Analysis of the retention profiles of poly(acrylic acid) with Co(II) and Ni(II)

Bernabé L. Rivas*, Ignacio Moreno-Villoslada

Department of Polymers, Faculty of Chemistry, University of Concepción,
Casilla 3-C, Concepción, Chile

SUMMARY

The mathematical description of the retention profiles of metal ions by water-soluble polymers using the Liquid-Phase Polymer Based Retention (LPR) technique is discussed for the system poly(acrylic acid)-Ni(II), and poly(acrylic acid)-Co(II). Two experiences have been done under constant and variable conditions. The dissociation constants are calculated from the theoretical expressions of the experimental retention profiles.

INTRODUCTION

The study of the metal complexing properties of water-soluble polymers has gained considerable importance in terms of their potential applications. A complete description of polymer-metal complexes and some of their applications have been done by Tsuchida and Nishide (1). Many water-soluble polymer types have been synthesized by homo- and copolymerization as well as by polymer-analogous reactions, and their properties to form metal complexes have been analyzed (2-4).

The Liquid-Phase Polymer Based Retention (LPR) technique, which has been recently approved by the IUPAC (5), is employed to test the interactions of metal ions with water-soluble polymers. This technique uses water-soluble polymers in combination with membrane filtration. It is based on the separation of ions bound to water-soluble polymers with chelating or ion-exchange groups from non-bound ions. The ultrafiltration cell is equiped with a membrane with a known exclusion rating. Noncomplexed metal ions are passed through the membrane due to their small molecular size. In contrast, the polymeric species, precursor polymer, and polymer-metal complexes, with substantial larger size than the membrane pores, are retained in the cell solution. By the use of this ultrafiltration membrane efficient and selective separation of inorganic ions can be achieved (4, 6-12).

By this technique a profile for the metal ion retention in the cell by the polymer is obtained. The retention profile of a given system is susceptible of variation with external variables such as polymer concentration, ionic strength, nature of the metal ions, and pH (13). Different mechanisms responsible for retention by membrane-based separations may be proposed. These mechanisms ought to give account of both mathematical expressions of the profiles and the dependence of external variables. Geckeler et al. (14) have found an expression of the retention based on reaction kinetics in partially open systems, where a reversible reaction in

---

* Corresponding author

combination with an irreversible metal ions transfer across the membrane is responsible for metal retention.

The aim of this paper is to evaluate the experimental results for the retention of Co(II) and Ni(II) with poly(acrylic acid) by the model proposed by Geckeler et al.

EXPERIMENTAL PART

Reagents

Poly(acrylic acid) was synthesized by radical polymerization in DMF with AIBN as initiator. The polymer was dissolved in water and fractionated by ultrafiltration over three membranes with an exclusion rating of 3,000, 10,000, and 100,000 g mol^{-1} (Filtron), respectively. The fractions were washed with water and lyophilized. Three fractions were obtained corresponding to the following molecular weight ranges: 3,000 to 10,000; 10,000 to 100,000; and over 100,000 g mol^{-1}.

Standard metal ion solutions of 1,000 ppm (Merck) were used.

Equipment

The unit used for retention studies consisted of a filtration cell with a magnetic stirrer, a membrane with an exclusion rating of 10,000 g mol^{-1} (Filtron), a reservoir, a selector, and a pressure source.

Metal ion concentrations were measured by atomic absorption spectrometry on a Perkin Elmer 3100 spectrometer. The pH was controlled by pH meter (H. Jürgens & Co).

Procedure

Polymeric fractions in the range over 100,000 g mol^{-1} (80 mg) were dissolved in bidistilled water, and NaNO$_3$ (255 mg) and metal solutions (400μg of each metal ion) were added. The solutions were brought to 20 mL of total volume and the pH was adjusted. The solutions are stored overnight. The pH of the cell and the reservoir solutions were adjusted to the same value. Filtration runs were carried out by washing the solutions with an aquous solution of NaNO$_3$ (experiment 1) or water (experiment 2) stored in the reservoir under a total pressure of 3 bar using an ultrafiltration membrane with an exclusion rating of 10,000 g mol^{-1}. The total volume in the cell was kept constant. Fractions were collected by filtration and the metal ion concentrations analyzed.

RESULTS AND DISCUSSION

Retention profiles of the system poly(acrylic acid) with Co(II) and Ni(II) in the presence of 0.15 M of NaNO$_3$ (experiment 1)

Recent theoretical work by Geckeler et al. (14) in the field of polymer-assisted metal ion retention has derived expressions for the retention profiles based on the kinetic theory of reactions in partially open systems, where a reversible reaction in combination with an irreversible transfer of the metal ions across the membrane is responsible for metal retention. The following model was used:

$$ML_n \Leftrightarrow M + nL$$
$$\downarrow$$
$$M_f$$
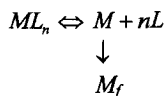
where M = metal in the cell solution, L = ligand, M_f = metal in the filtrate, and ML_n = metal-ligand complex.

The kinetic differential equations that describe this model are given by the system:

$$\frac{dR_1}{dZ} = k_1 TR_2 - k_2 T[L]^n R_1 - k_m R_1 \qquad (1)$$

$$\frac{dR_2}{dZ} = k_2 T[L]^n R_1 - k_1 TR_2 \qquad (2)$$

where T is the time employed for the elution with a volume V_0, R_1 and R_2 are the retention values for M and ML_n respectively, and k_m is the coefficient of membrane retardation.

Applying the mass balance, expressed as

$$R = R_1 + R_2 \qquad (3)$$

the following expression is obtained:

$$dR / dZ = - k_m R_1 \qquad (4)$$

indicating that the retention profile is a function of the coefficient of membrane retardation, and the free metal ion concentration.

The ligand concentration can be considered constant as it is in large excess, and a conditional apparent constant, K'_{app}, of the dissociation that involves the ligand concentration can be given by the expression:

$$K'_{app} = [M] / [ML_n] \qquad (5)$$

where $[M]$ is the concentration of metal ions not bound to the polymer and $[ML_n]$ is the concentration of metal ions bound to the polymer. Another expression of this constant is:

$$K'_{app} = R_1 / R_2 \qquad (6)$$

As $R = R_1 + R_2$, R_1 can be written as a function of R and K'_{app}:

$$R_1 = \frac{R}{1 + \dfrac{1}{K'_{app}}} \qquad (7)$$

Combining equations (4) and (7) the retention is, then, given by Geckeler's formula:

$$d\ln R = -k_m a\, dZ \qquad (8)$$

where a must be written in terms of the conditional apparent constant of dissociation:

$$a = \cfrac{1}{1 + \cfrac{1}{K'_{app}}} \qquad (9)$$

Integrating eq. (8) yields

$$R = \exp(-kZ) \qquad (10)$$

where k is a constant. As k_m is considered the coefficient of membrane retardation, a should be considered the coefficient of polymer retardation, and k should be considered the total coefficient of retardation.

The same conclusions are reached without the use of kinetic equations. As

$$d\ln R = -\frac{[M]_f}{[M]_c}\, dZ \qquad (11)$$

and $[M]_c = [ML_n] + [M]$ and $k_m = [M]_f / [M]$, equation (11) becomes equation (8).

The definition of k_m differs from Geckeler's et al. where they include in the denominator not only the free metal ions but all the metal ions, bound or not bound to the polymer, in the cell.

It is evident from the theoretical expressions that the retention profile of a system whose mechanism responsible for the retention is given by the model must be a curve that tends to zero for high values of Z, and a single straight line in logarithmic scale.

The retention profiles for the system poly(acrylic acid) (0.055 M) at pH 5 with Co(II) and Ni(II) in the presence of 0.15 M of $NaNO_3$ are lines that tends to zero for high values of Z, and a single straight line in logarithmic scale. Then the system could be evaluated with the model analyzed previously. Table 1 shows the equations that should represent the experimental retention profiles of Co(II) and Ni(II). These equations describe the experimental retention profiles with relative deviations of the experimental results from the calculated values not greater than 5% for Co(II) and 4% for Ni(II). From the blanks and the retention profiles of this polymer with these metal ions at pH 1, it is concluded that the coefficient of membrane retardation equals one, that is to say, there is no membrane retardation observed. From the values of k in these examples the apparent constants are calculated and they are also shown in Table 1.

The dissociation constant at these conditions, K'_{diss}, can be calculated, since

$$K'_{diss} = K'_{app} \, [L]^n \tag{12}$$

Table 1. Expression of the calculated functions describing the experimental retention profiles, the apparent constant of the equilibrium responsible for retention, the dissociation and the formation constants for poly(acrylic acid) with Co(II) and Ni(II).

metal ions	polymer concentration (M)	calculated functions	k	K'_{app}	n	K'_{diss} (M)	β'_1 (M)
Co(II)	0.055	$R = \exp(-0.123\ Z)$	0.123	0.14	1	$7.7 \cdot 10^{-3}$	$1.3 \cdot 10^2$
	0.275	$R = \exp(-0.027\ Z)$	0.027	0.028			
Ni(II)	0.055	$R = \exp(-0.097\ Z)$	0.097	0.11	1	$6.0 \cdot 10^{-3}$	$1.7 \cdot 10^2$
	0.275	$R = \exp(-0.021\ Z)$	0.021	0.021			

Giving values to n, different k are obtained. Changing the polymer concentration from 0.055 M to 0.275 M, the k obtained for $n = 1$ gives a theoretical expression of the retention profile that corresponds to the experimental curve (15). The value of the dissociation constants and their inverse, the formation constants β'_1, are also shown in Table 1. Figure 1 shows the experimental retention profiles of this polymer with these metal ions at 0.055 M, and the plot of the theorethical functions calculated 0.055 M and 0.275 M.
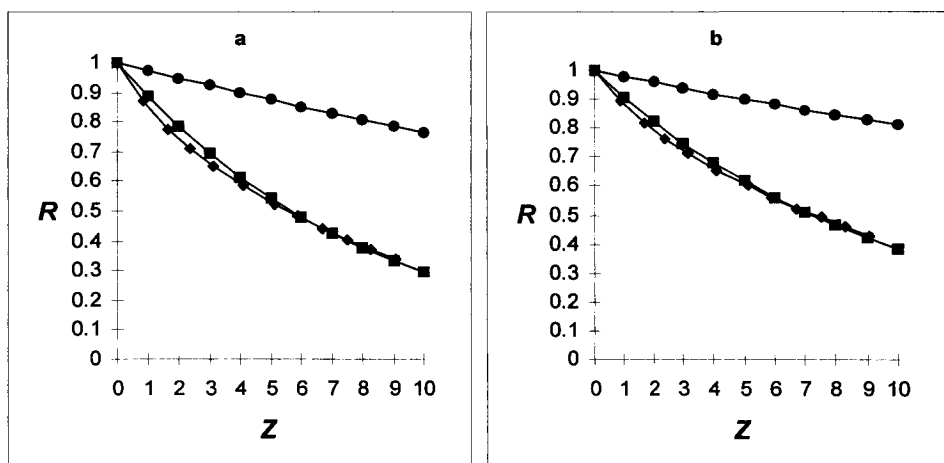

Figure 1. Retention profiles with poly(acrylic acid) at pH 5 in the presence of constant concentrations of NaNO$_3$ of a) Co(II): (—●—) experimental; (—■—) plot of the function $R = \exp(-0.123\ Z)$; (—◆—) plot of the function $R = \exp(-0.027\ Z)$ and b) Ni(II): (—●—) experimental; (—■—) plot of the function $R = \exp(-0.097\ Z)$; (—◆—) plot of the function $R = \exp(-0.021\ Z)$

Retention profiles of the system poly(acrylic acid) with Co(II) and Ni(II) in the presence of variable amounts of NaNO₃ (experiment 2)

The analysis of other retention profiles show that in many cases they do not fit this pattern. At Z values high enough a remaining residue of metal ions is frequently found which cannot be eluted by filtration at the same pH. This remaining percentage is called the retention capacity of a polymer. Thus, the retention profile does not tend to zero and is not a single straight line in the logarithmic scale. This is the case of the retention profile of Co(II) and Ni(II) with poly(acrylic acid) under conditions where the amounts of NaNO₃ present are varing with elution. The retention profiles are shown in Figure 2. The curves do not tend to zero at high values of Z, neither are they straight lines in the logarithmic scale. This fact may be interpreted by two assumptions: a) a change of the conditional constants with Z attributed to the change on the concentration of NaNO₃, b) the existence of a metal ion fraction that is irreversibly bound to the polymer.

On the other hand, curve fitting of these curves yields expressions of the type

$$R = x_0 + x_1 \exp(- k_1 Z) \tag{13}$$

where x_0, x_1, and k_1 are empirical parameters that correspond to the function which better describes the experimental data. They are summarized in Table 2. The plots of the calculated functions are also shown in Figure 2. These equations describe the experimental retention profiles with relative deviations of the experimental results from the calculated values not greater than 0.5 % for Co(II) and 0.6 % for Ni(II).
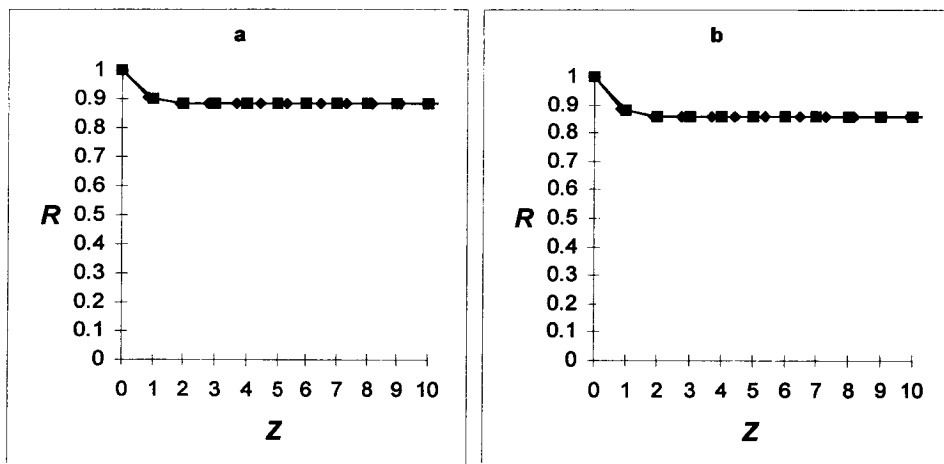

Figure 2. Retention profiles with poly(acrylic acid) at pH 5 with varing concentrations of NaNO₃ of a) Co(II): (—◆—) experimental; (—■—) plot of the function $R = 0.856 + 0.144 \exp(- 1.86\ Z)$ and b) Ni(II): (—◆—) experimental; (—■—) plot of the function $R = 0.883 + 0.117 \exp(- 1.79\ Z)$

According to the assumption b)

$$x_0 = R_3 \qquad (14)$$

and

$$k_1 = k \qquad (15)$$

where R_3 is the retention associated with this remaining metal fraction. But the empirical value of k_1 is greater than one, and k cannot be greater than one. This eliminates the possibility of a model where the existence of a metal ion fraction irreversibly bound to the polymer takes part on the total metal ion retention.

Table 2. Expression of the calculated functions describing the experimental retention profiles, the apparent conditional constants for three values of Z.

metal ions	x_0	x_1	k_1	calculated functions	Z	K'_{app}
Co(II)	0.856	0.144	1.86	$R = 0.856 + 0.144 \exp(-1.86\,Z)$	0.5	0.131
					1.0	0.050
					2.0	0.008
Ni(II)	0.883	0.117	1.79	$R = 0.883 + 0.117 \exp(-1.79\,Z)$	0.5	0.101
					1.0	0.040
					2.0	0.007

Thus, the deviation of $\ln R$ from linearity may be explained by means of a change on the conditional constants with Z attributed to the change on the concentration of $NaNO_3$. If this is true, an expression of K'_{app} as a function of Z may be obtained. The concentration of any forms of the ligand not bound to the metal studied may be still considered constant, since the ligand is in large excess. Equation (8) is still valid, but now K'_{app} turns into a function of Z. From equations (8) and (13) an expression is easily derived for the apparent conditional constants that expresses it as a function of the empirical parameters and Z:

$$K'_{app}(Z) = \cfrac{1}{\dfrac{k_m}{k_1} + \dfrac{x_0 k_m}{k_1 x_1 \exp(-k_1 Z)} - 1} \qquad (16)$$

Three apparent conditional constants are given for three Z values in Table 2.

CONCLUSIONS

The mathematical description of the retention profiles of metal ions by water soluble polymers by the Liquid-Phase Polymer Based Retention (LPR) technique has been discussed for the systems poly(acrylic acid)-Ni(II), and poly(acrylic acid)-Co(II). The LPR technique allows the calculation of the dissociation constants. From the retention profiles of Ni(II) and Co(II) with poly(acrylic acid) under different experimental conditions the apparent conditional constants have been calculated.

ACKNOWLEDGEMENTS

REFERENCES

1.   E. Tsuchida, H. Nishide, *Adv. Polym. Sci.*, **24**, 1, (1977)
2.   J.H. Barnes, G. F. Esslemont, *Makromol. Chem.*, **177**, 307, (1976)
3.   T. Hamaya, K. Hiratani, *Macromol. Chem. Phys.*, **195**, 2739, (1994)
4.   B.L. Rivas, K.E. Geckeler, *Adv. Polym. Sci.*, **102**, 171, (1992)
5.   B.Ya Spivakov, V.M. Shkinev, K.E. Geckeler, *Pure Appl. Chem.*, **66**, 631, (1994)
6.   K.E. Geckeler, G. Lange, H. Eberhardt, E. Bayer, *Pure Appl. Chem.* **52**, 1883, (1980)
7.   K.E. Geckeler, R. Zhou, B.L. Rivas, *Angew. Makromol. Chem.*, **193**, 195, (1991)
8.   B.L. Rivas, S.A. Pooley, M. Soto, H.A. Maturana, K.E. Geckeler, *J. Appl. Polym. Sci.*, (accepted)
9.   B.L. Rivas, S.A. Pooley, M. Soto, K.E. Geckeler, *J. Polym. Sci., Part A, Polym. Chem.*, (in press)
10.   G. del C. Pizarro, B.L. Rivas, K.E. Geckeler, *Polym. Bull.*, **37**, 525, (1996)
11.   B.L. Rivas, G.V. Seguel, K.E. Geckeler, *Angew. Makromol. Chem.*, **238**, 1, (1996)
12.   K.E. Geckeler, R. Zhou, A. Fink, B.L. Rivas, *J. Appl. Polym. Sci.*, **60**, 2191, (1996)
13.   B.L. Rivas, I. Moreno-Villoslada, *J. Appl. Polym. Sci.*, (accepted)
14.   K.E. Geckeler, E. Bayer, B.Ya. Spivakov, V.M. Shkinev, V.I. Golovanov, *Macromol. Theory Simul.*, **5**, 357, (1996)
15.   M. Soto, *Thesis, University of Concepción*, (1996)