

# Competition of Divalent Metal Ions with Monovalent Metal Ions on the Adsorption on Water-Soluble Polymers

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The interactions of water-soluble polymers with metal ions are treated as surface phenomena in which different metal species compete with each other to bind to the polymer surface. The adsorption isotherms for the system poly(sodium 4-styrenesulfonate)/Cd<sup>2+</sup>/Na<sup>+</sup> are obtained by ultrafiltration of the polymer at constant ionic strength in the presence of 0.15, 0.10, 0.05, 0.02, and 0.01 M NaNO<sub>3</sub> solutions, respectively. A change in the rate of release of divalent metal ions by the polymer is detected which is attributable to a change in the polymer conformation. A Michaelis-Menten-like mathematical development is shown for the competition of both metal ions.

## 1. Introduction

Water-soluble polymers undergo interactions with solvent and other high- and low-molecular-weight species present in aqueous solutions.<sup>1–12</sup> Due to these interactions, macromolecules in solution exhibit, beyond their chemical structure, different properties as conformation of the polymer chains, excluded volume, surface activity, or formation of higher-order structures as aggregates, gels, etc. The potential analytical and technological applications of water-soluble polymers in combination with metal ions make the study of such systems, viz., the interactions between the species, of interest. Apart from the potential ability of some polyelectrolytes to form coordinating bonds with metal ions, all polyelectrolytes undergo electrostatic interactions with other ions. In polyelectrolyte theory, when long-range electrostatic interactions are dominant, polyelectrolytes are assumed to bind counterions nonspecifically,<sup>13–16</sup> and they are considered to move freely around the axis of the polymer chain. Thus, the electrostatic water-soluble polymer metal ion interaction may be regarded as an adsorption phenomenon of counterions on the surface of the polymer domain. In previous papers<sup>17,18</sup> it has been shown that the ultrafiltration technique in a batch-like method allows obtaining the amounts of metal ions bound to the polymer in every instant during filtration, as well as the amounts of metal ions free in the solution. In this sense, the interaction of Cd<sup>2+</sup> with poly(sodium 4-styrenesulfonate) at variable ionic strength<sup>17</sup> and at constant ionic strength<sup>18</sup> has been studied. The values of this distribution of metal ions around the polyelectrolyte surface are strongly dependent on the ionic strength. Negatively charged polyelectrolytes interact with positively charged divalent metal ions stronger than with monovalent ones, but an excess of the latter may yield in a displacement of the former from the polymer surface. A competition between the positive species present in the solution is established to bind the negatively charged polymer surface.

In this paper, the interaction of poly(sodium 4-styrenesulfonate) with Cd<sup>2+</sup> will be evaluated by ultrafiltration at constant ionic strength in the presence of 0.15, 0.10, 0.05, 0.02, and 0.01 M NaNO<sub>3</sub> solutions, respectively. The system is evaluated under the steady-state approximation and a mathematical development is shown to calculate the dissociation constants following a Michaelis-Menten-like formalism applied to competitive reactions in enzymes.

## 2. Theory

**2.1. The System.** The reaction involved in the interaction of a water-soluble polyelectrolyte and two metal ions may be understood following Scheme 1. An element of polymeric surface (*dPS*) is in equilibrium with the two metal ions in a way that only one of the species is able to be bound to that *dPS* at a given instant. The concentration of one of the species (*M*<sub>1</sub>) is maintained constant during filtration, while the concentration of the other species is changing during filtration following an irreversible transfer across the membrane. The sum of the interaction of all the elements of polymer surface is related to the amounts of metal ions that are bound to the polymer in every instant. Let *c*<sub>Z</sub><sup>b</sup> be the concentration of metal ions of valence *Z* bound to the polymer and *C*<sub>Z</sub> the value of the molarity of metal ions of valence *Z* not bound to the polymer chains.

**2.2. Metal Ion Distributions.** The distributions of metal ions bound to the polymer or free in the solution, i.e., *c*<sub>Z</sub><sup>b</sup> and *C*<sub>Z</sub>, may be calculated experimentally.<sup>18</sup> The metal ion concentration experimentally measured for each filtration fraction collected (*c*<sub>Z</sub><sup>f</sup>) corresponds to the concentration of the solution at a given instant between the two *F* values that limit the filtration fraction (*ΔF*). When constant *ΔF* are taken, it is normally found an exponential decay if *c*<sub>Z</sub><sup>f</sup> is represented versus *F*, so that

$$\langle c_Z^f \rangle = \langle c_Z^f \rangle^{\text{init}} \exp(-jF) \quad (1)$$

where *j* is a parameter and the superscript “init” is referred to the initial value (for *F* = 0). This is related to an exponential

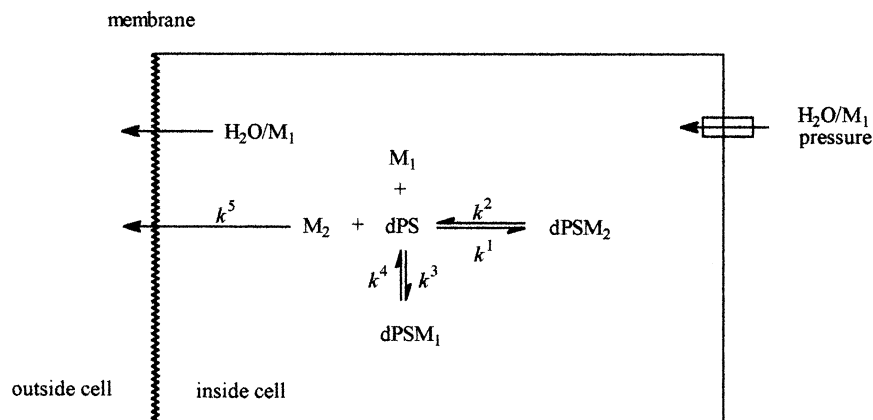
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## SCHEME 1



decay on the instantaneous  $c_Z^f$  during filtration, so that

$$c_Z^f = c_Z^{\text{finit}} \exp(-jF) \quad (2)$$

where

$$c_Z^{\text{finit}} = -\frac{j\langle c_Z^f \rangle^{\text{init}} \Delta F}{1 - \exp(j\Delta F)} \quad (3)$$

As

$$c_Z^f = k_Z^m C_Z \quad (4)$$

where  $k_Z^m$  is the coefficient of membrane retardation which is considered to be unity unless another value is indicated, the values of  $C_Z$  follow the relation

$$C_Z = C_Z^{\text{init}} \exp(-jF) \quad (5)$$

where

$$C_Z^{\text{init}} = c_Z^{\text{finit}} / k_Z^m$$

The values of  $c_Z^b$  are calculated by subtraction of  $C_Z$  from the concentration of metal ions inside the cell.

**2.3. The  $j$  Parameter.** The  $j$  parameter has a physical meaning. It gives a measure of the capacity of the polymer phase to transfer metal ions to the aqueous phase during filtration. If  $j < 1$ , the equilibrium in the solution inside the cell is furnishing metal ions to the aqueous phase from the polymer phase while they are being filtered out of the cell during filtration; on the contrary, if  $j > 1$ , apart from the loss of metal ions in the aqueous phase because of filtration, the polymer is capturing free metal ions from the solution. In the particular case that  $j = 0$ , the aqueous phase solution recuperates the same amount of metal ions that are filtered. When  $j = 1$ , the amounts of metal ions bound to the polymer do not change during filtration and the free metal ions are filtered out of the ultrafiltration cell.

**2.4. Competitive Reactions.** Following a Michaelis-Menten-like formalism applied to competitive reactions in enzymes, the equilibrium situation at the steady state, when a divalent and a monovalent metal ion coexist in solution, is described by the formula

$$k^2 C_2 [dPS] - k^1 [dPSM_2] + k^5 C_2 = 0 \quad (6)$$

where  $k^i$  are the velocity constants according to Scheme 1,  $[dPS]$  is the concentration of polymeric surface elements that keep

free, and  $[dPSM_2]$  is the concentration of polymeric elements that are bound to  $M_2$ . When  $k^5 \ll k^2 [dPS]$ ,

$$C_2 [dPS] = K_2^{\text{diss}} [dPSM_2] \quad (7)$$

where  $K_Z^{\text{diss}}$  is the apparent thermodynamic dissociation constant for the equilibrium. As

$$[dPS_T] = [dPS] + [dPSM_2] + [dPSM_1] \quad (8)$$

where  $[dPS_T]$  is the concentration of total polymeric surface elements, substituting and reordering

$$C_2 [dPS_T] - C_2 [dPSM_1] = (K_2^{\text{diss}} + C_2) [dPSM_2] \quad (9)$$

According to the equilibrium established for the monovalent metal ion

$$C_1 [dPS] = K_1^{\text{diss}} [dPSM_1] \quad (10)$$

following that

$$C_2 [dPS_T] - K_2^{\text{diss}} [dPSM_2] C_1 / K_1^{\text{diss}} = (K_2^{\text{diss}} + C_2) [dPSM_2] \quad (11)$$

or

$$[dPSM_2] = \frac{[dPS_T] C_2}{K_2^{\text{diss}} \left( 1 + \frac{C_1}{K_1^{\text{diss}}} \right) + C_2} \quad (12)$$

The concentration of divalent metal ions bound to the polymer in every instant is proportional to  $[dPSM_2]$ . Then

$$c_2^b = k [dPSM_2] = \frac{c_2^{\text{bmax}} C_2}{K_2^{\text{diss}} \left( 1 + \frac{C_1}{K_1^{\text{diss}}} \right) + C_2} \quad (13)$$

where  $k$  is the proportionality constant and  $c_2^{\text{bmax}}$  is the maximum amount of metal ions that may condense on the polymer surface. Equation 13 may be linearized to

$$\frac{1}{c_2^b} = \frac{K_2^{\text{diss}}}{c_2^{\text{bmax}}} \left( 1 + \frac{C_1}{K_1^{\text{diss}}} \right) \frac{1}{C_2} + \frac{1}{c_2^{\text{bmax}}} \quad (14)$$

### 3. Experimental Section

**3.1. Reagents.** Commercially available poly(sodium 4-styrenesulfonate) (PSS) (Aldrich, synthesized from the para-

TABLE 1: Values of the Experimental Variables

experiment	polymer concentration (M)	NaNO <sub>3</sub> concentration <sup>a</sup> (M)	initial Cd <sup>2+</sup> concentration (M)	pH <sup>a</sup>
PSS-Cd <sup>2+</sup> -01	0.01	0.150	0.005	5
PSS-Cd <sup>2+</sup> -02	0.01	0.100	0.005	5
PSS-Cd <sup>2+</sup> -03	0.01	0.050	0.005	5
PSS-Cd <sup>2+</sup> -04	0.01	0.019	0.005	5
PSS-Cd <sup>2+</sup> -05	0.01	0.010	0.005	5

<sup>a</sup> Values for both the cell solution and the reservoir solution.

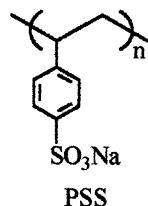


Figure 1. Structure of poly(sodium 4-styrenesulfonate).

substituted monomer) was treated as described elsewhere.<sup>17</sup> NaNO<sub>3</sub> and Cd(NO<sub>3</sub>)<sub>2</sub> (Merck) were used to prepare metal ion solutions. The pH was adjusted with NaOH and HNO<sub>3</sub>.

**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 Dalton (Filtron, Pall Gelman), a reservoir, a selector, and a pressure source. Metal ion concentrations were measured by atomic absorption on a Unicam Solar M5 spectrometer. The pH was controlled on a H. Jürgens & Co. pH meter.

**3.3. Procedure.** Polymeric molecular weight fractions over 100 000 Dalton were dissolved in twice distilled water, and metal salts were added to obtain the concentrations showed in Table 1. The exact polymer amounts used are also listed in Table 1. The solutions were brought to 20 mL of total volume, the pH was adjusted (see Table 1), and the solutions placed into the ultrafiltration cell. The pH and the concentration of NaNO<sub>3</sub> of the aqueous solution contained in the reservoir were adjusted to the same value as in the cell solution. The filtration runs were carried out over a membrane with an exclusion rating of 5000 Dalton under a total pressure of 3 bar, keeping constant the solution volume 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 were analyzed.

## 4. Results and Discussion

**4.1. Ultrafiltration.** The water-soluble poly(sodium styrenesulfonate) (PSS) has been taken as model of a polyelectrolyte polymer (see Figure 1). Ultrafiltration of PSS in the presence of Cd<sup>2+</sup> at five different values of constant ionic strength (see Table 1) yields five sets of experimental  $\langle c_2^f \rangle$  which may be represented versus  $F$  in logarithmic scale, as it can be seen in Figure 2. The profiles of the representations show deviations from linearity, except in the case of PSS-Cd<sup>2+</sup>-01, so that, the system does not follow eq 1. This may be interpreted postulating a dependency of  $j$  on  $F$ . As the ultrafiltration runs carry on, the  $j$  values diminish, indicating that the polymer releases metal ions at a higher rate. We have found for the experiments PSS-Cd<sup>2+</sup>-02 to PSS-Cd<sup>2+</sup>-05 two domains of linearity, and the linear adjustments are shown in Table 2, as well as the linear regression factors.

**4.2. Metal Ion Distributions.** The distributions of metal ions bound to the polymer or free in the solution in every instant

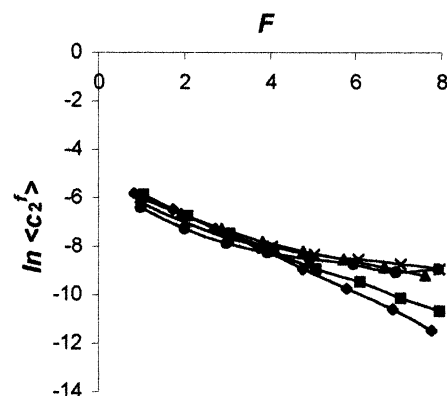


Figure 2. Plot of  $\ln \langle c_2^f \rangle$  versus  $F$ : (◆) PSS-Cd<sup>2+</sup>-01; (■) PSS-Cd<sup>2+</sup>-02; (▲) PSS-Cd<sup>2+</sup>-03; (●) PSS-Cd<sup>2+</sup>-04; (×) PSS-Cd<sup>2+</sup>-05; for linear adjustments see Table 2.

can be calculated by means of eqs 2–5. Then, five sets of  $c_2^b$  and  $C_2$  values are obtained, and  $1/c_2^b$  can be represented versus  $1/C_2$ , according to eq 14. In Figure 3 the results for every experiment are shown by plotting  $1/\theta_2$  versus  $1/C_2$ , where  $\theta_2$  represents the equilibrium binding fraction of the bound divalent counterions per fixed polyion charge, i.e.,  $\theta_2 = c_2^b/c^p$ , where  $c^p$  is the polymer concentration expressed in mole of charged monomeric units per liter. Straight lines are found in all cases with good linear regressions as it can be seen in Table 2. The comparison between the different isotherms follow the expected results for a Michaelis-Menten-like formalism applied to competitive reactions in enzymes. Slight differences are found in the ordinate at the origin, then in  $c_2^{b_{\max}}$ . The respective values of  $\theta_2^{\max} = c_2^{b_{\max}}/c^p$  are also shown in Table 2. The values of  $K_2^{\text{diss}}$  and  $K_1^{\text{diss}}$  should be calculated from the slope of the straight lines ( $m$ ) since, from eq 14

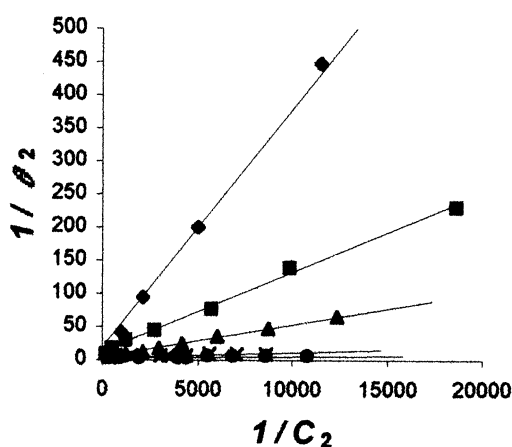
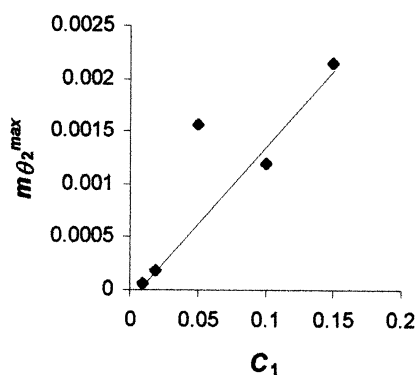
$$m\theta_2^{\max} = K_2^{\text{diss}} + \frac{K_2^{\text{diss}}}{K_1^{\text{diss}}} C_1 \quad (15)$$

The result is shown in Figure 4 where  $m\theta_2^{\max}$  is plotted versus the constant concentration of monovalent metal ions ( $C_1$ ). Good linear regression is found if the values corresponding to PSS-Cu<sup>2+</sup>-01 are not considered, but an approximately zero negative value for  $K_2^{\text{diss}}$  is found.

**4.3. The Polymer Surface.** In the above sections we have shown that the  $j$  parameter diminishes during filtration. Such a fact may be due to a conformational change on the polymer chains: the filtration of metal ions and their subsequent release from the polymer induces an increase of the net negative charge on the polymer surface and then in an expansion of the chains in order to increase the total surface, minimizing the electrostatic repulsions. Related with this, the decrease on the surface charge density of the polymer induces a decrease on the strength of the interactions with the metal ions, and in consequence, their easier release to the solution from the polymer domain during filtration, decreasing the  $j$  values found. It is important to note that if a constant  $j$  value is taken for the whole  $F$  domain, linearity is lost when plotting  $1/c_2^b$  versus  $1/C_2$ . So, it seems that the equilibrium constants  $K_2^{\text{diss}}$  and  $K_1^{\text{diss}}$  are dominating the behavior of the systems. On the other hand, expansion of the polymer would increase the capacity of fixing metal ions, and comparing the different experiments, expansion is related with the presence of less monovalent metal ions in solution. That could explain that higher  $\theta_2^{\max}$  values are found for lower ionic strengths.

**TABLE 2: Values of the Linear Adjusted Functions and  $\theta_2^{\max}$ .  $y_1 = \ln \langle c_2^f \rangle$ ;  $y_2 = 1/\theta_2$ ;  $x_2 = 1/C_2$** 

experiment	linear adjustment (Figure 2)	square linear regression ( $R^2$ )	linear adjustment (Figure 3)	square linear regression ( $R^2$ )	$\theta_2^{\max}$
PSS–Cd <sup>2+</sup> -01	$y_1 = -0.8087 F - 5.0735$	0.9990	$y_2 = 0.0359 x_2 + 16.381$	0.9992	0.06
PSS–Cd <sup>2+</sup> -02	$y_1 = -0.7961 F - 5.0492$	0.9996	$y_2 = 0.0120 x_2 + 10.405$	0.9958	0.10
	$1.06 \leq F \leq 3.09$				
	$y_1 = -0.6326 F - 5.651$	0.9994			
	$4.09 \leq F \leq 7.95$				
PSS–Cd <sup>2+</sup> -03	$y_1 = -0.6857 F - 5.3335$	0.9959	$y_2 = 0.0049 x_2 + 3.1594$	0.9982	0.32
	$0.97 \leq F \leq 2.89$				
	$y_1 = -0.3804 F - 6.3421$	0.9977			
	$3.84 \leq F \leq 7.62$				
PSS–Cd <sup>2+</sup> -04	$y_1 = -0.7121 F - 5.5245$	0.9908	$y_2 = 0.0007 x_2 + 3.6665$	0.9737	0.27
	$1.00 \leq F \leq 3.02$				
	$y_1 = -0.2293 F - 7.1310$	0.9907			
	$4.05 \leq F \leq 7.95$				
PSS–Cd <sup>2+</sup> -05	$y_1 = -0.7363 F - 5.7130$	0.9935	$y_2 = 0.0002 x_2 + 3.3147$	0.9530	0.30
	$1.00 \leq F \leq 3.00$				
	$y_1 = -0.2257 F - 7.3908$	0.9883			
	$3.94 \leq F \leq 5.94$				

**Figure 3.** Plot of  $1/\theta_2$  values as a function of  $1/C_2$ : (◆) PSS–Cd<sup>2+</sup>-01; (■) PSS–Cd<sup>2+</sup>-02; (▲) PSS–Cd<sup>2+</sup>-03; (●) PSS–Cd<sup>2+</sup>-04; (×) PSS–Cd<sup>2+</sup>-05; lines: linear adjustments (see Table 2).**Figure 4.** Dots: plot of  $m\theta_2^{\max}$  values as a function of  $C_1$ ; line: linear adjustment:  $y = 0.0145x - 0.0001$  (square linear regression factor = 0.99).

## 5. Conclusions

The equilibrium distributions of divalent metal ions have been experimentally obtained by ultrafiltration at constant ionic

strengths for the system poly(sodium 4-styrenesulfonate)/Cd<sup>2+</sup>/Na<sup>+</sup>. The polymer was ultrafiltered in the presence of 0.005 M of Cd(NO<sub>3</sub>)<sub>2</sub> and 0.15, 0.10, 0.05, 0.02, and 0.01 M NaNO<sub>3</sub> solutions, respectively. In the course of the ultrafiltration the rate of release of divalent metal ions by the polymer changes due to a change on its conformation. The metal ion distributions follow a Michaelis-Menten-like pattern applied to competitive reactions in enzymes.

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