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ORIGINAL PAPER

Polymer-enhanced ultrafiltration: counterion distribution and its relation with the divalent metal-ion retention properties by sulfonic acid polyelectrolytes

Manuel Palencia · Bernabé Rivas · Eduardo Pereira

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Abstract The distribution of divalent counterions and its relation with the retention properties of sulfonic polyelectrolytes were analyzed, and the results were interpreted under the light of the counterion condensation theory using two-zone model and Donnan's equilibria. In this regard, poly(vinyl sulfonic acid) and sodium poly(styrene sulfonate) solutions at pH 6.0 were diafiltered by the liquid-phase polymer-based retention technique. Metal-ion retention and distribution around polyelectrolyte chains were obtained from the diafiltration experiment as well as the maximum retention capacity (MRC) for each polymer. The MRC values obtained were 0.30, 0.15, 0.21, and 0.26 mmol of metal-ion per mmol of polymer for PVSA–Cu^{2+}, PVSA–Cd^{2+}, PSS–Cu^{2+} and PSS–Cd^{2+}, respectively. The excess of ions added, the volume in the inside cell, and the order of addition of the ions contacted with the polymer were important factors defining the form of the retention profile.

Keywords Counter ion distribution · Polyelectrolytes · Retention profile · Enrichment method · Washing method · Two-zone model

Abbreviations

A	Proportionality factor of C_p and C_c (dimensionless)
ε	Solvent dielectric constant (dimensionless)
ε_0	Vacuum permittivity (F/m)

M. Palencia · B. Rivas (✉)
Department of Polymer, Faculty of Chemistry, University of Concepción, Casilla 160-C, Concepción, Chile
e-mail: brivas@udec.cl

E. Pereira
Department of Analytic and Inorganic Chemistry, University of Concepción, Casilla 160-C, Concepción, Chile

θ	Fraction of ions bound to the polymer chains (dimensionless)
μ	Metal-ion/polymer ratio (mmol of M^{n+}/mmol polymer)
Ω	Distribution function (dimensionless)
ξ	Fixed charge density parameter (dimensionless)
C_0	Metal-ion concentration in the cell at $F = 0$ (mmol/L)
C_0^*	Initial concentration of metal-ions contacted with the polymer (mmol/L)
C_c	Free metal-ion concentration in the cell (mmol/L)
C_{bulk}	Concentration in the bulk of the polymeric solution (mmol/L)
C_{ext}	Concentration in the external zone according to two-zone model (mmol/L)
C_{int}	Concentration in the internal zone according to two-zone model (mmol/L)
e	charge (C)
f_0	Fraction of ions which can be eluted (dimensionless)
f_{ext}	Fraction of ions which is slowly bound to the polymer chain (dimensionless)
f_{int}	Fraction of ions which is strongly bound to the polymer chain (dimensionless)
f_{bulk}	Fraction of ions which is free in solution (dimensionless)
f_{state1}	Fraction of ions in the state 1 according to two-state model (dimensionless)
F	Filtration factor (dimensionless)
F_{sat}	Filtration factor at V_{sat} (dimensionless)
g	Ratio of free metal-ions in the bulk of the solution with respect to the amount of ions detectable in the permeate (dimensionless)
g_a	Parameter g as function of association constant (dimensionless)
g_d	Parameter g as function of dissociation constant (dimensionless)
K_B	Boltzmann constant (m^2kg/sK)
K_d	Dissociation constant (dimensionless)
K_m	Adsorption constant of metal-ion on the membrane (dimensionless)
K_{ext}	Dissociation constant between external zone and bulk of solution (dimensionless)
K_{int}	Dissociation constant between internal and external zones (dimensionless)
L_B	Bjerrum length (nm)
N_{bulk}	Number of moles in the bulk of the solution (mmol)
N_m	Number of moles adsorbed on the membrane (mmol)
N_p	Number of moles in the permeate (mmol)
N_{bound}	Number of moles bound the polymer chain (mmol)
r	Molar binding ratio (mmol of M^{n+}/mmol polymer)
R_p	Retention of metal-ions by the polymer (dimensionless)
R_{syst}	Retention of metal-ions by the filtration system (dimensionless)
t	Time (s)
T	Temperature (°C)
V_p	Volume of permeate (mL)
V_c	Volume in the inside cell (mL)
V_{sat}	Volume of saturation during enrichment experiment (mL)
Z	Valence of counterion (dimensionless)

Introduction

A polyelectrolyte (PEL) is a polymer composed of macromolecules in which a substantial portion of the constitutional units contains ionic, ionizable groups, or both [1]. Many biologically important substances exhibit PEL behavior; examples are nucleic acids, globular proteins, and polysaccharides. They are used in separation processes, wastewater treatment, catalysis, medicine, and cosmetics among others. PELs have the ability to chelate or exchange metal-ions. This property facilitates their use to recover and/or to separate metal-ions from aqueous solution, and they have increasingly become an important focus of research in the last few years [2–5]. Thus, a better understanding of PEL solutions and counterion distribution during specific retention processes is important for the polymer technology and science.

Liquid-phase polymer-based retention (LPR) is a membrane-based retention technique that uses water-soluble polymer (WSP) to remove ions from aqueous solution. Different authors frequently use LPR to study polymer–ion interaction under different experimental conditions [6–10]. In LPR, with an adequate selection of the filtration membrane, the ions that interact strongly with the retained WSP's functional groups cannot pass through the filtration membrane due to their combined high molecular weight; in contrast, ions with a weak or null interaction are eluted through it [6, 11, 12]. The binding and elution process are described as a chemical reaction, where a reversible reaction in combination with an irreversible transfer of the metal-ions through the membrane is responsible for ion retention [7–9].

Two methods are usually used in LPR: the *washing method* (ionic strength can (or not) be maintained constant) and the *enrichment method* [6]. In the washing method, a certain amount of polymer and metal-ion solutions with known concentrations are placed in the feed inside an ultrafiltration cell through which a water stream is passed. Different authors have presented the conventional theory and mathematical description for this method [6, 11, 12].

In the enrichment method, the macromolecular solution is placed in a stirred cell, and a metal-ion solution is continuously added from a pressurized reservoir. During the process, permeate is removed at the same rate, maintaining the volume in the feed cell and the polymer concentration constant all the time. When the polymer bonding groups are saturated by their interaction with the metal-ion in the solution, the maximum retention capacity (MRC) of the polymer is achieved and the process cannot continue [6, 13, 14].

Three types of main interactions can be considered according to interacting species: (1) *polymer–metal-ion interaction*, (2) *membrane–metal-ion interaction*, and (3) *polymer–membrane interaction* [15]. If PELs and divalent metal-ion solutions are contacted, the ion distribution in the filtration cell is governed by the polymer–metal-ion interactions and the electrostatic attraction between PEL chains and counterions in solutions can be discussed by *counterion condensation theory* (CCT) [3, 16].

There are several approaches to describe counterion condensation in PEL solutions by cell models. In the first approach, *two-state counterion condensation model* (Oosawa–Manning condensation theory), the counterions are separated into '*free*' and '*condensed*'. Free counterions can explore the solution volume, and the condensed counterions are located within a small volume surrounding the polymer backbone [16].

In this model, fixed charge density (ξ) is characterized in terms of a dimensionless parameter ξ,

$$\xi = \frac{L_B}{b} = \frac{e^2}{4\pi\varepsilon\varepsilon_0 k_B T b} \tag{1}$$

where e is the electron charge, ε is the solvent dielectric constant, ε_0 is the vacuum permittivity, k_B is the Boltzmann constant, T is the temperature, and b is the average backbone separation of unit charges. The Bjerrum length L_B is the required displacement of two-unit charges to match their mutual electrostatic interaction energy to the medium's thermal energy kT ($L_B = 7.13$ at 25 °C in water) [17, 18], even though the two-state approximation for counterion distribution in a PEL solution is an oversimplification of the real situation.

A more rigorous description of counterion distribution can be obtained in the framework of the so-called *Katchalsky's cell model* [3]. To avoid some of the limitations of this cell model and to describe counterion distribution in dilute solutions, Deshkovski–Obukhov–Rubinstein developed a *two-zone model*. In this model, the volume occupied by charged rods is divided into two types of regions. The inner regions are cylindrical zones around the charged rods with the diameter in the order of the length of rods. The outer regions are spherical zones outside the cylindrical regions that extend up to the distance between chains [3, 19]. Since this two-zone model is relatively recent, only theoretical descriptions of the model have been reported, and this model has yet to be compared with experimental results [3, 19].

On the other hand, using Marinsky's Donnan-based concepts, a PEL phase can be assumed in the vicinity of the polyion chain, and ion binding in this system is expressed as the ion exchange of counterions between the PEL phase and the bulk solution phase [20–22]; thus, the distribution equilibrium of mobile ions (counterions and co-ions) between the two phases can be conceptualized as a Donnan's relation.

$$\mathrm{M}^{n+}_{\mathrm{bound}} \rightleftarrows \mathrm{M}^{n+}_{\mathrm{free}} \tag{2}$$

where $\mathrm{M}^{n+}_{\mathrm{bound}}$ and $\mathrm{M}^{n+}_{\mathrm{free}}$ are metal-ions bound to the polymer and free in solution, respectively. Working from this assumption, the interaction between PELs and divalent metal-ions has been studied [23–25].

This article analyzes the distribution of divalent ions and its relation with the retention properties of different sulfonic PEL solutions using the LPR technique and a mathematical description of elution the process based in the two-zone model developed by Deshkovski–Obukhov–Rubinstein and Marinsky's Donnan-based concepts. We also analyze the effect of metal-ion excess on the interpretation of retention profile obtained by the washing method using CCT.

Mathematical description of washing method

A polyion is assumed to be a simple rod with uniformly smeared charge in the continuum dielectric system, and the mobile counterions are treated as finite-sized spheres with a hard-core potential [26].

During LPR by washing method, a metal ion solution is contacted with a WSP in the ultrafiltration cell (at $t = 0$, being $t =$ time); then while the system is operated under steady-state conditions, a volume of solvent enters and an equal volume of solution simultaneously leaves from the cell, maintaining constant the volume in the cell throughout the experiment until the polymer retention, R_p, is achieved (t_f).

At $t = 0$ and $t = t_f$, polymer/metal system can be described by two different approaches considering the specific features of the equilibrium binding of macromolecules with metal ions in solution [27]. In the first, the central species is a metal ion (M) with which a few functional groups of the chain (L) are successively or simultaneously reacted and reactions are assumed to be independent of each other

$$\mathrm{M} + n\mathrm{L} \rightleftarrows \mathrm{ML}_n \tag{3}$$

In another model, the central species is a macromolecule as matrix with a certain number of binding sites. In this case, the formation of complex in solution can be described by sets of equilibria [27], where P is the coil of polymer and N is the maximum number of metal ions capable of binding with one coil, thus

$$\mathrm{PM}_{n+1} + \mathrm{M} \rightleftarrows \mathrm{PM}_n \quad (n = 1, 2, \ldots N) \tag{4}$$

On the other hand, if the non-equilibrium state is considered, this is $0 < t < t_f$, according to CCT, it can be assumed that a fraction of the added metal-ions is distributed around polyelectrolyte chains in the "state 1" (*polymeric domain*) and these are retained by the polymer, while another fraction is distributed in the bulk (state 2) and these are eluted through the membrane into the permeate. Thus, the following mass balances are possible with respect to free ions in the bulk:

$$\left.\begin{array}{l} \text{Case 1: } N_{\mathrm{bulk}}(t) = N_0 - N_m(t) - N_p(t) + N_{\mathrm{bound}}(t) \\ \\ \text{Case 2: } N_{\mathrm{bulk}}(t) = N_0 - N_m(t) - N_p(t) - N_{\mathrm{bound}}(t) \end{array}\right\} \tag{5}$$

where N_{bulk}, N_0, N_m, N_p, and N_{bound} are the mole of metal-ions in the bulk, initially placed in the cell, adsorbed on the membrane, in the permeate and in the polymer domain (being "$+N_{\mathrm{bound}}$" if metal-ions go from polymeric domain to bulk and "$-N_{\mathrm{bound}}$" if metal-ions go from bulk to polymeric domain), respectively.

If the membrane is inert ($N_m = 0$), and considering Eq. 2, it can be written:

$$\left(\frac{K_d - 1}{K_d}\right) V_c \mathrm{d}C_{\mathrm{bulk}} = -V_p \mathrm{d}C_p - C_p \mathrm{d}V_p \mapsto \text{case 1} \tag{6}$$

$$\left(\frac{1 + K_d}{K_d}\right) V_c \mathrm{d}C_{\mathrm{bulk}} = -V_p \mathrm{d}C_p - C_p \mathrm{d}V_p \mapsto \text{case 2} \tag{7}$$

where K_d is the dissociation constant related to polymer–ion equilibrium by applying of Marinsky's Donnan-based concepts, C_{bulk} and C_p are the metal-ion concentration in the bulk and in the permeate with respect to the volume inside the cell (V_c) and inside the permeate (V_p), respectively. A parameter g can be defined by two different expressions:

$$\frac{dC_p}{C_p} = \frac{-g dV_p}{\alpha V_c + g V_p}; \quad g = \begin{cases} g_d = \dfrac{K_d}{K_d - 1} & \text{case 1} \\ g_a = \dfrac{K_d}{1 + K_d} & \text{case2} \end{cases} \tag{8}$$

Solving the equation,

$$C_p = \frac{\alpha V_c C_0}{\alpha V_c + g V_p} \tag{9}$$

where α is a parameter that relates C_p with C_c ($dC_c = \alpha dC_p$) to correct the effect of different dilution factors in the cell and the permeate; and C_0 is the metal-ion concentration detectable in the permeate at $t = 0$ [28].

Materials and methods

Reagents

Commercially available poly(vinyl sulfonic acid) (PVSA, solution 25%, M_w: 250.000 g/mol, Aldrich) and sodium poly(styrene sulfonate) (PSS, M_w: 200.000 g/mol, Aldrich) were used as WSP. Copper and cadmium nitrates (analytical grade from Merck) were used to prepare metal-ion solutions.

Equipment

Retention experiments were carried out in a filtration unit with stirred-cell (Millipore, model 8050) under inert atmosphere (N_2). Figure 1 describes the components of filtration system. Disk-shaped membranes of polyethersulfone (PES) were used in all the experiments (Biomax PBGC; nominal cut-off of 10 kDa; 44.5 mm in diameter; manufactured by Amicon Bioseparations-Millipore Co). The metal-ion concentration in permeate was determined by atomic absorption spectrometry (AAS) through a spectrometer UNICAM Solaar 5M Series.

Experiment by washing method

A detailed description of each experiment is shown in the Table 1. In cases where only one metal-ion was analyzed, 10 mL of polymer solution was contacted with 20 mL of solution of Cu^{2+} or Cd^{2+} for each experiment. To study the effect in the presence of two metal-ions, 10 mL of polymer solution was contacted with 10 mL of solution of Cu^{2+} and 10 mL of solution Cd^{2+} (in the order indicated) for each experiment. Previously, the pH of the respective solutions and washing water in the reservoir were adjusted to 6.0 using 0.1 M HNO_3 and 0.1 M NaOH solutions. The system was operated at 300 kPa of pressure and 200 rpm surface stirring rate. Permeate fractions with a volume of 20 mL were collected, and the metal-ion concentrations were analyzed by flame AAS.

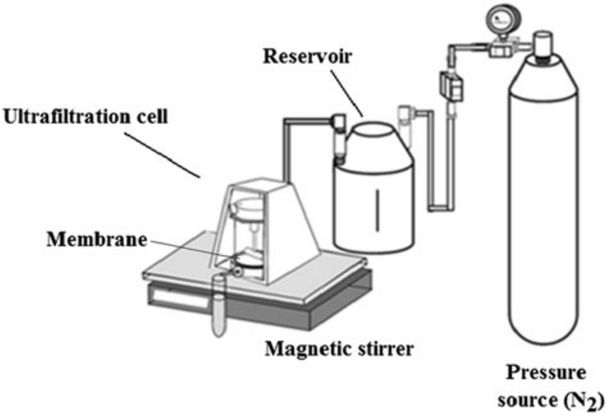

Fig. 1 Filtration system components used during LPR experiments

Table 1 Composition of the filtration experiments carried out by washing method

Polymer	*P* (mmol/L)	[Cu^{2+}] (mmol/L)	[Cd^{2+}] (mmol/L)	V_c (mL)
PVSA	13.3	4.11	0.00	30.0
	13.3	0.00	2.02	30.0
	12.1	1.87	0.92	33.0
PSS	11.4	3.52	0.00	35.0
	11.8	0.00	1.78	34.0
	11.8	1.81	0.89	34.0

Polymer concentration (*P*) refers to repeat unit, and all concentrations have been corrected taking account the end volume in the filtration cell

Experiment by enrichment method

A detailed description of each experiment is shown in the Table 2. In these experiments, a PEL solution (PVSA and PSS) at pH 6.0 was placed in the inside of the ultrafiltration cell, and a solution of metal-ion nitrates (nitrates of Cu^{2+} and Cd^{2+}) at pH 6.0 was placed into the reservoir; the pH was adjusted by adding HNO_3 and NaOH solutions. An experimental blank was performed before and after each experiment. These blank runs consisted in the filtration of the metal-ion solution under the same experimental conditions but in the absence of polymer. The system was operated at 300 kPa of pressure, using pressurized nitrogen, and at 100 rpm

Table 2 Composition of the filtration experiments carried out by enrichment method

Polymer	*P* (mmol/L)	[Cu^{2+}] (mmol/L)	[Cd^{2+}] (mmol/L)	V_c (mL)
PVSA	40.0	6.16	0.00	20.0
	40.0	0.00	5.69	20.0
PSS	40.0	6.20	0.00	25.0
	40.0	0.00	5.52	30.0

Polymer concentration (*P*) refers to repeat unit, and all concentrations have been corrected taking account the end volume in the filtration cell surface stirring rate. Permeate fractions were collected, and the metal-ion concentrations were analyzed by AAS.

Results and discussion

Washing method: retention profiles

A retention profile shows the changes in the metal-ion retention of the system (R_{syst}) as a function of filtration factor ($F = V_p/V_c$) under specific experimental conditions; this is a common form to describe the results obtained from the washing method in the LPR technique. If the membrane can be considered as an inert component, when R_{syst} is independent of F ($F \rightarrow \infty$), the observed retention value is a consequence of the polymer–metal-ion interaction, and therefore: $R_{syst} = R_p$. Thus, the retention profiles for individual ions indicate that PVSA and PSS show good retention properties for Cu^{2+} and Cd^{2+} under the experimental conditions ($R_p > 80\%$).

Although metal/polymer ratios (μ) in each case were equal with respect to the metal-ions studied ($\mu_{PVSA–Cu} = \mu_{PSS–Cu} = 0.31$ and $\mu_{PVSA–Cd} = \mu_{PSS–Cd} = 0.15$), it can be seen that $R_{p,PSS} > R_{p,PVSA} > 80\%$ in all cases (Fig. 2a). Given that the

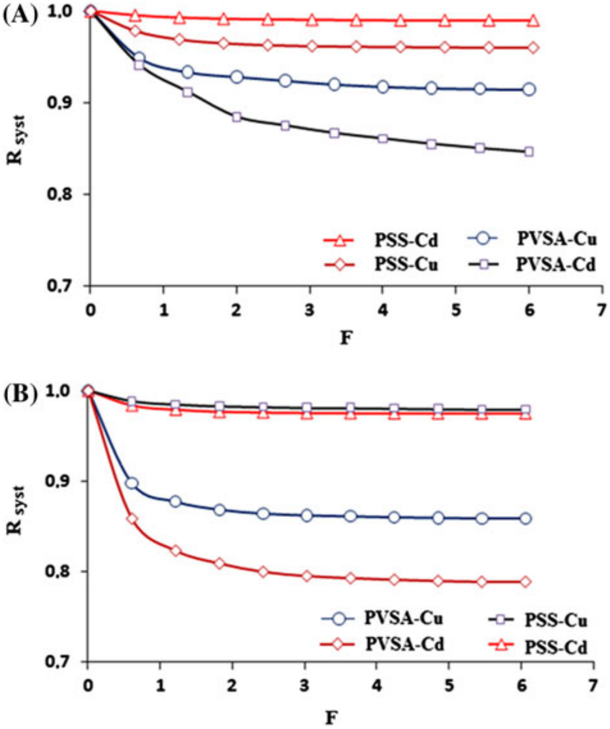

Fig. 2 **a** Retention profile for individual metal-ions (Cu^{2+} and Cd^{2+}) with poly(vinyl sulfonic acid) (PVSA) and poly(styrene sulfonate) (PSS) at pH 6.0. **b** Retention profile for metal-ions (Cu^{2+} and Cd^{2+}) contacted simultaneously with poly(vinyl sulfonic acid) PVSA and PSS at pH 6.0

nature of interaction between metal-ions and sulfonic groups is only electrostatic [29, 30], the obtained results could be explained by a larger negative charge on the sulfonic groups of PSS as a result of resonance effects.

However, μ is the same, and the metal-ion concentration (C_0^*) is different; C_0^* is the amount of reference used to calculate the R_{syst}. Thus, for two PELs with the same retention capability, at an initial concentration higher than the maximum metal-ion concentration that can be retained, the calculated R_{p} value should be smaller at higher concentrations as a result of a higher excess of ions added.

On the other hand, for PVSA, $R_{\mathrm{p,Cu}} > R_{\mathrm{p,Cd}}$ and for PSS $R_{\mathrm{p,Cd}} > R_{\mathrm{p,Cu}}$. Since the hydrated ionic radii of Cu^{2+} (419 pm) are smaller than Cd^{2+} (426 pm) [31], the surface charge density for Cu^{2+} is higher than Cd^{2+}, and therefore it is expected that $R_{\mathrm{p,Cd}} < R_{\mathrm{p,Cu}}$ as consequence of an weaker electrostatic interaction. Since this result is not observed for PSS, other factors (in addition the metal/polymer ratio and electrostatic potential) could be masking the real behavior of polymer–metal-ion interaction in the profile. The effects of polymer and metal-ion concentration have been previously studied and reported for this kind of experiments [29]. Basically, the retention ability is increased by increasing the molecular weight or by decreasing metal/polymer ratio, where this depends on the initial amount of contacted metal-ions with the polymer solution (C_0^*) and on MRC of the polymer.

New experiments contacting simultaneously Cu^{2+} and Cd^{2+} with a single WSP, using a lower ion/polymer ratio but maintaining the same proportion ($\mu_{\mathrm{WSP-Cu}} = 2\ \mu_{\mathrm{WSP-Cd}}$), obtained similar results. In this case, the total amount of metal-ion species was an intermediate amount used in the initial experiments with a single metal-ion. These results can be summarized as: $R_{\mathrm{p,PSS}} > R_{\mathrm{p,PVSA}}$ in all cases, for PVSA $R_{\mathrm{p,Cu}} > R_{\mathrm{p,Cd}}$ and for PSS $R_{\mathrm{p,Cd}} \approx R_{\mathrm{p,Cu}}$ (see Fig. 2b).

In general, it is clear that the information obtained from the retention profile has limited application and that retention behavior in individual ion experiments cannot be used to infer a priori the retention profile behavior for mixtures of ions. In addition, since the form of the curve depends on the metal-ion excess added, the horizontal behavior of retention profile cannot always be obtained from a small number of data.

The concentration profile behavior was obtained from retention data, and Eq. 9 can be used to calculate the value of R_{p} if the horizontal behavior of the elution curve is not been achieved (see Fig. 3). In addition, the total detectable concentration in the permeate (C_0) at $F = 0$ and g were obtained and these are showed in the Table 3. The results indicate that retention profile depends on polymer–metal-ion interaction (which is described by parameter g), the MRC and contacted ratio (which defines if there is an excess of metal-ions with respect to amount of polymer used), and the volume of solution in the inside of the cell, although other factors (e.g., pH and ionic strength of solution) are not considered by the model.

Enrichment method

At the beginning of LPR by enrichment, a very strong interaction between the PELs and metal-ions in solution takes place. In these experiments, μ is continuously

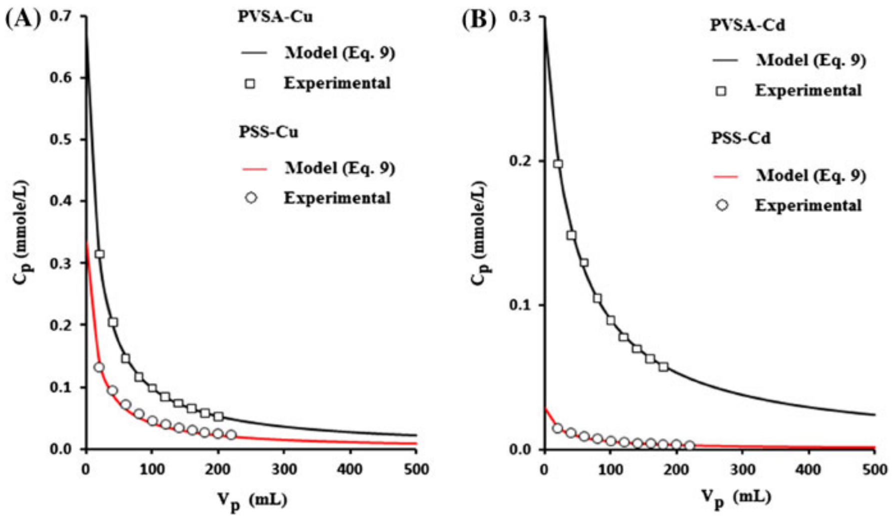

Fig. 3 Concentration profile for metal-ions (**a** Cu^{2+} and **b** Cd^{2+}) contacted simultaneously with poly(vinyl sulfonic acid) (PVSA) and poly(styrene sulfonate) (PSS) at pH 6.0 obtained by Eq. 9

Table 3 Parameters obtained by Eq. 9 for each experiment by washing method

Polymer–metal system	$g(\alpha C_0)^{-1}$	C_0^{-1}	g	R_p (%)	Coefficient correlation
PVSA–Cu^{2+}	2.603	1.494	0.61	83.7	0.9997
PVSA–Cd^{2+}	2.603	3.780	0.24	87.0	0.9986
PVSA–Cu^{2+} (Cd^{2+})	2.372	1.581	0.63	73.8	0.9977
PVSA–Cd^{2+} (Cu^{2+})	4.834	1.617	0.79	66.1	0.9999
PSS–Cu^{2+}	6.229	2.984	0.97	90.5	0.9989
PSS–Cd^{2+}	4.916	3.823	0.57	98.5	0.9987
PSS–Cu^{2+} (Cd^{2+})	23.948	15.257	0.67	96.5	0.9995
PSS–Cd^{2+} (Cu^{2+})	40.394	12.353	0.79	91.2	0.9994

increased, increasing binding molar ratio (r, mole of metal-ions retained by the polymer per mole of polymer used) as a function of F. Figure 4 presents the respective enrichment curves for the systems studied. V_{sat} corresponds to the inflexion point in the enrichment curve, and it can be determined by different methods. In our case, using experimental data, the changes in C_p were calculated and plotted as a function of V_p; Thus, from the critical points in the resulting curves, the V_{sat} was obtained for each case, and the MRCs were calculated.

The MRCs obtained were: 0.30 and 0.21 for Cu^{2+} and 0.15 and 0.26 for Cd^{2+} by PVSA and PSS, respectively. Thus, the following order was established for MRC with respect to V_{sat}: PVSA–Cu > PSS–Cd > PSS–Cu > PVSA–Cd.

During the enrichment method, V_c is strongly relevant because when a fraction of metal-ion solution enters into the cell from reservoir, it is diluted in the V_c, decreasing the effective concentration of ions that interact with the polymer chains.

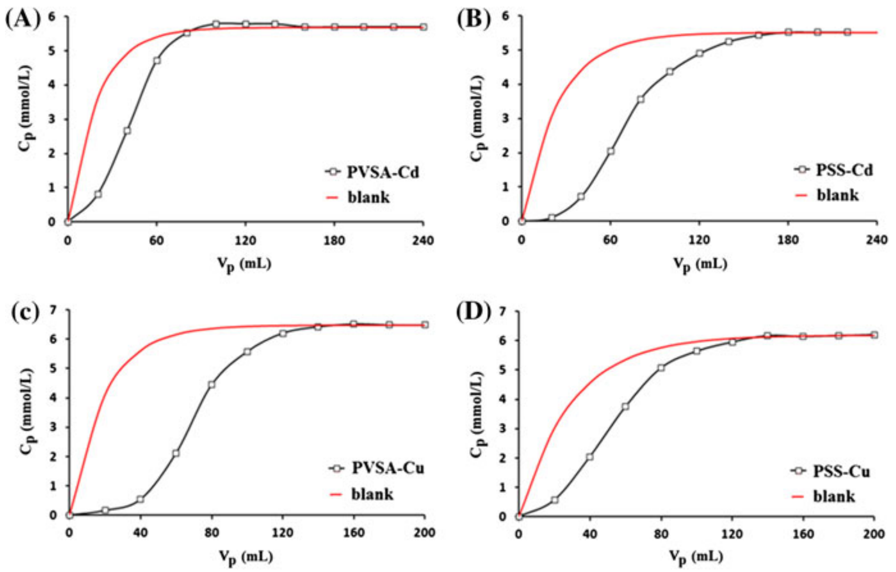

Fig. 4 Enrichment curves for: **a** PVSA–Cd, **b** PSS–Cd, **c** PVSA–Cu, and **d** PSS–Cu

A lower metal-ion concentration results in a decrease of μ and V_p, while the same remaining concentrations of metal-ions in the bulk will be also lower, and consequently V_{sat} appears displaced to the right. In the same system, a higher V_{sat} is related to higher C_p, which is related to a lower concentration of metal-ions bound to the WSP. However, this decrease is offset by a larger V_{sat}, and consequently the effect of V_c on MRC is not obvious. Therefore, the MRC values obtained in different experiments must be carefully compared, and the possible effects of V_c on V_{sat} should be corrected.

Retention properties and counterion distribution models

Since R_p is the fraction of metal-ions that cannot be eluted, it can be considered to be equivalent to the metal-ions fraction that is distributed in the polymeric domain (θ), i.e., this is the metal-ion fraction distributed in "state 1" (f_{state1}) according to the Manning model or the one distributed in the "internal zone" (f_{int}) according to the two-zone model. In either case, since the amount of metal-ions experimentally distributed around the polymeric chain does not depend on the model used, it is expected that $\theta = f_{\text{state1}} = f_{int}$; Therefore, from the retention profile, it is established that

$$\theta = \lim_{F \to \infty} \left(R_{\text{syst}}\right) = R_p \tag{10}$$

On the other hand, C_0 and g do depend on the counterion distribution model used. Thus, with the Manning model, metal-ions can be only distributed in two states: as either "state 1" metal-ions that are retained during filtration or as "state 2"

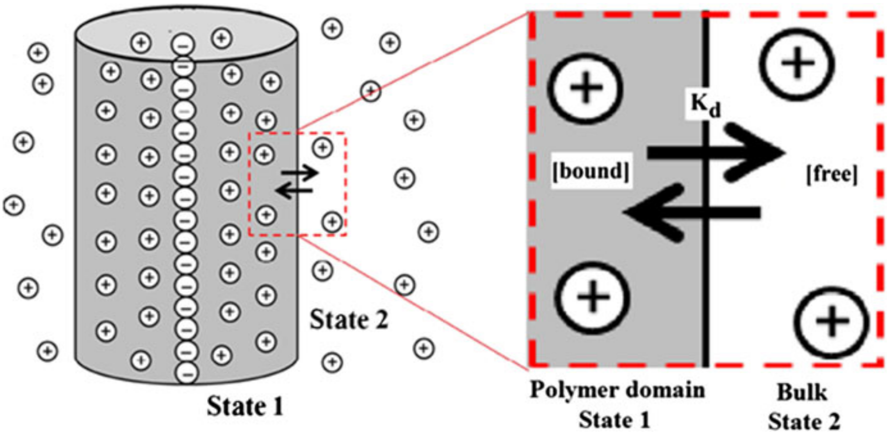

Fig. 5 Representation of two-state model and Marinsky's Donnan equilibrium for the interpretation of LPR experiment by washing method

metal-ions free in solution that are eluted, thus resolving metal-ion distribution from R_p. Still, the Manning model cannot explain the changes in curve concavity since the curves obtained from the enrichment experiments suggest that a metal-ion fraction is strongly bound ($C_p \approx 0$) and another is weakly bound to the polymer chain ($C_p > 0$, concave upward),. Furthermore, another fraction in excess is distributed in the bulk of the solution (concave downward). These weakly and freely distributed ions should also be detected in the permeate during a washing experiment.

Based in Manning's theory and Marinsky's Donnan-based concepts, a chemical equilibrium between condensed ions in the state 1 and uncondensed ions in the state 2 is commonly assumed (see Fig. 5) [7].

With this improved model, a part of metal-ions in the state 1 can dissociated from the polymeric domain into the bulk and detected in the permeate. Theoretically, since g is given by g_a and it is clear from Eq. 8 that g_a is the counterion fraction in the state 2 ($g_a = f_0 = C_0/C_0^*$), R_p should therefore be equal to "$1 - g_a$" for values of $g < 1$. However, LPR experiments indicate that $R_p \neq 1 - g_a$ ($1 - g_a = 0.39$ and 0.76 for PVSA–Cu and PVSA–Cd, respectively; and 0.12 and 0.46 for PSS–Cu^{2+} and PSS–Cd^{2+}, respectively).

On the other hand, according to the two-zone model, two Donnan equilibria can be defined and these can be characterized by an internal constant (K_{int} = [external zone]/[internal zone]) and by an external constant (K_{ext} = [bulk]/[internal zone]). The internal zone is the polymeric domain which is assumed to be a rod-like polyion, and the ions in this zone interact strongly with the polymer; the external zone is a spherical zone around the internal zone, the ions in this zone interact weakly with the polyion by residual charge; if an excess of ions are present, this excess is distributed in the bulk (see Fig. 6).

Applying Eq. 9 and by considering of two-zone model, metal-ion distribution (Ω) during LPR experiments can be determined by

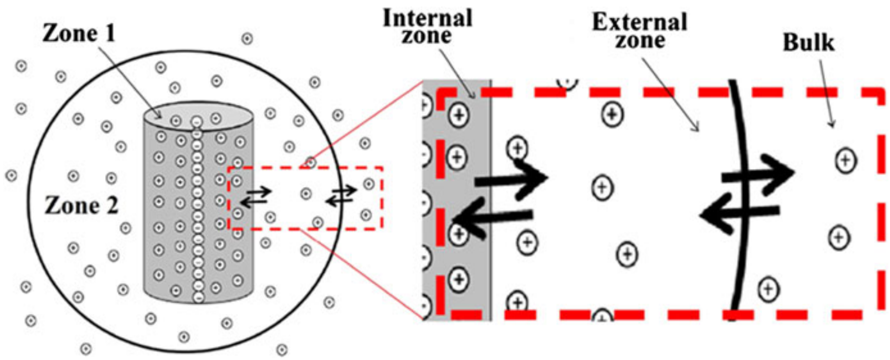

Fig. 6 Representation of two-zone model and Marinsky's Donnan equilibria for the interpretation of LPR experiment data by washing method

$$\Omega(g_a, f_0) = \begin{cases} f_{\mathrm{bulk}} = g_a \cdot f_0 \\ f_{\mathrm{int}} = 1 - f_0 \\ f_{\mathrm{ext}} = (1 - g_a) \cdot f_0 \end{cases} ;\ being \quad g_a = \frac{g_d}{2g_d - 1} \tag{11}$$

where the subscripts "int", "ext," and "bulk" indicate the internal, external, and free in solution fractions around PEL chains.

Under this treatment, f_0 is the metal-ion fraction that can be eluted, and therefore it is measured in the permeate; $C_0^* = C_{\mathrm{int}} + C_{\mathrm{ext}} + C_{\mathrm{bulk}}$, $C_0 = C_{\mathrm{ext}} + C_{\mathrm{bulk}}$, and g_a is an experimental parameter, which cannot be directly associated to R_p, that can be defined as *the amount of ions in excess or free in the bulk of the solution with respect to the amount of ions detectable in the permeate*. This is,

$$g_a = \frac{C_{\mathrm{bulk}}}{C_{\mathrm{bulk}} + C_{\mathrm{ext}}} \tag{12}$$

Note that the two-state and two-zone models converge when the amount of metal-ions in the external zone is negligible, i.e., when the internal zone is in a condition of electroneutrality. In this case, the condensed ions are distributed only in the internal zone, and uncondensed ions are freely distributed in the bulk.

By applying Eq. 11, metal-ion distributions previous to the elution process during washing experiments were obtained (see Table 4). From values of f_{int} for individual ions with each polymer, r can be calculated. If the charge number is considered to be independent of the nature of ion (in the washing method), it is observed that total charges in the end experiments corresponds to an intermediate value in an approximately linear tendency with respect to the first experiments. This result suggests that total saturation of the internal zone was not achieved since an increase in added charge was associated to an increase of r.

According to the above results, there is no a significant difference between retention effectiveness of Cu^{2+} or Cd^{2+} by PVSA and PSS at pH 6.0 under the experimental conditions evaluated, although a small difference in the values of r_{PSS} and r_{PVSA} for the same ions suggests that the polymer–ion interaction between PSS–M^{n+} is more favorable than that between PVSA–M^{n+}.

Table 4 Distribution of metal-ion according to Eq. 11 for each studied systems

Polymer-metal system	f_{int}	f_{ext}	f_{bulk}	r
PVSA–Cu^{2+}	0.84	0.06	0.02	0.26
PVSA–Cd^{2+}	0.87	0.02	0.11	0.13
PVSA–Cu^{2+} (Cd^{2+})	0.82	0.06	0.12	0.13
PVSA–Cd^{2+} (Cu^{2+})	0.81	0.04	0.15	0.06
PSS–Cu^{2+}	0.91	0.01	0.08	0.28
PSS–Cd^{2+}	0.98	0.01	0.01	0.15
PSS–Cu^{2+} (Cd^{2+})	0.97	0.01	0.02	0.15
PSS–Cd^{2+} (Cu^{2+})	0.91	0.02	0.07	0.07

Moreover, if the polymer–ion interaction is favorable when a metal-ion solution is contacted with a polymer solution, ions are distributed in the internal zone and a considerable fraction of ions is distributed in the bulk when $\mu >$ MRC. Since the relative amount of ions distributed in the external zone depends on the residual charge, contributing these and "free" ions in the bulk to C_0, then $f_{\mathrm{int}} \approx 1$ if $\mu \approx$ MRC. Our results show that when PSS was used as the WSP, $f_{\mathrm{int}} \approx 1$; therefore, it can be concluded that MRC was not achieved.

Since $f_{\mathrm{int}} < 1$ for PVSA, MRC can be compared with r_{PVSA}. Cu^{2+} obtained $r_{\mathrm{PVSA–Cu}} = 0.27 \approx \mathrm{MRC} = 0.30$ and Cd^{2+} obtained $r_{\mathrm{PVSA–Cd}} = 0.14 \approx \mathrm{MRC} = 0.15$, indicating a concordance between the experimental data and the model generated data for the washing method (under interpretation of two-zone model) and enrichment experiments.

From the above results, it is concluded that the enrichment experiments can be best understood using the two-zone model. When $V_p < V_{\mathrm{sat}}$, the ions added to the system displace the initial counterions ("*native*" or "*true*") in the internal zone of PEL molecules. Since this displacement can be associated to K_D, a fraction of ions is therefore present in the bulk and these can be measured in the permeate. C_0 is possible due to competition with water molecules and the anions of the salt added (NO_3^-) by metal-ions or functional groups of the PEL in the case of water molecules. With the increase of ions in the cell, the concentration increases in the external zone and in the bulk; therefore, the enrichment curve form is ascendant. If $V_p = V_{\mathrm{sat}}$, MRC has been achieved and the curve's form changes its concavity (from concave upwards to concave downwards); if $V_p > V_{\mathrm{sat}}$, the added ions only contribute significantly to increase f_{bulk} and the curve's form is ascendant from the inflexion point to the point where the metal-ion concentration is achieved in the reservoir.

Conclusions

The mathematical description of the LPR technique by washing method was evaluated and interpreted from the perspective of the two-zone model. Three regions around the PEL chain can be described: an internal zone where ions interact strongly with the polymer, an external zone where weakly interacting ions are distributed, and the bulk of solution where the polymer–metal interaction is negligible but ions can be present. With only limited experimental data, this model can reproduce the retention profile and can be used to calculate the distribution of ions in the different regions considered.

One limitation, in the case of the washing method, is that the information obtained in retention experiments for individual ions cannot be used to infer the retention profile behavior for mixtures of ions. Important factors to consider are the excess of ions added and the order of addition if several ions are contacted with the polymer.

A positive aspect of this model is that when washing experiments are carried out under saturation conditions and $r = \mathrm{MRC}$ at V_{sat}, the results of different LPR methods can be related, and enrichment curves by counter ions distribution models of PEL solutions can be interconnected with distribution information obtained from washing method. Furthermore, the above results confirm that washing and enrichment methods used in LPR experiments can be understood using the two-zone model.

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