free in the solution.

In order to quantify the separation process, metal species retention versus the filtration factor is plotted. The binding and elution processes may be formulated as a chemical reaction, where reversible reaction in combination with an irreversible transfer of metal ions across the membrane is responsible for metal ion retention (see Scheme 1). Retention (R) is defined for any species as the fraction per unit of the species under study remaining in the cell during filtration. The filtration factor (Z) is defined as the volume ratio of the filtrate (Vf) versus volume in the cell (Vo). The metal ion (M) remaining in the cell during filtration is equal to the sum of the metal ion bound to the polymer chain and the metal ion free in the solution.

Figure 2 shows the effect of the pH on the retention profile of P(APSA) for different metal ions. It is observed as the pH increases, retention increases. As APSA is a strong acid, these groups are deprotonated at low pH, then at pH = 3 the sulfonate group are present and a high interaction occurs with divalent metal ions and trivalent metal ions, increasing continuously at pH = 5 and pH = 7 rising values close to 100% for all divalent metal ions. Only Ag(I) shows a weak interaction. It could be explained for a low charge density of this ion or means Pearson's Principle due to sulfonic acid are classified as hard base and Ag(I) is a soft acid.



Scheme 1.
Ultrafiltration processes with polymer and metal ions.

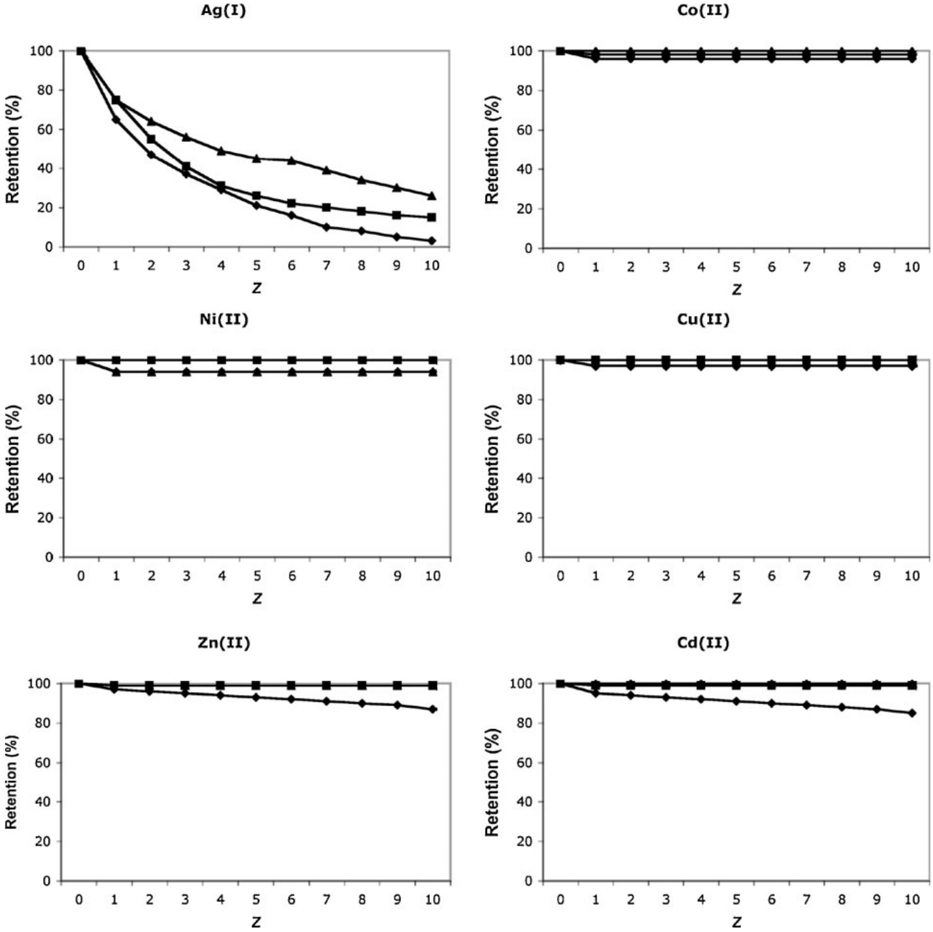


Figure 2.
P(APSA) retention profiles for different metal ions at pH = 3 (◆), pH = 5 (■) and pH = 7 (▲).

Interactions of metal ions with water-soluble polymers are mainly due to electrostatic forces and the formation of coordinating bonds. Other weak interactions may appear such as trapping metal ions in the bulk of the polymer phase. The features of coordination between polymers and metal ions may be described by the usual coordination theories, but some special aspects may be considered. In addition to the solubility in aqueous media of polymers containing APSA, a considerable increase in its metal ion interaction respect its homopolymers could be observed due to deprotonation of sulfonic acid groups at low pH (see Figure 3). For acid comonomers it is observed a cooperation effect between strong and weak acids for metal ions retention. Then P(AM) increases its interaction at pH = 5 for Ag(I) from 5% to >77%, Co(II) from 20% to 100%, Zn(II) from 38% to 100%, Cd(II) from 60% to >99%, only Cu(II) keep a similar behavior with a retention of 100% for P(AM) and P(APSA-*co*-AM). P(AGA) shows in an increase in the retention for Ag(I) from 5% to 98%, Co(II) from 26% to 85%, Zn(II) from 48% to 89%, Cd(II) from 36% to 83%, and Pb(II) maintains a high retention with 92% for P(AGA) and 98% for P(APSA-*co*-AGA). For neutral comonomers the solubility increases significantly but

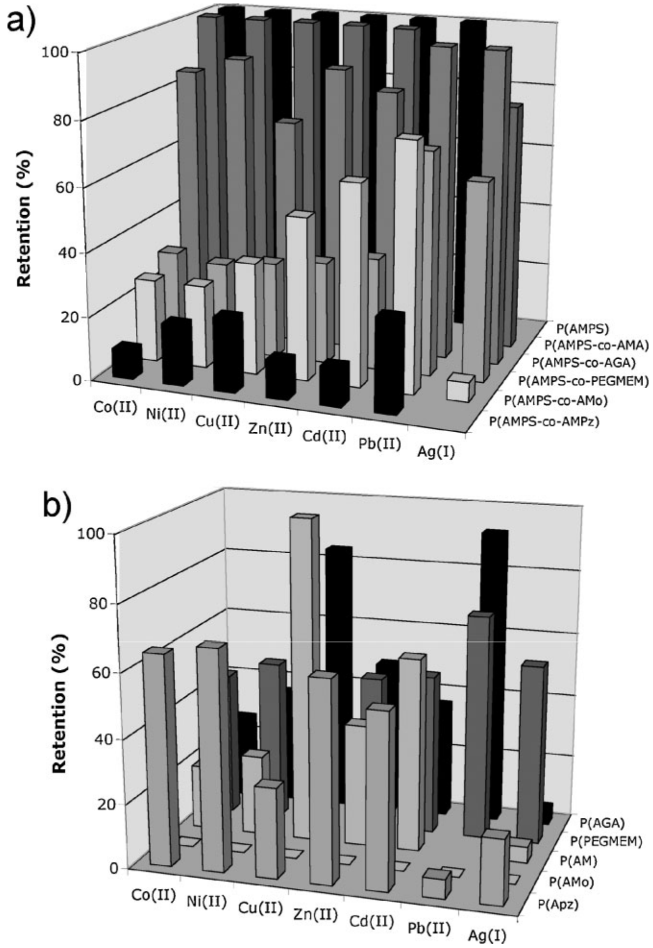


Figure 3.
Comparison of maximum retention of a) P(AMPS) and its copolymers, b) homopolymers at pH = 5 and Z = 10.

a cooperation mechanism for metal ion retention is not observed. For P(APz) the following changes for the retention values are observed: Co(II) from 65% to 9%, Zn(II) from 62% to 12%, Cd(II) from 54% to 12%, Cu(II) from 28% to 23%, only for Pb(II) it is observed an increase from 6% to 29%. P(AMo) don't show a polychelatogen behavior and the retention ability is lower than 1%, and P(APSA-*co*-AMo) retentions are the following: Ag(I) 6%, Co(II) 26%, Ni(II) 27%, Cu(II) 35%, Zn(II) 51%, Cd(II) 63%, and Pb(II) 77%, which are lower than those retention values of P(APSA). For P(PEGMEM), only for Ag(I) (56%–62%) and Pb(II) (65%–68%) was observed a similar retention behavior between the homopolymer and P(APSA-*co*-PEGMEM). The other metal ions show a decrease in its retentions, Co(II) from 45% to 30%, Ni(II) from 50% to 28%, Cu(II) from 40% to 30%, Zn(II) from 48% to 32%, and Cd(II) from 50% to 35%.

Figure 4 shows the suggested polymer-ligand-metal ion interactions that involve the sulfonate group, weak acid groups, and neutral groups. This explanation means that this mechanism should be occurring at pH 5, where the majority of the ligand groups are deprotonated. Although

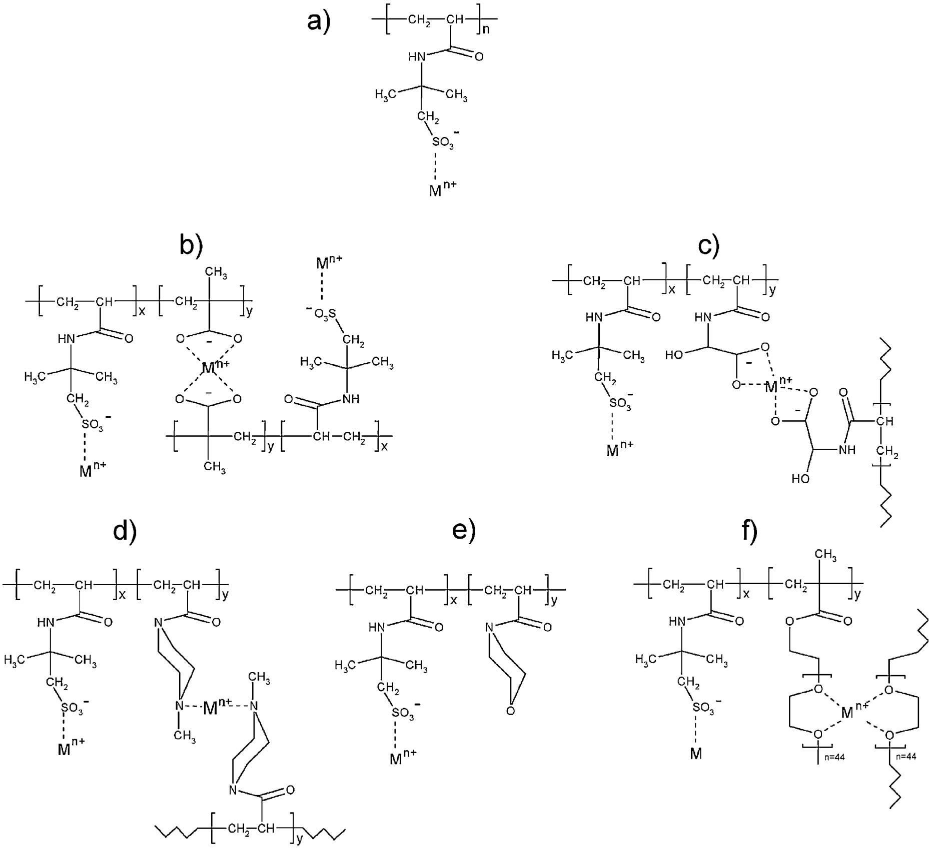


Figure 4.
Suggested polymer-ligand-metal ion interactions for a) P(APSA), b) P(APSA-*co*-AMA), c) P(APSA-*co*-AGA), d) P(APSA-*co*-APz), e) P(APSA-*co*-AMo), and f) P(APSA-*co*-PEGMEM).

interactions though amide group can be present for these polymers.[23–24]

Conclusions

The metal ion retention properties of water soluble copolymers containing the moiety 2-acrylamido-2-methyl-1-propane sulfonic acid, APSA, through LPR technique were investigated. The retention capability depended strongly on the structure of the polyelectrolyte, arrangement of comonomers at main chain, pH, and the filtration factor, Z. Z gave also a qualitative measurement of the strenght of the polymer-metal ion interaction. APSA allowed increased metal ion interaction of weak acid, meanwhile APSA did not improve the metal ion interaction of neutral monomers under these experimental conditions.

Acknowledgements: The authors thank to FONDECYT (Grant No 1070542) for financial support. AM thanks to CIPA the Fellows.

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