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Functional Water Soluble Polymers with Ability to Bind Metal Ions

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Summary: Water-soluble polymers containing amine, carboxylic acid, and sulfonic acid groups were investigated as polychelatogens through the liquid phase polymer-based retention, LPR technique, under different experimental conditions. The metal ions investigated are: Ag(I), Cu(II), Co(II), Ni(II), Ca(II), Hg(II), and Cr(III). An important effect of the pH and the ligand type was observed on the metal ion retention. As the pH increases the metal ion retention increases. Two types of metal ion interactions are involved: coordination and electrostatic.

Keywords: functionalization of polymers; water-soluble polymers

Introduction

Water-soluble polymers (WSP) containing ligands at the main or side chains have been investigated for the removal of metal ions in the homogeneous phase.[1-6] These chelating polymers, termed *polychelatogens*, have been prepared by functionalizing various basic polymers. Water-soluble polymers are commercially available or can be synthesized by different routes. Among the most important requirements for technological applications of these polymers, are their high solubility in water, 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. The macromolecules can be homo- or copolymers, and may contain one or more coordinating and/or charged groups. These groups are placed at the backbone, or at the side chain, directly or through a spacer group. Using these polychelatogens in combination with membrane filtration, higher efficiency and selectivity of membrane separations can be achieved.

Polyelectrolytes may be distinguished from chelating polymers (polychelatogens). The former have charged groups, or easily ionizable groups in aqueous solution, while the latter bears

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functional groups with the ability to form coordination bonds. The most investigated ligands present in the polychelatogens are amines, carboxylic acids, amides, alcohols, aminoacids, pyridines, thioureas, iminos, *etc.* Among them, polymers containing amino groups have been extensively studied by ultrafiltration, particularly the functional poly(ethyleneimine). This heterochain polymer contains three different types of amino groups: secondary and tertiary groups in the main chain and secondary and primary amino groups in the side-chain. The ratios are between 1:1:1 and 1:2:1 for the primary, secondary, and tertiary species, varying depending on the degree of branching. The most studied polyelectrolytes include those with carboxylic acid, phosphoric acid, sulfonic acid, or amonio groups in their structure.

A water-soluble polymer solution may be considered a two phase system. The polymeric functional groups keep separated by a distance contained in a range so that they present a local high and nearly constant concentration. The water-soluble polymers undergo interactions with solvent and other high and low-molecular weight species present in the aqueous solutions. Due to these interactions, macromolecules in solution exhibit, beyond their chemical structure, different properties such as conformation of the polymer chains, excluded volume.

Membrane filtration processes can be successfully used for the separation of inorganic species and for their enrichment from dilute solutions with the aid of a water-soluble polymer. This technique is called the *liquid-phase polymer based retention*, LPR, technique. Ultrafiltration is fast-emerging as a new and versatile technique in separation technology, concentration, purification, and separation processes. 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 the low molecular weight of small species, such as metal ions.

This technique uses solutions of polychelatogens in combination with membrane filtration where selective separations of metal ions can be achieved. When solutions of mixtures of metal ions are put in contact with the polymer solution, a profile for the retention of the different metal ions by the polychelatogen during the filtration, can be obtained.

A series of polymers have been designed and investigated with respect to the analytical determination of metal ions. Poly(ethyleneimine)-based reagents have been used in many studies as complexing ligands, as well as a versatile source of chelating derivatives for removing metal ions from aqueous solutions by means of complexation-ultrafiltration (UF). [4, 5, 7-24] 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.[10] Poly(acrylic acid) and copolymers with acrylamides[13-14], N-maleyl glycine [15], N-vinyl-2-pyrrolidone[14], poly(2-acrylamido-2-methyl-1-propane sulfonic acid)[16], poly(N-acryloyl-N-methyl piperazine)[17], as well as mixtures of two polychelatogens [18] were investigated in their ability to bind di- and trivalent cations.

Liquid-Phase Polymer-Based Retention (LPR) Technique

The method, *liquid-phase polymer based retention* (LPR) is based on the retention of certain ions by a membrane which 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 (see figure 1).

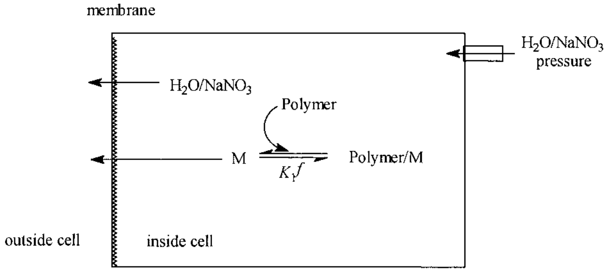


Fig. 1. Ultrafiltration process.

Different modes of separation by LPR can be used for inorganic ions. To separate the components of a small volume sample in analytical chemistry (relative preconcentration), the liquid sample is placed in the polymer containing cell solution and then washed with water (washing method). The pH is adjusted to a value at which the ions of interest are retained and the other species are removed. The washing method can also be applied to purify a macromolecular compound by eliminating the microsolutes maintaining a constant volume in the cell.

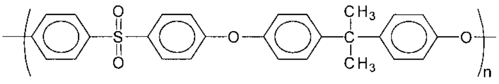
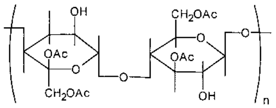
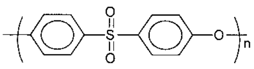
To achieve enrichment of the metal ions, their solution can be passed from a reservoir to a smaller volume filtration unit in the presence of a complexing polymer. This concentration method (enrichment method) is designed for metal recovery from dilute technological solutions and for absolute preconcentration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

The main features of a *liquid-phase polymer-based retention* system are a membrane filtration, reservoir and a pressure source, *e.g.* a nitrogen bottle. Conventional stirred filtration cells or a specially designed tangential-flow cell equipped with a pump can be used. Essential parameters are the molecular mass exclusion rate in wide pH range (1-12), an appropriate permeate flow rate (0.5-12 mL min^{-1}), retentate volume (2-50 mL) and gas pressure 300 kPa, are suitable in most cases. A polymer concentration of 0.5-5 weight-% in the cell solution is more appropriate for both retentions of elements and their subsequent determination in the retentate. The most usual molecular mass cut-off ranged between 1000 and 300000 Daltons. A nominal exclusion rate of 10 kg mol^{-1} proved to be convenient for polymers having a molecular mass ranging between 30 and 50 kg mol^{-1}.

The advantages of this method are the use of the separation, owing to the use of a selective binding, and the low energy requirements involved in UF.

The most common ultrafiltration membranes are based on cellulose acetate (CA), polysulfone (PS), poly(ether sulfone) (PES), polyacrylonitrile (PAN) and polyvinyldiene (PVD). Although CA-based membranes are less prone to fouling and typically have a higher flux than PS membranes at equivalent rejection, PS membranes are used in many applications because of higher stability (see table 1).

Table 1. Molecular structure of ultrafiltration membranes.

Name	Molecular structure
Poly(sulfone)	
Cellulose acetate	
Poly(ethersulfone)	
Poly(ethylene)	$-(CH_2)_n-$
Poly(vinyldiene fluoride)	$-(CH_2CF_2)_n-$

Moreover, hydrophobic polymers and membranes can be modified to increase flux and reduce fouling. These membrane modification techniques include the following: entrapping a hydrophilic moiety, reacting the base polymer with hydrophilic pendant groups, blending polymers, modifying the membrane surfaces, modifying the membrane charge and grafting the ceramic membranes.

Ultrafiltration is based on the same principle as reverse osmosis but with much larger pore sizes (0.001-0.1 μm). Because of the low or negligible osmotic pressure of macrosolutes, ultrafiltration operates at very low pressures (30-80 psi).

Ultrafiltration membrane separation depends on membrane pore size, solute-membrane interaction, and shape and size of the macromolecule. For maximum separation efficiency, there should be a 10-fold difference in the sizes of the species in order to be separated. In addition, because all ultrafiltration membranes have a certain pore size distribution, the molecular mass cut off (MMCO) of the membrane (defined as the molecular weight at which 90% of the macromolecular solute is rejected by the membrane) should be at least one-half that of the smallest macromolecule that must be rejected.

In order to quantify the separation process, retention of the metal species is plotted versus the filtration factor. 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. Retention (R_Z) is defined for any species as the fraction per unit of the species under study remaining in the cell during filtration. The filtration factor (F) is defined as the volume ratio of the filtrate (V^f) versus volume in the cell (V^c). The metal ion (M) 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. These values are a function of F, *i.e.*, the extent of the filtration run. Then, when the volume inside the ultrafiltration cell is kept constant during filtration, retention may be formulated as follows:

$$R_Z(F) = \frac{c_Z^{free}(F) + c_Z^{bound}(F)}{c_Z^{init}} \qquad (1)$$

where c_Z^{free} is the concentration of M free in the solution, c_Z^{bound} is the concentration of M bound to the polymer, and c_Z^{init} is the initial metal concentration. Z is the valence of the metal ion considered.

The Nature of the WSP-Metal Ion Interactions

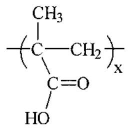
Interactions of metal ions with water-soluble polymers are mainly due to electrostatic forces and the formation of coordinating bonds. Other weak interactions may appear as trapping metal ions in the bulk of the polymer phase.

The coordination features between polymers and metal ions may be described by the usual coordination theories, but some special aspects may be considered. When intrachain complexes are predominant, it is normally recognized the existence of a polymer domain with near constant concentration of ligands, since the distances between them are kept in a narrow range for a given polymer chain. This is responsible that the chelating reaction appears as a one-step reaction. For relative low ligand amounts in the solution, completely complexed metal ions may coexist with free, uncomplexed ones.

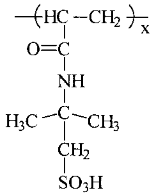
Polychelatogens

Poly(ethyleneimine) PE, poly(ethyleneimine-*co*-epichlorohydrine) PEE, poly(methacrylic acid) PMA, poly(2-acrylamido-2-methyl-1-propane sulfonic acid) PAPSA, were synthesized, except the commercial PE and PEE, from the respective monomers by radical polymerization. Subsequently the polymers were purified by dissolving in water and passing through the ultrafiltration membrane with a molecular mass cut-off 3.000 D. The final product was lyophilized.

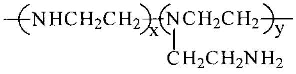
The structures of the polychelatogens are the following:



PMA

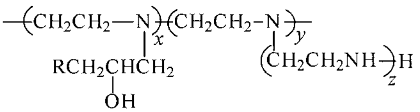


PAPSA



$$-(NHCH_2CH_2)_x(\underset{CH_2CH_2NH_2}{N}CH_2CH_2)_y-$$

PE



$$-(CH_2CH_2-\underset{RCH_2\underset{OH}{C}HCH_2}{N})_x(CH_2CH_2-\underset{(CH_2CH_2NH)_zH}{N})_y-$$

PEE

Procedure to Study the Metal Ion Binding Properties

The membrane filtration Filtron, poly(ether sulfone)] was carried out in a system described previously. [4,11] For the determination of the complex binding ability, 0.02 M aqueous solution of the polychelatogen was prepared and adjusted to the corresponding pH by addition of diluted HNO_3 or NaOH. The solutions of polymer and metal nitrates (0.0008 M) were placed into the filtration cell. The total volume in the cell was kept constant at 20 mL. The system was pressurized by nitrogen gas and kept constant at 300 kPa during the membrane filtration. The filtration fraction (Z = 1-10) was recollected and the concentration of metal ions in the filtrate was determined by atomic absorption spectrometry. Z is defined as the ratio of the volume in the filtrate (V_f) and the volume of the cell solution (V_o).

Polymer-metal Ion Retention Properties

Retention can be plotted versus the filtration factor, Z, and a retention profile is obtained. R is the fraction per unit of metal ions remaining in the cell. As an example, figure 2 shows several retention profiles obtained for different metal ions by PE.

The polymer metal ion interaction is pH-dependent. In strongly acidic solutions no complexation takes place. At pH=3 no metal ion was significantly retained. The highest ability is observed at pH 7 for all the metal ions. At this pH it is very important the strong amine-metal ion interaction as at Z = 10, the retention is kept over 80 % for C(II), Cd(II), Cu(II), Ni(II), Zn(II), and Co(II). The PE shows only a poor afinity for Pb(II).

The polychelatogen PEE shows a lower metal ion retention capability than that PE. It is due to that the copolymer includes hydroxyl groups which are more weak ligands compaired with amino groups. As an example, figure 3 shows the retention behavior for Ni(II) by PE and PEE.

The PMA shows also an important effect of the pH on the metal ion retention. At pH = 5, the highest retention (100%) was obtained for Cu(II) ions. Cr(III) ions precipitate at this pH and were not investigated. At pH = 7, the Ag(I), Cd(II), Co(II), Ni(II) were retained in a 100%. At such pH all the carboxylic acids are dissociated and the carboxylate groups form more stable complexes with the divalent cations. Cu(II) precipitates at this pH, hence it was not investigated.

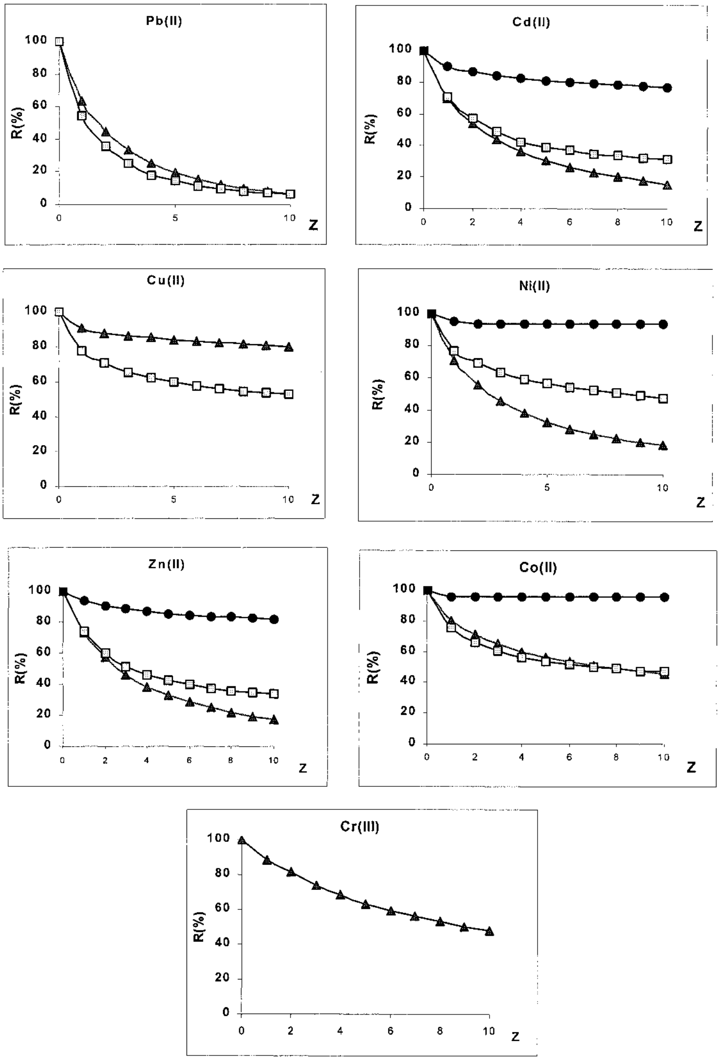


Fig. 2. Retention profiles for poly(ethyleneimine) PE at pH 3; (σ); 5 (ν), and 7 (λ).

On the contrary, the polychelatogen PAPSA shows for all metal ions a high metal ion retention which is not very dependent on the pH.

It is well known that the filtration factor, Z, is a measurement of the strength of the ligand-metal ion interaction. At Z high enough values, a remaining residue of metal ions is frequently found which cannot be eluted by filtration at the same pH and under the same conditions. Therefore, figure 4 shows that the metal ions Ag(I), Ni(II), Co(II), Cd(II), and Zn(II) form very stable complexes with carboxylate groups at pH=5 and pH=7. At pH=3 the strongest complex was formed with Cr(III). Hg(II), Cu(II), and Cr(III) was not investigated in all pH ranges to avoid precipitation.

Figure 5 shows the metal ion binding properties of the polychelatogens containing the three ligand types. These experiences were carried out at pH = 7 corresponding to the maximum retention and Z = 10. PAPSA is the polychelatogen which shows the strongest interactions with the metal ions and the PEE the weaker ligand-metal ion interactions. Cd(II) ion forms very stable complexes with amino groups coming from PE.

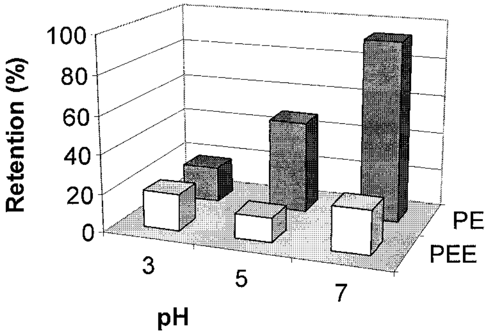


Fig. 3. Retention of Ni(II) by the polychelatogens PE and PEE at different pH.

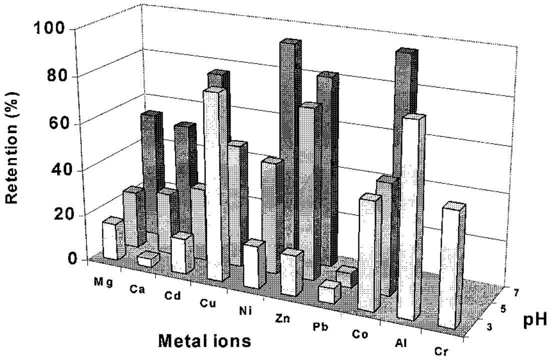


Fig. 4. Metal ion retention of PE at different pH and Z=10.

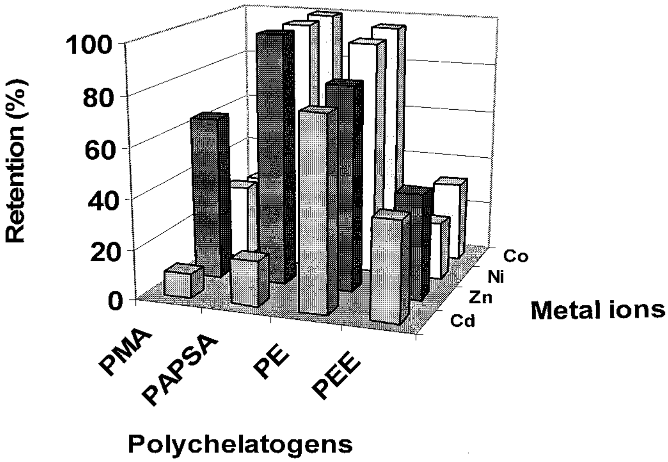


Fig. 5. Metal ion retention for the polychelatogens at Z = 10 and pH = 7.

The capacity of soluble polymer complexing agents is influenced by various factors, mainly steric and statistical ones. Usually there is not only intramolecular, but also intermolecular complexation because the coordination number of metal ions is greater than two. The dependence of capacity on concentration of the polymer solution differs from polymer to polymer. Generally, sterical hindrance diminishes the capacity if a certain concentration of solution is exceeded.

Polymer-metal Ion Interaction Mechanism

It is strongly related with the dissociation degree of the polychelatogens. Thus, for PE and PMA, at pH 5 most of the ligand groups are as free amine, and carboxylate respectively. Therefore, these groups form polymer-metal complexes, which are shown in figures 6a) and 6b). APSA is deprotonated at lower pH than that of carboxylic acid. Due to that APSA shows a higher metal ion retention capability. For this polychelatogen, the polymer-metal ion interaction is only an electrostatic type (see figure 6c).

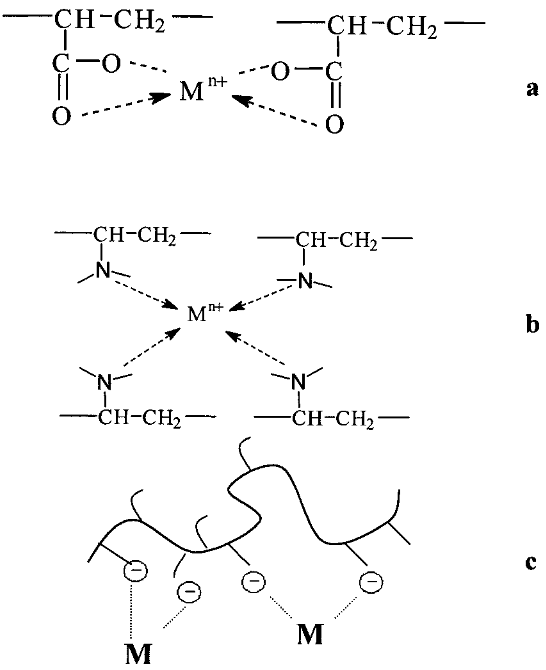


Fig. 6. Possible polymer-metal ion interaction mechanism for a) carboxylate group (complexes formation), b) amine type complexes, and c) sulfonate group (electrostatic interaction).

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