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Polymer 45 (2004) 1771–1775
polymer
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Interactions of polyelectrolytes bearing carboxylate and/or sulfonate groups with Cu(II) and Ni(II)

Bernabé L. Rivas[a,*], L. Nicolás Schiappacasse[a], U. Eduardo Pereira[a],
Ignacio Moreno-Villoslada[b]

[a]*Department of Polymers, Faculty of Chemistry, University of Concepción, Casilla 160-C, Concepción, Chile*
[b]*Instituto de Química, Facultad de Ciencias, Universidad Austral de Chile, Casilla 567, Valdivia, Chile*

Received 24 September 2003; received in revised form 15 December 2003; accepted 21 January 2004

Abstract

The interactions between the water-soluble polyelectrolytes poly(acrylic acid) (PAA) and poly(vinyl sulfonic acid) (PVS), and Cu(II) and Ni(II) are studied by the liquid-phase polymer-based retention (LPR) technique. Assuming a Ni(II)–PVS interaction of electrostatic nature, the nature of the Ni(II)–PAA interaction is found to be electrostatic, while Cu(II)–PAA interactions imply the formation of coordinative bonds. The charge related formation constants for the systems Ni(II)–PAA, Ni(II)–PVS, and Cu(II)–PVS are found to be 57.57×10^2, 43.4×10^2, and $60.5 \times 102\ M^{-1}$, respectively in a 0.010 M $NaNO_3$ aqueous solution at pH 5, and 1.4×10^2 for both systems containing Ni(II) and $1.3 \times 10^2\ M^{-1}$ for the system Cu(II)–PVS in a 0.10 M $NaNO_3$ aqueous solution at pH 5.

Keywords: Polyelectrolyte; Polymer–metal ion interaction; Linear charge density

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1. Introduction

Polyelectrolytes (PEs), polymers with a high concentration of ionic groups or ionogenes, have the ability to chelate or exchange metal ions [1–4]. 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 [5,6].

The polyelectrolyte–metal ion interaction can be only electrostatic or include the formation of coordination 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 in two groups: intrinsic and extrinsic to the polymer. The former includes the polymer structure in terms of composition and geometry, which affects the flexibility of the chains in solution: branches of the chain, chemical nature of the functional groups, and their distribution at the polymer chain, etc. The second group includes the charge and type of the metal ion, pH of the solution, ionic strength, temperature, and dielectric constant of the medium [7].

The study of the polyelectrolyte–metal ion interaction can be carried out by different techniques such as potentiometry [8–13], spectrophotometry [9,11,12, 14–18], viscosimetry [11,14,15], conductometry [12,15, 19], light scattering [20–22], and voltammetry [23]. In our laboratory we have used the liquid-phase polymer-based retention (LPR) technique [24]. This technique combines the use of water-soluble polymers with ultrafiltration membranes, which separate low molecular mass species as free ions from high molecular mass compounds as the precursor polymer and polymer–metal complexes (PMC). It is assumed that the only separation mechanism is the size exclusion by the ultrafiltration membrane. The LPR technique has important technological applications [25, 26]. The projection of its use has the great challenge of increasing the selectivity of the water-soluble polymer (WSP) used towards binding specific metal ions [3,27–30].

The LPR technique has demonstrated to be an excellent tool to quantitatively study the polymer–metal ion interaction [31–33]. By application of the LPR technique by the

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[*] Corresponding author. Tel.: +56-41-204256; fax: +56-41-245974.
E-mail address: brivas@udec.cl (B.L. Rivas).

0032-3861/$ - see front matter © 2004 Published by Elsevier Ltd.
doi:10.1016/j.polymer.2004.01.032

washing method a retention profile is obtained. This corresponds to a plot of retention (R) versus the filtration factor, (F) where R is defined as the ratio between the amount of metal ions in the ultrafiltration cell at every instant and the initial amount of metal ions, and F is defined as the ratio between the filtrate volume V_f and the volume in the ultrafiltration cell, V_o. This retention profile gives information about the affinity of the metal ions to bind the polyelectrolytes.

Despite the advance in the study of the polyelectrolyte–metal ion interaction through the LPR technique, there are still non-solved questions such as how to differentiate purely electrostatic interactions from others involving coordinative bonds. In this paper, we analyze the nature of the interactions of polyelectrolytes bearing carboxylate and sulfonate groups on their structure with Cu(II) and Ni(II) by means of the LPR technique.

2. Experimental part

2.1. Materials

The commercial polymers poly(acrylic acid) (PAA) and poly(vinylsulfonic acid) (PVS), (both Aldrich) were purified and fractionated by ultrafiltration. PAA has, according to Aldrich, $M_w = 250,000$, therefore a fraction between 100,000 and 1,000,000 Da was chosen. A fraction between 10,000 and 50,000 Da was studied for PVS. The salts $NaNO_3$, $Cu(NO_3)_2$, and $Ni(NO_3)_2$ (p.a. grade, Merck), were used as received. The solutions were prepared with twice distilled water whose conductivity was lower than $1\ \mu S\ cm^{-1}$.

2.2. Equipment

The ultrafiltration equipment has been previously described [24,27]. It has a filtration cell with a membrane with a defined molar mass cut off (MMCO) (Filtron, Pal Gelman), a reservoir for the washing solution, a selector, and a pressure source (see Fig. 1). The metal ion concentration was determined by atomic absorption spectrometry through a spectrometer UNICAM Solaar 5M Series.

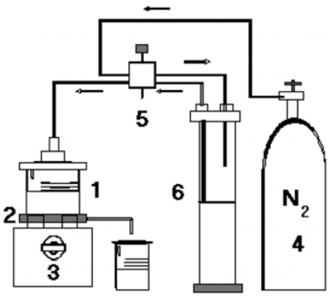

Fig. 1. Ultrafiltration equipment: (1) filtration cell; (2) ultrafiltration membrane; (3) magnetic stirrer; (4) pressure source; (5) selector; (6) reservoir.

2.3. Procedure (Washing method)

50.0 mL of a solution containing 5.0×10^{-3} equiv./l of a water-soluble polymer, 0.010 or 0.10 M of $NaNO_3$, and 1.0×10^{-4} M of metal ions were placed into the ultrafiltration cell provided with a ultrafiltration membrane with a MMCO of 5000 Da (Filtron, Pal Gelman). The pH was adjusted to 5.0 with dilute HNO_3. A washing solution (0.010 or 0.10 M of $NaNO_3$ in water at pH 5.0) was passed under pressure (3 kPa of N_2), from the reservoir through the cell solution. All the experiments were carried out at constant ionic strength. As the in- and out flux are rapidly equalled, the initial volume (50.0 mL) is kept constant during the experiment. Ten fractions of 10 mL were collected and then 10 more of 20.0 mL. Each fraction was collected in graduated tubes, and the corresponding metal ion concentration was determined.

3. Results and discussion

The polyelectrolytes PAA and PVS are high flexible linear polymers whose functional groups are linked directly to the backbone; they show good chemical and physical stability, very good solubility in water, and a high capacity to incorporate metal ions due to the high local concentration of functional groups. They also exhibit specific properties: PVS is a strong polyelectrolyte, and is deprotonated in a wide range of pH, while PAA is a weak polyelectrolyte that deprotonates from pH 3.5 to pH higher than 6. In terms of the Pearson's concept of hard- and soft-acids and bases, the carboxylate groups are soft 'bases', while sulfonate groups are relative hard 'bases'.

On the other hand Cu^{2+} is a soft acid, while Ni^{2+} is a relative hard acid. As a general rule, hard acids coordinate better with hard bases and soft acids with soft bases. The hard base–hard acid interaction is a charge-controlled one, resulting mostly from a favourable electrostatic interaction between a donor and an acceptor, respectively, with a high and a low orbital electronegativity. However, the interaction between a soft acid and a soft base normally leads to the covalent coordination of a donor with a low orbital electronegativity and an acceptor with a high orbital electronegativity. Then, a strong interaction between Cu^{2+} and PAA is expected to be found in ultrafiltration experiments due to their high ability of forming coordination bonds.

In Fig. 2(a) the retention profiles for Ni(II) and Cu(II) in contact with PAA and PVS are shown for two different ionic strength values [30]. When the solutions present low $NaNO_3$ concentration, a great difference appears in the retention profiles of Cu(II) and Ni(II) by PAA, which is in agreement with the discussion made above: due to the formation of

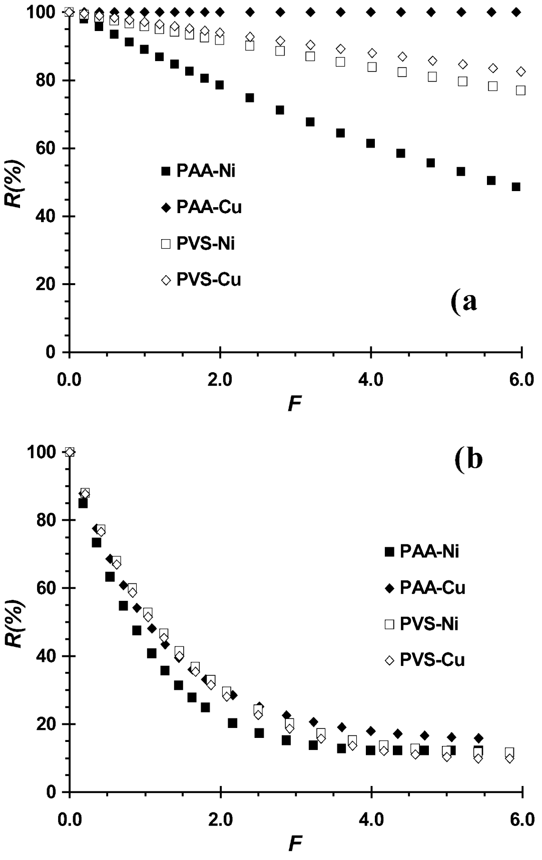

Fig. 2. Retention profiles for Ni(II) (squares) and Cu(II) (rhombus) with PAA (filled symbols) and PVS (open symbols) at different $NaNO_3$ concentrations: (a) 0.010 M $NaNO_3$, (b) 0.10 M $NaNO_3$.

strong coordination bonds all the initial Cu(II) is retained by the polymer. No significant differences are observed in the retention of both metal ions by PVS, but note that retention of Ni(II) by PVS is higher than that produced by PAA.

By increasing the 1:1 electrolyte concentration in one order of magnitude (see Fig. 2(b)), the ability of retention of both polymers decreases noteworthy, a fact that is attributed to strong shielding effects of the charges of the polyion and the metal ions as well as ion binding competition [33,34].

In order to find out which is the nature of the Ni^{2+}–PAA interaction we explore the hypothesis that it is only electrostatic. As the electric field produced by a polyelectrolyte is determined by its linear charge density, the results obtained in ultrafiltration experiments should be related with the corresponding linear charge densities. The lower ability of PAA to bind Ni(II) with respect to PVS may be explained in terms of the lower charge density of the polycarboxylate, since at pH 5 it is not completely dissociated. The linear charge density parameter of a polyelectrolyte ξ is given by:

$$\xi = l_B/b \tag{1}$$

where l_B, the Bjerrum's length, corresponds to the distance at which the electrostatic and thermal energies are equalled (in water at 25 °C is = 7.16 Å), and b is the distance that separates two fixed charges on the chain (for completely charged vinyl polymers is equal to 2.52 Å). For PAA, ξ is calculated according to:

$$\xi = 2.84\alpha \tag{2}$$

where α is the dissociation degree of the polyacid. At pH 5.0 PVS shows a ionization degree of 100%, yet in absence of a single salt, (see Fig. 3(c)), a 5 mM PAA solution exhibits an ionization degree of 25% when 0.01 M of $NaNO_3$ is present (see Fig. 3(a)), and 40% when its concentration increases 10 times (see Fig. 3(b)) [35].

Copolymerization of acrylic acid (AA) with vinylsulfonate (VS) yields macromolecules whose charge densities are higher than that of PAA. For these P(AA-*co*-VS) copolymers, ξ is obtained from:

$$\xi = 2.84(\tau_S + \alpha\tau_A) \tag{3}$$

where τ_S and τ_A are the molar fractions of the comonomers VS and AA, respectively ($\tau_S + \tau_A = 1$), and α is the dissociation degree of the carboxylic groups. Strictly speaking, at the same pH α is lower in the copolymers than in the homopolymer due to that the $(pK_a)_{ap}$ increases with the content of the ionizable groups at the chain [36]. Nevertheless, $\alpha = 0.4$ and 0.25 are still used at pH 5.0 for the copolymer in the presence of 0.10 and 0.01 M of $NaNO_3$, respectively. In Eq. (3) it is assumed that the distribution of charges at the backbone is uniform, without considering the microstructure of the copolymer [37]. Table 1 shows the values of the linear charge density parameter for the different homo- and copolymers studied.

We define the charge related formation constant (K_f^{ξ}) of a PMC as the apparent formation constant calculated considering the effective concentration of charged monomers in solution. This allows calculating and comparing the relative strength of the charged groups towards binding a metal ion. It can be calculated by ultrafiltration. The retention profiles corresponding to the interaction of a metal

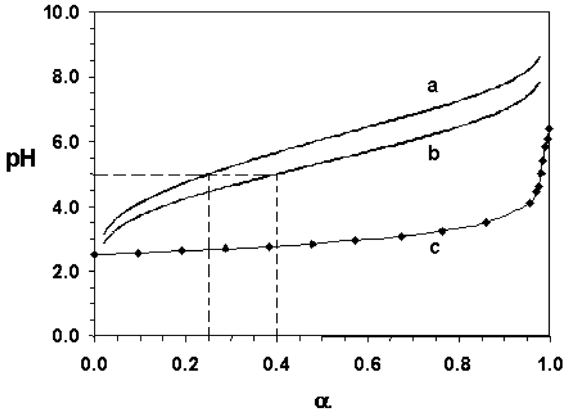

Fig. 3. Titration curves of: (a) PAA (4.71×10^{-3} equiv./l) in 0.01 M $NaNO_3$; (b) PAA (4.71×10^{-3} equiv./l) in 0.1 M $NaNO_3$; (c) PVS (5.5×10^{-3} equiv./l) in the absence of $NaNO_3$.

Table 1
Values of the linear charge densities (ξ), retention coefficient (k), and charge related formation constants (K_f^ξ) for the systems studied

Experiment	System	[NaNO$_3$] (M)	Molar fraction of AA in the polymer	α (for carboxylic units)	Linear charge density parameter	k ($\times 10^2$)	K_f^ξ ($\times 10^{-2}$) M^{-1}[a]
1	Ni(II)–PAA	0.010	1	0.25	0.71	12.2 ± 0.4	57.6 ± 0.5
2	Ni(II)–PAA	0.10	1	0.4	0.576	78 ± 6	(1.4 ± 0.2)
3	Ni(II)–P(AA-*co*-VS)	0.010	0.56	0.25	1.65	9.6 ± 0.3	32.4 ± 1.1
4	Ni(II)–P(AA-*co*-VS)	0.10	0.56	0.4	1.89	76 ± 6	(1.0 ± 0.2)
5	Ni(II)–PVS	0.010	0	–	2.84	4.4 ± 0.1	43.4 ± 1.3
6	Ni(II)–PVS	0.10	0	–	2.84	59 ± 3	(1.4 ± 0.2)
7	Cu(II)–PVS	0.010	0	–	2.84	3.2 ± 0.1	60.5 ± 1.8
8	Cu(II)–PVS	0.10	0	–	2.84	61 ± 3	(1.3 ± 0.2)

[a] In parenthesis, values with relative error >10%.

ion with a WSP may be adjusted to the plot of a function

$$R = \exp(-kZ) \tag{4}$$

where k is the constant retention coefficient [31,32]. The charge related formation constant is calculated following the general expression

$$K_f^\xi = \frac{\lfloor M^{2+}\rfloor_\mathrm{p}}{(\tau_\mathrm{S} + \alpha\tau_\mathrm{A})[L][M^{2+}]_\mathrm{ac}} = \frac{2.84}{\xi[L]}\left(\frac{1}{k} - 1\right) \tag{5}$$

where $[M^{2+}]_\mathrm{p}$ is the concentration of the metal ion bound to the polymer and $[M^{2+}]_\mathrm{ac}$ is the concentration of the metal ion free in solution [38]. $[L]$ corresponds to the concentration of monomeric units of both comonomers, while $(\tau_\mathrm{S} + \alpha\tau_\mathrm{A})[L]$ corresponds to the effective concentration of charged functional groups on the polymer. Table 1 summarizes the values of the K_f^ξ for PMCs formed with Ni(II) as well as the corresponding K_f^ξ for the system Cu(II)–PVS. The charge related formation constant of the system Cu(II)–PAA is too large to be quantified by ultrafiltration at these conditions. We have previously reported [39] that the values of the K_f^ξ will be confident if $k \leq 0.4$. In this case this condition is satisfied only when $[\mathrm{NaNO_3}] = 0.010$ M. By increasing the concentration of the single salt, the new retention coefficients are higher than the limit value expected and the respective constants allow only a qualitative analysis of the results. It can be seen that, at the same conditions, the linear charge density charge related formation constants for the PAA complexes are very similar to those for the PVS complexes. Assuming that the interactions with PVS are of pure electrostatic nature, it could be also inferred that the interaction of $\mathrm{Ni^{2+}}$ with PAA is also an electrostatic interaction.

4. Conclusions

The interactions between the water-soluble polyelectrolytes, poly(acrylic acid), PAA and poly(vinyl sulfonic acid), PVS, and Cu(II) and Ni(II) were studied by ultrafiltration. On the basis of the differences in charge densities of the polyelectrolytes and in the concentration of single salt present in solution, it was pointed out that the interaction PAA–Ni(II) is basically electrostatic, and charge related formation constants for the systems Ni(II)–PAA, Ni(II)–PVS, and Cu(II)–PVS were found to be 57.57×10^2, 43.4×10^2, and 60.5×102 M^{-1}, respectively in a 0.010 M NaNO$_3$ aqueous solution at pH 5, and 1.4×10^2 for both systems containing Ni(II) and 1.3×10^2 M^{-1} for the system Cu(II)–PVS in a 0.10 M NaNO$_3$ aqueous solution at pH 5.

Acknowledgements

The authors thank FONDECYT (Grant No. 1030669 and

No. 1020198) and the Dirección de Investigación of the Universidad Austral de Chile (Grant No. S-200126) for their financial support. N.Sch. thanks CONICYT for providing PhD fellowship.

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