

Binding of Cd^{2+} and Na^+ Ions by Poly(sodium 4-styrenesulfonate) Analyzed by Ultrafiltration and Its Relation with the Counterion Condensation Theory

B. L. Rivas* and I. Moreno-Villoslada

Department of Polymers, Faculty of Chemistry, University of Concepción, Casilla 160-C, Concepción, Chile

Received: January 26, 1998; In Final Form: April 22, 1998

A complete mathematical model that describes the metal ion retention profiles in ultrafiltration experiments of solutions of high molecular weight polymers and metal ions is given on the basis of polymer–metal ion interactions. The model allows the calculation of the free metal ion fraction and the fraction of metal ions bound to the polymer, as well as the equilibrium constants. Interactions between polyelectrolytes and metal ions are usually described by Manning's counterion condensation theory. The experimental results for the retention of Cd^{2+} in the presence of Na^+ by the polyelectrolyte poly(sodium 4-styrenesulfonate) (PSS) are in agreement with the predictions derived from Manning's counterion condensation two-variable theory.

1. Introduction

Research on functional polymers is of great interest in polymer science. Polymers with complexing or ion exchange groups have been used for the removal of metal ions from diluted solutions and implicate potential technical applications. Cross-linked insoluble resins are the most developed polymers for these applications.^{1–3} However, there are certain disadvantages in the two-phase process such as reactions in heterogeneous phase and long contact times. The use of polymers in solution in metal separation science has been less studied. A number of techniques have been described^{4–6} to recover metals from water using water-soluble polymers. Many types of water-soluble polymers have been synthesized by homo- and copolymerization as well as by polymer-analogous reactions.^{6–11} These reactions yield polymers that may show both complexing or ion exchange groups on their structure.

Polyelectrolytes are an important group of study among the hydrophilic polymers. These polymers are widely studied in relation to their properties in solution. They undergo electrostatic interactions with counterions, and it is noted that even infinitely diluted solutions of polyelectrolytes contain small counterions to the polyion. There has been great interest in studying the distribution of small ions around the polyion, as it provides crucial information about the functioning of polyelectrolytes in technological and in vivo processes.^{12–17} The interactions between polyanions and small ions in solution are generally described considering the counterion condensation theory of G. S. Manning.^{12,13,18} Experimental and theoretical results of investigations involving several polyions such as poly(4-styrenesulfonic acid) and DNA^{19–22} have proved to be explained by the theory. Fewer data are available for polyelectrolyte solutions in which a mixture of monovalent and divalent counterions in variable relative concentrations is present. These systems are described quite well by the Manning's two-variable theory.¹² Furthermore, Nordmeier et al.²³ have found good correlations between their experimental results and theoretical predictions for poly(sodium 4-styrenesulfonate). The liquid-phase polymer based retention (LPR) technique, recently approved by the IUPAC,²⁴ has been frequently used by the

authors to detect polymer–metal ion interactions.^{25–29} This technique uses solutions of polymers and metal ions in combination with membrane filtration. Metal ions with high interaction rates with the polymer are retained by the polymer, which is not able to pass through the ultrafiltration membrane, while other ions are eluted through the membrane. When solutions of mixtures of metal ions are put in contact with the polymer solution, a profile of the retention of the different metal ions by the polymer during filtration can be obtained. Some features about the pattern of these profiles have been recently discussed.²⁹ Crucial information may be extracted from these profiles, such as the value of the dissociation constants or the concentration of ions bound to the polymer in every instant.

In this paper a complete mathematical description of the metal ion retention profiles in ultrafiltration experiments of solutions of high molecular weight polymers and metal ions is given on the basis of polymer–metal ion interactions. In addition, the information obtained from the retention profiles of a mixture of mono- and divalent metal ions by poly(sodium 4-styrenesulfonate) is analyzed on the basis of Manning's theories.

2. Theory

2.1. Manning's Theory. Manning's theory represents the solution of a polyelectrolyte in water as composed by a polyelectrolyte domain, in which counterions are nonspecifically bound (territorially bound or condensed) to the polyion and by uncondensed mobile ions diffused in the zone outside the polyion domain. The condensed counterions closest to the polymer chain should be dehydrated and the farthest should retain the fully hydrated state. Territorially bound counterions are accumulated around the polyion skeleton within a volume V_p where they are assumed able to move. The uncondensed mobile ions in the solution are treated by the Debye–Hückel approximation. Extensive experimental and theoretical literature indicates that this condensed layer of counterions on the polyelectrolytes prevents the contour length charge density of the polyionic chain from exceeding a definite critical value. Some assumptions are made to enunciate this theory: (a) the real polyelectrolyte chain is modeled as an infinite regular linear array of infinite fixed univalent point charges of spacing b , (b) interactions between two or more polyions are negligible, (c)

* To whom correspondence should be sent.

the permittivity ϵ_r in the condensation volume of the polyelectrolyte is that of the pure solvent. The central parameter of this theory is the dimensionless charge-density parameter ξ . It holds

$$\xi = e^2/\epsilon k_B T b \quad (1)$$

where b is the distance between two charged groups on the polyion, ϵ is the dielectric constant of the solvent, e is the elemental charge, T is the Kelvin temperature, and k_B the Boltzmann constant. In the simple condensation theory, where the existence of a single counterion species is assumed, the formulation of the free energy of the system, G_{sys} , taking into account the mixing of free counterions, bound counterions, and solvent molecules, yields in equilibrium conditions the following expression:

$$1 + \ln[10^3 \theta_Z / (V_p C_Z)] = -2Z\xi(1 - Z\theta_Z) \ln[1 - \exp(-\kappa b)] \quad (2)$$

that relates the equilibrium binding fraction of the bound counterions per fixed polyion charge, θ_Z , with the charge-density parameter ξ . C_Z is the molarity in excess counterion of valence Z , κ is the Debye–Hückel screening parameter, and the ratio $10^3 \theta_Z / V_p$ is the molarity of the counterions bound within the volume V_p , where V_p is given in cm³/mol (of polymer charge).

This theory provides a limiting law since in the limit $C_Z \rightarrow 0$, the value of θ_Z is given by the expression

$$\lim_{C_Z \rightarrow 0} \theta_Z = \frac{1}{Z} \left(1 - \frac{1}{Z\xi} \right) \quad (3)$$

that is to say, in the limit of infinite dilution, θ_Z counterions per fixed polyion charge will remain bound to the polymer chain.

An analogous treatment is performed when two species of counterions of different valence are present, in the so-called Manning's two-variable theory. Considering a mixture of monovalent and divalent counterions, where $\theta_1 \gg \theta_2$, the equilibrium values for θ_1 and θ_2 are given by the following two expressions:

$$1 + \ln[10^3 \theta_1 / (V_p C_1)] = -2\xi(1 - \theta_1 - 2\theta_2) \ln[1 - \exp(-\kappa b)] \quad (4)$$

$$\ln[10^3 \theta_2 / (V_p C_2)] = 1 + 2 \ln[10^3 \theta_1 / (V_p C_1)] \quad (5)$$

where the subscripts 1 or 2 represent the mono- or divalent metal ion, respectively. Again, when $C_1 \rightarrow 0$ and $C_2 \rightarrow 0$, a limiting expression is found from eq 4:

$$\xi = (1 - \theta_1 - 2\theta_2)^{-1} \quad (6)$$

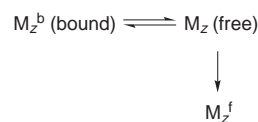
Equations 4 and 5 represent a 2×4 equation system, where the four variables are θ_1 , θ_2 , C_1 , and C_2 . Manning's two-variable theory is relevant because it combines all the variables and puts them in relation with ξ .

2.2. Ultrafiltration Process and the Retention Profiles.

The ultrafiltration is carried out in a steady-state mixed flow reactor as described in the Experimental Section.

The binding and elution processes may be formulated as a chemical reaction, where reversible reaction in combination with an irreversible transfer of the metal ions across the membrane is responsible for metal retention, following Scheme 1: where M_Z^b is the amount of metal ions bound to the polymer and M_Z is the amount of free or nonbound metal ions of valence Z in

SCHEME 1



the cell solution. The retention R_Z is defined for each species of metal ions as the fraction per unit of metal ion remaining in the cell, i.e., $R_Z = M_Z^c / M_Z^{\text{init}}$, where M_Z^c is the absolute amount of metal ions in the cell and M_Z^{init} is the initial total absolute metal amount. The subscript Z always refers to the valence of the metal ion. The filtration factor F is defined as the volume ratio of the filtrate, V^f , versus the volume of the solution in the cell, V^c . The amounts of metal ion remaining in the cell during filtration consist of the sum of the metal ions bound to the polymer chain and the metal ions free in the solution. These values are function of F . Then, the retention may be formulated as follows:

$$R_Z(F) = \frac{C_Z(F) + \theta_Z(F)c_p}{c_Z^{\text{init}}} \quad (7)$$

where c_p is the polyion concentration expressed in moles of charged monomeric units per liter, and c_Z^{init} is the initial total metal ion concentration of valence Z , i.e., $c_Z^{\text{init}} = M_Z^{\text{init}} / V^c$. As the reactor may be considered a steady-state mixed flow reactor, the uniformly mixed system attains an equilibrium state in every instant throughout filtration. Retention can be plotted versus the filtration factor, and a retention profile is obtained. The filtrate is collected in n fractions of volume ΔV . R_Z is calculated experimentally by calculating the increment on the retention from the metal ion concentration in the n th volume fraction analyzed, since

$$\Delta R_Z = -c_Z^f \Delta V / M_Z^{\text{init}} \quad (8)$$

where c_Z^f is the metal ion concentration in the n th volume fraction of filtrate. Then, dividing and multiplying by V^c the following expression is obtained:

$$\Delta R_Z = -c_Z^f \Delta F / c_Z^{\text{init}} \quad (9)$$

The coefficient of membrane retardation, k_Z^m , is defined as the ratio concentration of metal ions in the filtrate versus concentration of free (not bound to the polymer) metal ions in the cell in every instant, $k_Z^m = c_Z^f / C_Z$, and represents the influence of the membrane in the retention process. Then, at the limit of small volume fractions,

$$dR_Z = -\frac{k_Z^m C_Z}{c_Z^{\text{init}}} dF \quad (10)$$

and dividing and multiplying by R_Z , since $R_Z = c_Z^c / c_Z^{\text{init}}$, where c_Z^c is the concentration of metal ions in the cell,

$$d \ln R_Z = -\frac{k_Z^m C_Z}{c_Z^c} dF \quad (11)$$

or, as $c_Z^c = C_Z + c_Z^b$, where c_Z^b is the concentration of metal ions bound to the polymer, i.e., $c_Z^b = \theta_Z c_p$,

$$d \ln R_Z = \frac{-k_Z^m}{1 + \frac{1}{K_Z^{\text{diss}}}} dF \quad (12)$$

where $K_Z^{\text{diss}} = C_Z/(\theta_Z c_p)$ is the dissociation constant of the equilibrium represented above in every instant. Assuming that k_Z^m is constant for any free metal concentration, the retention profile should tend to zero and should be a straight line in logarithmic scale, whose slope represents the coefficient of dF in eq 12. In other words, the retention profile should correspond to the plot of a function of the type

$$R_Z = \exp(-\alpha F) \quad (13)$$

The experimental results obtained by the authors²⁸ do not agree with the above theoretical conclusions. In most cases the retention profile corresponds to a function of the type

$$R_Z = u_Z + v_Z \exp(-k_Z F) \quad (14)$$

where u_Z , v_Z , and k_Z are experimental parameters. This fact may be interpreted by two hypotheses: (a) When the metal solution is put in contact with the polymer, a fraction (u_Z) of the metal ions binds irreversibly to the polymer, while the rest of the metal ions should behave according to the reversible equilibrium represented in Scheme 1. It is easily demonstrated that in this case a limiting condition should be accomplished. Since

$$d \ln R_Z = -\frac{k_Z^m C_Z}{C_Z + c_Z^b + c_Z^{*b}} dF = -\frac{k_Z v_Z \exp(-k_Z F)}{u_Z + v_Z \exp(-k_Z F)} dF \quad (15)$$

where c_Z^{*b} is the metal ion concentration irreversibly bound to the polymer, evaluating at $F = 0$, where $R_Z = 1$, it holds that

$$k_Z v_Z = \frac{k_Z^m C_Z}{C_Z + c_Z^b + c_Z^{*b}} \quad (16)$$

Then, dividing and multiplying by c_Z^{init} , it is obtained that

$$k_Z v_Z = \frac{k_Z^m C_Z / c_Z^{\text{init}}}{u_Z + v_Z} \leq k_Z^m v_Z$$

and so, as $k_Z^m \leq 1$, it is finally concluded that

$$k_Z \leq k_Z^m \leq 1 \quad (17)$$

(b) During filtration, a change occurs in the dissociation constant with F , attributed to a change in the concentration of the metal ions present in the solution. In this second case, it holds when $F = 0$ that

$$\frac{k_Z^m}{1 + \frac{1}{K_Z^{\text{diss}}(F)}} = k_Z v_Z \quad (18)$$

and taking in account that the dissociation constant must be positive, the limiting law becomes

$$v_Z k_Z \leq k_Z^m \leq 1 \quad (19)$$

The value of k_Z is frequently found to be greater than 1, and

therefore, in those cases, the first hypothesis can be discarded. Thus, the deviation of $\ln R_Z$ from linearity may be explained by a change in the dissociation constant with F attributed to the change in the concentration of the metal ions present in the solution. That means that in every instant during filtration a new equilibrium state is achieved. An expression of K_Z^{diss} as a function of F may be obtained from equations 12 and 15:

$$K_Z^{\text{diss}}(F) = \frac{1}{\frac{k_Z^m}{k_Z} + \frac{u_Z k_Z^m}{v_Z k_Z \exp(-k_Z F)} - 1} \quad (20)$$

For F values high enough, K_Z^{diss} tends to zero, and so, a fraction (u_Z) of metal ions will remain bound to the polymer. Derivation of the logarithm of K_Z^{diss} leads to the expression

$$\frac{d \ln K_Z^{\text{diss}}}{dF} = \frac{-k_Z \frac{k_Z^m u_Z}{v_Z \exp(-k_Z F)}}{\frac{k_Z^m u_Z}{v_Z \exp(-k_Z F)} + (k_Z^m - k_Z)} \quad (21)$$

In the limit when $F \rightarrow \infty$, it is found that $d \ln K_Z^{\text{diss}}/dF \rightarrow -k_Z$. In fact, when F becomes greater than 1, the $(k_Z^m - k_Z)$ term becomes negligible and the slope of the plot becomes $-k_Z$. Then, k_Z may be defined as the absolute value of the variation of the logarithm of the dissociation constant with F when F is sufficiently large.

During filtration, all the variables θ_1 , θ_2 , C_1 , and C_2 are changing. From eqs 7 and 20, the values of these variables may be calculated as a function of F , yielding

$$\theta_Z(F) = \frac{R_Z c_Z^{\text{init}}}{[1 + K_Z^{\text{diss}}] c_p} = \frac{c_Z^{\text{init}}}{c_p} [u_Z + (1 - k_Z) v_Z \exp(-k_Z F)] \quad (22)$$

$$C_Z(F) = \frac{R_Z c_Z^{\text{init}} K_Z^{\text{diss}}}{[1 + K_Z^{\text{diss}}]} = c_Z^{\text{init}} k_Z v_Z \exp(-k_Z F) \quad (23)$$

where the assumption has been made that the influence of the membrane in the retention is negligible; that is to say, $k_Z^m = 1$.

The evaluation of eqs 14 and 23 in $F = 0$ yields two important relations:

$$v_Z = 1 - u_Z \quad (24)$$

$$k_Z v_Z = C_Z^0 / c_Z^{\text{init}} \quad (25)$$

where the numeric superscript denotes the value of F at which the variables are evaluated.

Again, the maximum value of $k_Z v_Z$ can be 1. When this occurs, the dissociation constant in $F = 0$ is ∞ , and none of the initial metal amount is condensed to the polymer chain. Instead, all the metal ions of valence Z remain free in the solution. On the other hand, the evaluation of eq 22 for F values high enough yields the conclusion that

$$u_Z = \theta_Z^\infty c_p / c_Z^{\text{init}} \quad (26)$$

2.3. Consequences of Manning's Theory on the Ultrafiltration Parameters. If the nature of the interaction of the polyelectrolyte is purely electrostatic, Manning's theory should relate all the parameters u_Z , v_Z , and k_Z with the charge-density

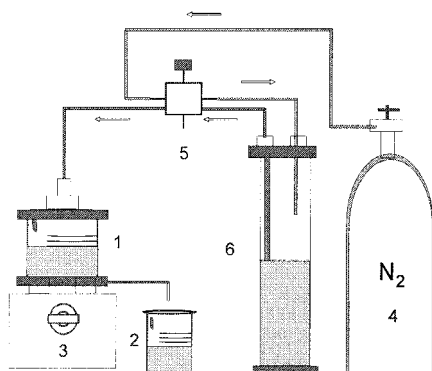


Figure 1. Retention unit. (1) Filtration cell containing the polymer and metal ion solution. (2) Membrane filtrate. (3) Magnetic stirrer. (4) Pressure trap. (5) Selector. (6) Reservoir.

parameter. For a mixture of mono- and divalent metal ions this is done as follows: First, eq 6 is written as

$$\xi = [1 - (u_1 c_1^{\text{init}}/c_p) - 2(u_2 c_2^{\text{init}}/c_p)]^{-1} \quad (27)$$

On the other hand, from eq 5 it holds

$$d \ln K_2^{\text{diss}}/d \ln C_1 = 2[1 - d \ln \theta_1/d \ln C_1 + 0.5 d \ln V_p/d \ln C_1] \quad (28)$$

Again, for F values high enough, as the ionic strength diminishes, Manning's model considers that the change in θ_1 and V_p with $\ln C_1$ is negligible. From eq 23 it holds that $d \ln C_1/dF = -k_1$, and then

$$k_2/k_1 = 2 \quad (29)$$

Then, from eqs 27 and 29 derived from Manning's two-variable theory, it can be concluded that the evolutions of the mono- and divalent metal ions during filtration are not independent events, but related in last instance by the charge-density parameter.

3. Experimental Section

3.1. Reagents. Commercially available poly(sodium 4-styrenesulfonate), 20 wt % solution in water (Aldrich, synthesized from the para-substituted monomer), was fractionated by ultrafiltration over three membranes with an exclusion rating of 3000, 10 000, or 100 000 g/mol (Filtron), respectively. The fractions were washed with water and lyophilized. Three fractions were obtained corresponding to the following molecular weight range: 3000–10 000; 10 000–100 000; and over 100 000 g/mol. Metal nitrates were used to prepare metal solutions.

3.2. Equipment. The unit used for retention studies consisted of a filtration cell with a magnetic stirrer, a membrane with an exclusion rating of 3000, 10 000, or 100 000 g/mol (Filtron), a reservoir, a selector, and a pressure source (see Figure 1). Metal ion concentrations were measured by atomic absorption on a Perkin Elmer 3100 spectrometer. The pH was controlled on an H. Jürgens & Co. pH meter.

3.3. Procedure. The procedure of the experiment discussed in section 4.3. is given. Other experiments in section 4.1. and 4.2. follow the same procedure with the quantities indicated in the text. Polymer (molecular weight fraction over 100 000 g/mol, 83 mg, 0.4 mmol sulfonate groups) and NaNO_3 (255 mg) were dissolved in bidistilled water, and 3.4×10^{-4} M solution (4 mL) $\text{Cd}(\text{NO}_3)_2$ was added. The solution was brought

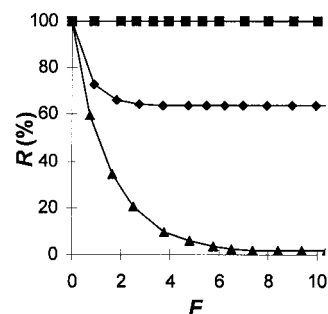


Figure 2. Retention profiles of Cd^{2+} (a) in the absence of NaNO_3 (■); (b) in the presence of 0.4 M NaNO_3 and subsequent elution with water (◆); (c) in the presence of 0.4 M NaNO_3 and subsequent elution with 0.4 M NaNO_3 water solution (▲).

to 23 mL of total volume. The pH of the cell solution and the reservoir containing only water were adjusted to pH 5. The filtration runs were carried out over a membrane with an exclusion rating of 3000 g/mol under a total pressure of 3 bar, maintaining constant a total volume of 23 mL in the cell by creating a continuous flux of liquid through the cell solution from the reservoir. Filtration fractions were collected and the metal concentrations analyzed. Measurements of the fraction volumes are given with an experimental maximum error of 0.5%, while measurements of the metal ion concentrations are given with a maximum error of 0.2%.

4. Results and Discussion

4.1. Influence of the NaNO_3 Concentration on the Retention Profile. The idea of the change in the equilibrium conditions and subsequent change in the values of the dissociation constants with the filtration factor by changing the concentration of NaNO_3 is supported by some experimental results. Three filtration runs were done where the initial concentrations of divalent metal ions were identical. In one of them, 3.6 μmol of $\text{Cd}(\text{II})$ was put in contact with 0.4 mmol of PSS in the absence of NaNO_3 , and the filtration was carried out by elution with water. In another experiment, 3.6 μmol of $\text{Cd}(\text{II})$ was put in contact with the same quantities of polymer in the presence of 0.4 M NaNO_3 , and the filtration was carried out by elution with water. In the last experiment, the same amounts of $\text{Cd}(\text{II})$ were put in contact with the polymer in the presence of 0.4 M NaNO_3 , and the filtration was carried out by elution with 0.4 M NaNO_3 solution. For the first experiment all the metal ions were retained in the solution (see Figure 2), resulting in a null value for the dissociation constant, while for the latter no metal ion was retained, resulting in a dissociation constant whose value is infinite. For the second experiment, whose retention profile can be approximated to a function of the eq 14 type, the dissociation constant changes with F as the ionic strength is strongly changing.

Such a great influence of the NaNO_3 concentration suggests that the nature of the interaction is merely electrostatic and that Na^+ is actively participating in the retention "competing" with the divalent metal ion to enter the polyelectrolyte domain.

4.2. Influence of the Membrane. To calculate the participation of the membrane in the retention, an experiment was performed without polymer and with $c_1^{\text{init}} = 0.14$ M and $c_2^{\text{init}} = 0.0017$ M. It can be seen in Figure 3 that both Na^+ and Cd^{2+} do not interact with the membrane, since their retention profiles can be represented by the function $R_Z = \exp(-F)$. That implies that $k_Z^m = 1$ for both species.

4.3. Analysis of a Retention Profile. In this section, the retention profiles for a Na^+ and Cd^{2+} solution will be analyzed.

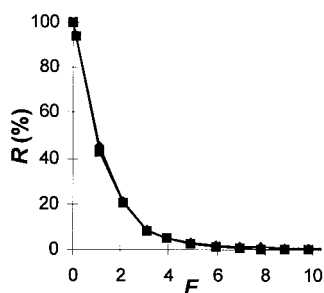


Figure 3. Retention profiles of Cd^{2+} (◆) and Na^{+} (■) in the absence of polymer.

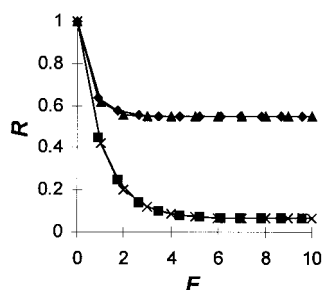


Figure 4. Experimental retention profiles of Cd^{2+} (◆) and Na^{+} (■) and the plot of the functions $R = 0.55 + 0.45 \exp(-1.90F)$ (▲) and $R = 0.064 + 0.936 \exp(-0.95F)$ (×).

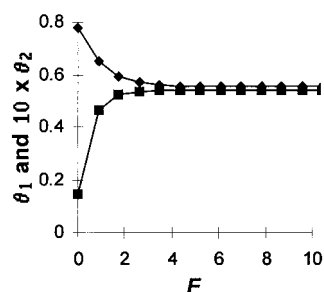


Figure 5. Equilibrium binding fraction of metal ion condensed per fixed polyon charge versus the filtration factor: (◆) θ_1 , (■) $10 \times \theta_2$.

The experiment was performed with $c_1^{\text{init}} = 0.14$ M, $c_2^{\text{init}} = 0.0017$ M, and $c_p = 0.017$ M. The retention profiles are shown in Figure 4. They adjust very well with the functions, whose plots also appear in Figure 4, $R = 0.55 + 0.45 \exp(-1.90F)$ for Cd^{2+} and $R = 0.064 + 0.936 \exp(-0.95F)$ for Na^{+} . Note that the coefficient of F in the first exponential is greater than 1, resulting in the implications stated in the Theory section. These profiles satisfy the property that $k_2/k_1 \equiv 2$, a condition derived from Manning's theory. The evaluation of eq 27 with the values of u_1 and u_2 obtained yields a value of $\xi = 2.95$, which is very close to the theoretical value 2.8. From eqs 22 and 23, the values of θ_1 , θ_2 , C_1 , and C_2 for the different F values are obtained, and they are plotted in Figure 5 and Figure 6, where the θ_2 and C_2 values are multiplied by a factor 10 and 100, respectively. Note the evolution of θ_1 , and θ_2 . For high concentrations of monovalent ions relative to divalent metal ions, they practically fill the condensation domain, and few divalent ions are condensed. The values of $(1 - \theta_1 - 2\theta_2)^{-1}$ as a function of F are shown in Table 1. Note that the limiting condition is exceeded. That means that the higher the ionic concentration is, the higher the number of condensed ions becomes. Lowering the amounts of monovalent ions permits the divalent metal ions to enter the polymer domain, and then, monovalent metal ions exit from it until the limiting condition eq 6 is achieved. The approximation of a sufficiently low ionic concentration can be made when the values of θ_1 and θ_2 are

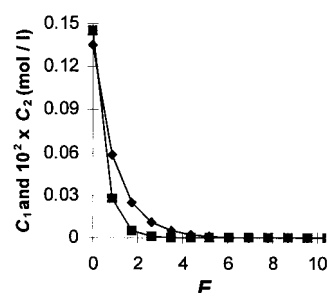


Figure 6. Equilibrium concentration of uncondensed Na^{+} and Cd^{2+} versus the filtration factor: (◆) C_1 , (■) $100 \times C_2$.

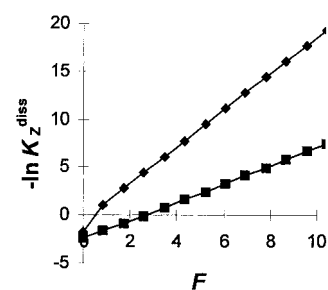


Figure 7. Plot of $-\ln K_1^{\text{diss}}$ (■) and $-\ln K_2^{\text{diss}}$ (◆) versus the filtration factor.

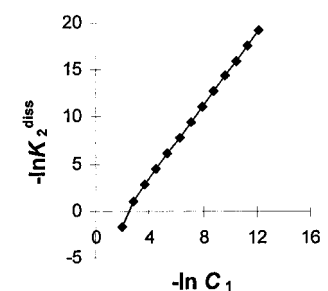


Figure 8. Plot of $-\ln K_2^{\text{diss}}$ versus $-\ln C_1$.

TABLE 1: Values of $(1 - \theta_1 - 2\theta_2)^{-1}$ as a Function of F

F	$(1 - \theta_1 - 2\theta_2)^{-1}$
0	5.16
0.97	3.88
1.74	3.33
2.61	3.11
3.48	3.02
4.35	2.98
5.22	2.96
6.09	2.96
7.83	2.95
8.7	2.95
9.57	2.95
10.4	2.95

practically constant. In this experiment, this can be considered achieved at $F = 5$, and it is related to the fact of C_Z tending to zero (see Figure 6). Nevertheless, it is observed that $d \ln K_Z^{\text{diss}}/dF$ becomes constant at very low F values (see Figure 7). From eq 23 it can be inferred that $d \ln C_1/dF$ is constant in the whole F range ($d \ln C_1/dF = -k_1$). Consequently $d \ln K_2^{\text{diss}}/d \ln C_1 = 2$ from very low F values, even before $F = 5$, i.e. for practically all C_1 values, as shown in Figure 8.

5. Conclusions

A mathematical description of the metal ion retention profiles in ultrafiltration experiments of solutions of high molecular weight polymers and metal ions is given on the basis of polymer-metal ion interactions. The model allows the calcula-

tion of the free metal ion fraction and the fraction of metal ions bound to the polymer, as well as the equilibrium constants. The expressions for these variables as functions of the experimental parameters describing the retention profiles are given. It is noted that at the limit of infinite elution a fraction of metal ions remains bound to the polymer. The metal ion distribution under these conditions satisfied the Manning's limiting law that $\xi = (1 - \theta_1 - 2\theta_2)^{-1}$. Another of Manning's predictions from his two-variable counterion condensation theory is also satisfied, as $d \ln K_2^{\text{diss}}/d \ln C_1 = 2$.

Acknowledgment. The authors thank the FONDECYT (Grants 1951104 and 2960068) for financial support. I.M.V. thanks the Dirección de Investigación of the University of Concepción (Grant 97088) for financial support and the Instituto de Cooperación Iberoamericana (Ministerio de Asuntos Exteriores) (Spain) for the MUTIS fellowship. The authors thank Prof. G. S. Manning from The State University of New Jersey for fruitful discussion.

References and Notes

- (1) Izatt, N. K.; Bradshaw, J. S.; Bruening, R. L.; Bruening, M. L.; Tarbet, B. J. *Pure Appl. Chem.* **1995**, *67*, 1069.
- (2) Rivas, B. L.; Maturana, H. A.; Pereira, E. *Angew. Makromol. Chem.* **1994**, *220*, 61.
- (3) Geckeler, K. E.; Lange, G.; Eberhardt, H.; Bayer, E. *Pure Appl. Chem.* **1980**, *52*, 1883.
- (4) Tomida, T.; Ikawa, T.; Masuda, S. *J. Chem. Eng. Jpn.* **1993**, *26*, 575.
- (5) Tomida, T.; Inoue, T.; Tsuchiya, K.; Masuda, S. *Ind. Eng. Chem. Res.* **1994**, *33*, 904.
- (6) Geckeler, K. E.; Lange, G.; Eberhardt, H.; Bayer, E. *Pure Appl. Chem.* **1980**, *52*, 1883.
- (7) Salamone, J. C.; Ahmed, I.; Rodriguez E. L.; Quach, L.; Watterson, A. C. *J. Macromol. Sci., Chem.* **1988**, *A25*, 811.
- (8) McCarthy, K. J.; Burkhardt, C. W.; Parazak, D. P. *J. Appl. Polym. Sci.* **1987**, *34*, 1311.
- (9) Nguyen, M. T.; Diaz, A. F. *Macromolecules* **1994**, *27*, 7003.
- (10) Kirsh, Yu. E.; Rahnanskaya, A. A.; Lukovkin, G. M.; Kabanov, V. A. *Eur. Polym. J.* **1974**, *10*, 393.
- (11) Kathmann, E. E.; McCormick, C. L. *J. Polym. Sci. Part A; Polym. Chem.* **1997**, *35*, 243.
- (12) Manning, G. S. *Q. Rev. Biophys.* **1978**, *11*, 179.
- (13) Manning, G. S. *J. Phys. Chem.* **1984**, *88*, 6654.
- (14) Bratko, D.; Vlasy V. J. *Phys. Lett.*, **1982**, *90*, 434.
- (15) Backet, R.; Rossky P. J. *J. Phys. Chem.* **1988**, *92*, 3604.
- (16) Le Bret, M.; Zimm, B. H. *Biopolymers* **1984**, *23*, 271.
- (17) Nordmeier, E. *Macromol. Chem. Phys.* **1995**, *196*, 1321.
- (18) Manning, G. S. *Physica A* **1996**, *231*, 236.
- (19) Joshi, Y. M.; Kwak, J. C. T. *Biophys. Chem.* **1981**, *13*, 65.
- (20) Mattai, J.; Kwak, J. C. T. *J. Phys. Chem.* **1982**, *86*, 1026.
- (21) Noda, I.; Tsuke, T.; Nagasawa, M. *J. Phys. Chem.* **1970**, *74*, 710.
- (22) Kowblansky, M.; Zema, P. *Macromolecules* **1981**, *14*, 166.
- (23) Nordmeier, E.; Dawe, W. *Polym. J.* **1991**, *23*, 1297.
- (24) Spivakov, B. Ya; Shkinev, V. M.; Geckeler, K. E. *Pure Appl. Chem.* **1994**, *66*, 631.
- (25) Geckeler, K. E.; Zhou, R.; Rivas, B. L. *Angew. Makromol. Chem.* **1991**, *193*, 195.
- (26) Rivas, B. L.; Pooley, S. A.; Soto, M.; Geckeler, K. E. *J. Polym. Sci., Part A, Polym. Chem.* **1997**, *35*, 2461.
- (27) Rivas, B. L.; Moreno-Villoslada, I. *J. Appl. Polym. Sci.* (in press).
- (28) Rivas, B. L.; Moreno-Villoslada, I. *J. Appl. Polym. Sci.* (in press).
- (29) Rivas, B. L.; Moreno-Villoslada, I. *Polym. Bull.* **1997**, *39*, 653.