# Competitive association of cations with poly(sodium 4-styrenesulfonate) (PSS) and heavy metal removal from water by PSS-assisted ultrafiltration

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**Abstract:** Complexing metal cations with water-soluble nano-sized ionic polyelectrolytes, combined with a separation process such as ultrafiltration (UF), is a potential strategy to remove or recover ionic heavy metals from water or wastewater. However, competition from naturally occurring cations (e.g., $Na^+$, $K^+$, $Ca^{2+}$ and $Mg^{2+}$) may adversely influence target cation removal. To investigate this competition effect, the affinities of both common aqueous cations commonly found in natural surface waters, groundwaters or wastewaters and toxic cationic metals for a typical, commercially available anionic polyelectrolyte, poly(sodium 4-styrenesulfonate) (PSS), were evaluated using a simple ion exchange model and a binary-system ultrafiltration process. Selectivity of these cations for PSS complexation decreased in the order $Ba^{2+} > Pb^{2+} > Sr^{2+} > Ca^{2+} > Cu^{2+} > Co^{2+} > Ni^{2+} > Mg^{2+} > H^+ > K^+ > Na^+ > Li^+$. For cations with same valence, their affinity for PSS is proportionally related to their ionic radii. Competitive interactions among different cations complexing with PSS were also investigated in a multi-ion experimental system and the results were compared with estimates obtained using a simple model based on binary-system selectivity coefficients and mass balances. The cation distribution observed in the experimental multi-ion system was consistent with the model calculations. Experimental results also indicate the model can be applied to predict heavy metal ($Cu^{2+}$ and $Pb^{2+}$) removal by PSS-assisted UF in a competitive multi-cation water environment. Greater removal of heavy metals was observed at higher ratios of PSS molecular weight to membrane molecular weight cut-off (MW/MWCO).

**Keywords:** Ultrafiltration; Selectivity coefficient; Polyelectrolyte; Heavy metal removal; Ion exchange.

## 1. Introduction

Ionic heavy metal contaminants in water such as lead, copper, cobalt and nickel can pose a severe threat to human health and the environment, even at low concentrations[1, 2], and can be difficult to remove from water in both natural and engineered environments[3]. A wide range of treatment technologies, including adsorption[4, 5], ion exchange[6, 7], precipitation[8], coagulation[9], electrochemical treatment[10], and membrane separation[11] have been used for heavy metal removal. Recently, separation processes based on ultrafiltration (UF) combined with nano-sized materials, including certain ionic polymers[12-15], surfactant micelles[16-18] and nanoparticles[19, 20], have been shown to offer a promising technological approach to remove these pollutants, and to recover valuable elements from water and wastewater. Association of ionic heavy metals with the added nano-materials through electrostatic interaction, chelation, or ion exchange, incorporates the metal ions into larger compounds. Ultrafiltration (UF) or similar separation processes can then be used to reject these nano-materials, simultaneously removing the complexed heavy metals[16].

Nano-sized water-soluble polyelectrolytes, polymers with repeated ionizable functional groups, have been used widely as scale inhibitors in oil production[21, 22], nanoparticle templates in material synthesis[23, 24], functional membrane and adsorbent modifiers[25, 26], and flocculants in water treatment[27, 28]. These polyelectrolytes also have been considered as potential nano-sized ion exchangers or adsorbents to facilitate removal of ionic pollutants from water and wastewater during membrane separation[15, 29-31]. High charge density on the polyelectrolytes generates a high electrostatic potential, which attracts counterions. The resulting polyelectrolyte-ion complex has a sufficiently high molecular weight to be easily eliminated by membrane filtration.

Previous studies examining removal of heavy metals with water soluble polyelectrolytes in membrane separation processes have mostly focused on single species heavy metal removal under varying operating conditions (e.g., pH, operating pressure, heavy metal concentrations, or polymer concentrations)[32, 33], ignoring competition from naturally occurring cations. However, the presence of alkali metals (e.g., $Na^+$ and $K^+$) and alkali earth metals (e.g., $Mg^{2+}$, $Ca^{2+}$, $Sr^{2+}$, and $Ba^{2+}$) in surface waters, groundwaters, and wastewaters can adversely influence the removal of target cations. Models[34, 35] have been developed for ion binding by water-soluble polymers, and cation exchange models for heavy metal removal by some ion-exchangers have also considered cation competition[36, 37]. However, studies focusing on competitive binding of cations by polyelectrolytes in complex ionic mixtures are still relatively sparse. Understanding how competition with naturally occurring cations will impact the complexation of heavy metal cations with anionic polyelectrolytes, and their subsequent removal by membrane filtration, is critical for evaluating and effectively applying polymer-assisted UF processes for heavy metal removal.

In this study, poly(sodium 4-styrenesulfonate) (PSS), a typical, commercially available anionic polyelectrolyte with sulfonate functional groups, was used as the nano-sized material in a PSS-assisted UF process. For modeling purposes, PSS can be treated as a cation exchanger. Selectivity coefficients for binding of different cations to PSS were determined using experimental data from binary PSS/UF systems and a simple model that considers the PSS as a pseudo-solid phase ion exchange material. A model was developed to predict cation distribution between the aqueous and the pseudo-solid (polymer) phases during UF separation in the presence of common aqueous-phase cations and selected heavy metals ($H^+$, $Li^+$, $Na^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$, $Sr^{2+}$, $Ba^{2+}$, $Pb^{2+}$, $Cu^{2+}$, $Ni^{2+}$, and $Co^{2+}$), based on competitive interactions between these cations in binding to PSS polymers and mass balances. This model was then used to predict heavy metal ($Cu^{2+}$ and $Pb^{2+}$) removal by PSS-assisted UF in waters of varying composition.

## 2. Materials and Methods

### 2.1 Materials

Three PSS polyelectrolytes with different molecular weights (MW), ~200 kDa (as 20 wt% in $H_2O$), ~70 kDa (powder) and ~1000 kDa (30 wt% in $H_2O$), were purchased from Sigma Aldrich, USA. Target cations used in these experiments included $Na^+$, $K^+$, $Li^+$, $H^+$, $Mg^{2+}$, $Ca^{2+}$, $Sr^{2+}$, $Ba^{2+}$, $Cu^{2+}$, $Pb^{2+}$, $Co^{2+}$, and $Ni^{2+}$. All cation solutions were prepared from their chloride salts (HCl for $H^+$), except for $Cu^{2+}$ and $Pb^{2+}$, which were prepared from $CuSO_4$ and $Pb(CH_3COO)_2$, respectively. All salts were ACS reagent grade and reagent water (18.2 MΩ/cm water prepared using a Milli-Q Direct 8 system) was used to prepare all aqueous solutions and for all experiments.

To determine selectivity coefficients, PSS was purified using dialysis to eliminate small molecules and oligomers that might otherwise have affected the test results[38]. The dialysis membranes, supplied by Biosharp (Hefei, China), had a molecular weight cut-off (MWCO) of 12,000 to 14,000 Da, and a diameter of 36 mm. Thirty g/L solutions of PSS (200 kDa and 70 kDa, 30 mL) were sealed in dialysis bags and placed in 200 mL water, dialyzing for 24 h to remove most of the low MW PSS. After dialysis, PSS in the permeate during the UF process (10,000 Da) was less than 0.03 mM (< 1 mg/L sulfur), based on elemental sulfur analysis of the permeate solution using inductively coupled plasma-optical emission spectrometry (ICP-OES, PerkinElmer, Optima 2000 DV).

### 2.2 Ultrafiltration

All experiments were conducted at room temperature with a total volume of 100 mL for each experiment. The cations and PSS were contacted for 0.5 hours before filtration. A dead-end ultrafiltration cell (Amicon, model 8200, USA) with a stirrer and cellulose membranes (Diaflo, USA) with a diameter of 62 mm and effective area of 28.7 cm$^2$ were used to separate the aqueous phase cations from those associated with the polymer phase (i.e., PSS). Membranes used in these experiments had MWCOs of 10,000 Da and 1,000 Da (10 kDa and 1 kDa). A filtration pressure of 30 psi was used for the 10 kDa membranes and 50 psi for the 1 kDa membranes, using nitrogen gas as the source of pressure. Subsamples collected before filtration and the first 10% volume of permeate (10 mL) were analyzed to determine cation concentrations.

### 2.3 Selectivity Coefficient Determination

The high charge density of polyelectrolytes results in a high electrostatic potential that attracts ions of the opposite charge[39]. A previous study has reported that PSS behaves like a strong-acid cation exchanger[38]. A simple ion exchange model, based on one used to describe ion exchange with surfactant micelles[16], was used to model PSS-cation interactions. This approach has been widely used to describe ion exchange on resins[40, 41], ionic membranes[42], nano-sized materials such as surfactant micelles and nanoparticles[19, 43], and natural absorbents[44]. The basic principle of cation association with PSS can be described by **equations 1 and 2**. A fraction of the initial counterion, $Na^+$, has a close association with the PSS functional groups, while the extent of PSS ionization can be determined by measuring free $Na^+$ in solution. When other cations are added into the solution, they also form associations with PSS, exchanging some portions of the PSS-associated $Na^+$ into the bulk solution until equilibrium is reached (**equation 3**). The selectivity coefficient ($K_{sel}$) of a given cation towards PSS with respect to $Na^+$ is defined as in **equation 4**. (The activity coefficient can be neglected if the aqueous concentration of ions is sufficiently dilute, and the PSS phase is considered an ideal phase.)

Measurement of the total and aqueous concentrations of sodium and the exchanging cation in the permeate allow calculation of $K_{sel}$ values using **equations 5** through **7**.

$$PSSNa \leftrightarrow PSS^{-} + Na^{+} \tag{1}$$

$$M^{n+} + nPSS^{-} \leftrightarrow PSS_{n}M \tag{2}$$

$$nPSSNa + M^{n+} \leftrightarrow PSS_{n}M + nNa^{+} \tag{3}$$

$$K_{sel} = \frac{[Na^{+}]_{aq}^{n}[M^{n+}]_{P}}{[Na^{+}]_{P}^{n}[M^{n+}]_{aq}} \tag{4}$$

$$\frac{[M^{n+}]_{P}}{[Na^{+}]_{P}^{n}} = \frac{[M^{n+}]_{aq}}{[Na^{+}]_{aq}^{n}} K_{sel} \tag{5}$$

$$[M^{n+}]_{P} = ([M^{n+}]_{total} - [M^{n+}]_{aq})/Q \tag{6}$$

$$Q = \sum n([M_{i}^{n+}]_{total} - [M_{i}^{n+}]_{aq}) \tag{7}$$

In these equations, $M^{n+}$ refers to target cations with charge n; $[M]_{total}$, $[M]_{aq}$ and $[M]_{P}$ represent the total concentration of cations (mole/L) present, the concentration of cations in the permeate (aqueous phase, mole/L), and the concentration of cations in the polymer phase (mole fraction of cations, mole/mole exchange sites of PSS), respectively; and Q is the total effective concentration of exchange sites on PSS (mole/L). For binary systems with purified PSS, Q can be calculated directly from aqueous phase measurements.

In the selectivity coefficient experiments, the total concentration of target cation was 1 mM, and the concentration of purified PSS (based on monomers) ranged from 1.8 to 4 mM. NaCl was added into the solution to achieve the same number of equivalent charges (i.e., for monovalent cations, [NaCl] = 1 mM; for divalent cations, [NaCl] = 2 mM). The pH of the test solution was adjusted to 5.5 by adding HCl to prevent any precipitation, and aqueous phase concentrations were measured following UF separation. Three replicates were carried out for each selectivity coefficient experiment, and the average values were reported. During ultrafiltration, some portions of free cations in the solution are also rejected due to the charge balance across the membrane. It is assumed that these rejected free cations do not strongly influence the ion exchange process[16].

### 2.4 Cation Measurements

Aqueous samples collected before filtration and from the permeate were analyzed for concentrations of $Na^+$ and target cation(s). Samples were diluted tenfold with 2% (volume) $HNO_3$ (Fisher Scientific PN A509) prior to analysis. Concentrations of all elements were determined using inductively coupled plasma-optical emission spectrometry (ICP-OES, PerkinElmer, Optima 2000 DV). Standard wavelengths for each cation and operating conditions were used[45]. Triplicate analyses were performed for each sample by ICP, and measurements accepted if all results were within 10% of the averaged value. Cation concentrations in the polymer phase were then determined using **equations 6** and **7**.

### 2.5 Distribution of Cations in Different Phases

The affinity of each cation for PSS in a multi-ion environment can be determined from the distribution of that cation between the aqueous and the polymer phases. The total normality of the bulk aqueous phase (C, eq/L) is defined by **equation 8**, and the equivalent fractions of cations in aqueous phase (x) and polymer phase (y) are represented by **equations 9 and 10**. “Ion exchange isotherms” can be determined by plotting *y* vs *x* to compare affinities of different cations to PSS.

$$C = \sum n[M_i^{n+}]_{aq} \qquad (8)$$

$$x = \frac{n[M_i^{n+}]_{aq}}{C} = \text{equivalent fraction of cation } M_i \text{ in solution} \qquad (9)$$

$$y = \frac{n[M_i^{n+}]_P}{Q} = \text{equivalent fraction of cation } M_i \text{ in the polymer phase} \qquad (10)$$

### 2.6 Model Development for Ionic Mixtures and Verification

A model (**Table 1**) was developed to calculate the concentrations of cations in the aqueous and the polymer phases, assuming that the selectivity coefficients of cations measured from binary systems were valid in a multi-cation system[16, 36]. The model equations were all solved by Microsoft Excel, using the built-in minimization algorithm “Solver” to iteratively minimize the sum of squared errors by adjusting initial guesses of unknown values[16]. A detailed sample calculation is provided in the **Supporting Information**.

To verify the model, mixture solutions with 1 mM $Mg^{2+}$, $Ca^{2+}$, $Sr^{2+}$, and $Cu^{2+}$, and 2 mM $Na^+$ and $K^+$ were prepared. Purified PSS was added and the solution was adjusted to pH 5.5, reacted and separated as described above for the selectivity experiments. PSS concentrations in these experiments ranged from 5 to 15 mM.

**Table 1.** Model equations for ionic mixture

| Equations$^\dagger$ |
|---|
| $[Na^+]_{total} = [PSS]_{total} + [Na^+]_0$ |
| $[M_i^{n+}]_{total} = [M_i^{n+}]_{aq} + [M_i^{n+}]_P Q$ |
| $Q = \sum n([M_i^{n+}]_{total} - [M_i^{n+}]_{aq}) = [PSS]_{total}$ |
| $K_{sel}{}_{M_i^{n+}}^{Na^+} = \frac{[Na^+]_{aq}^n [M_i^{n+}]_P}{[Na^+]_P^n [M_i^{n+}]_{aq}}$ |
| Where, $M_i$ represents Na, Li, K, H, Mg, Ca, Sr, Ba, Pb, or Cu<br>and $[Na^+]_0$ refers to initial concentration of $Na^+$ in water. |

$^\dagger$Known values: $[PSS]_{total}$, $[Na^+]_0$, $[M_i^{n+}]_{total}$, $K_{sel}$; unknown values: $[Na^+]_{total}$, $[M_i^{n+}]_{aq}$, $[M_i^{n+}]_P$, Q.

## 2.7 Heavy Metal Removal in Multi Cation Waters

Simulated heavy metal polluted water samples containing $Cu^{2+}$ or $Pb^{2+}$ were used to test the application of the speciation model for predicting heavy metal removal. The composition of the simulated water samples is shown in **Table 2**. For each solution, the pH was adjusted by adding either HCl or NaOH, while unpurified PSS was added at concentrations ranging from 0.3 to 6 g/L (i.e., 1.46 to 29.1 mM). The reaction and filtration procedures were the same as those described in Section 2.2.

**Table 2.** Cationic composition of simulated heavy metal polluted waters (pH = 5.5)

| Cations | Concentrations (mg/L) |
|---|---|
| $Na^+$ | 50 |
| $K^+$ | 50 |
| $Mg^{2+}$ | 50 |
| $Ca^{2+}$ | 100 |
| $Cu^{2+}$ or $Pb^{2+}$ | 50 |

The rejection fraction, or the fraction of each cation removed from the permeate solution, *R*, is defined by **equation 11**.

$$R = 1 - \frac{[C]_{permeate}}{[C]_{total}} \tag{11}$$

Here, $[C]_{permeate}$ and $[C]_{total}$ refer to the concentration of heavy metal in the permeate and the initial bulk solution, respectively.

Since an unpurified PSS solution was used in these studies to better represent an actual treatment system, the total number of effective exchange sites must be adjusted to account for smaller PSS molecules and oligomers that pass through the dialysis membrane. For these experiments, Q was calculated from **equation 12**.

$$Q = \alpha[PSS]_{total} \tag{12}$$

In this equation, $[PSS]_{total}$ is the total concentration of PSS in charge equivalents per L, based on an equivalent weight of 206 g/mole. The actual fraction of exchange sites that will be retained by the UF membrane in a PSS-assisted UF system, or $\alpha$, depends on PSS molecular weight distribution, membrane pore size and operating pressure[46], and has a maximum value of 1. Under the conditions of these experiments (200 kDa PSS, 10 kDa UF, and 30 psi operating pressure), the experimental value of $\alpha$ was measured as 0.80 (**Figure S2** in the **Supporting Information).**

## 3. Results and Discussion

### 3.1 Selectivity Coefficients of Cations Towards PSS in Binary Systems

**Figure 1** shows the regression plots used to calculate $K_{sel}$ for monovalent cations. A higher slope indicates a higher affinity for the polymer phase, with values greater than 1 indicating a greater affinity for $H^+$ and $K^+$ to complex with PSS, compared to $Na^+$ (slope = 1), while PSS binds $Li^+$ less strongly than $Na^+$. Overall, selectivity of monovalent cations for PSS decreases in the order $H^+ > K^+ > Na^+ > Li^+$.

**Figure 2** shows the selectivity experiment results for divalent cations (**Figure 2a** for $Mg^{2+}$, $Ca^{2+}$, $Sr^{2+}$, and $Ba^{2+}$, and **Figure 2b** for $Cu^{2+}$ and $Pb^{2+}$). Among the divalent cations, a higher slope indicates a greater affinity for PSS complexation. Overall, all divalent cations have a greater affinity for PSS than the monovalent cations, as shown by a much higher distribution of divalent cations than monovalent cations in the polymer phase in a binary-system (**Figure S3** in the

S**upporting Information**). This is due to their higher charge, which leads to greater electrostatic association between cations and the PSS.

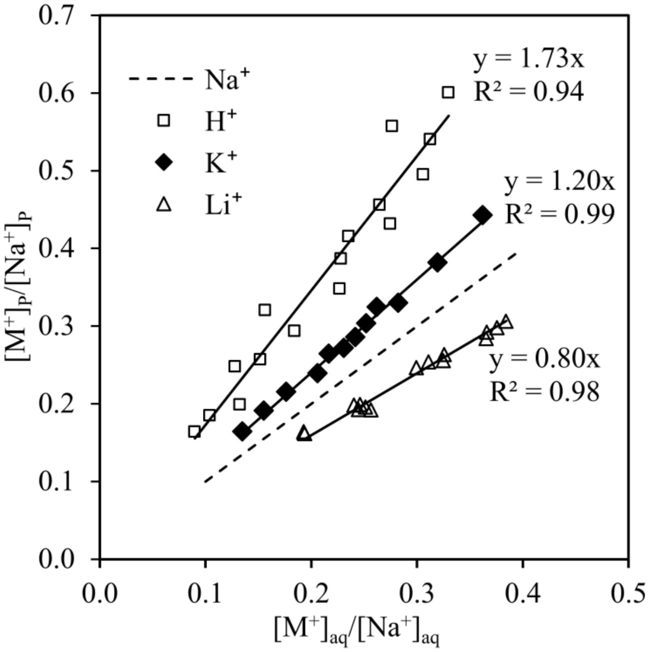

**Figure 1**. Selectivity coefficients for binding of monovalent cations to PSS, relative to $Na^+$

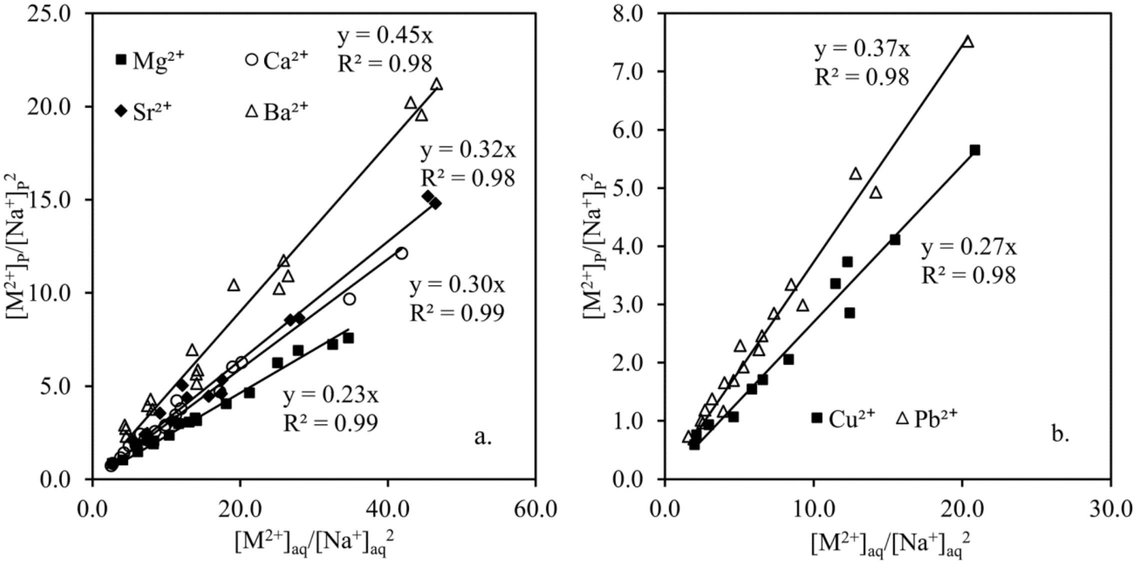

**Figure 2**. Selectivity coefficients for binding of divalent cations to PSS, relative to $Na^+$. a: alkali earth metals; b: cationic heavy metals

**Figure 3** compares the selectivity coefficient measurement for $K^+$ using 200 kDa and 70 kDa PSSs. It can be seen that polymer MW did not affect the affinity of $K^+$ for PSS (no significant difference at 95% confidence, $p = 0.135$). Similar results were obtained with the divalent cation $Ba^{2+}$ (**Figure S4** in the **Supporting Information**). Therefore, cation association with PSS does not appear to depend on polymer size within the apparent MW range tested. This is similar to results from Morlay *et al.*[29] who found similar metal binding properties for poly(acrylic acids) (PAA) of differing molecular weights.

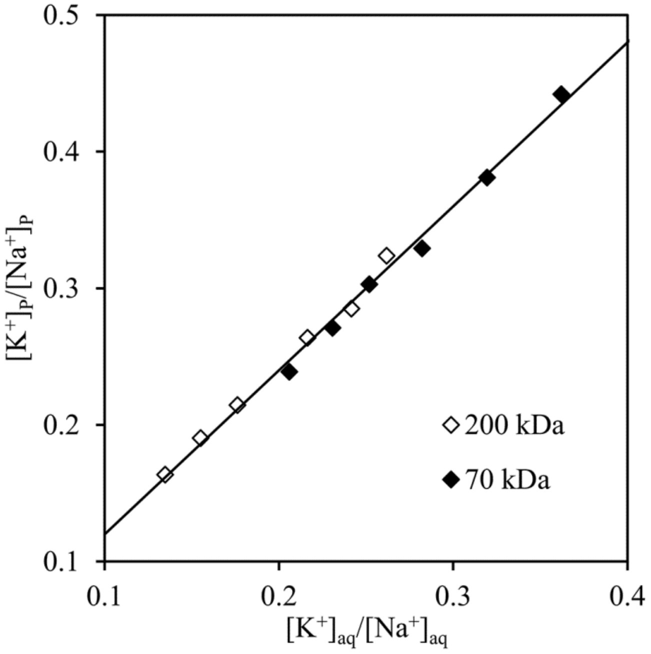

**Figure 3**. $K^+$ selectivity coefficient for PSSs of two different molecular weights

The values of $K_{sel}$ determined for different cations with PSS from single-cation experiments are reported in **Table 3**. $K_{sel}$ values for monovalent cations have an error of < 10% based on analysis of replicate experiments, while values for divalent cations have an error of < 15%. It can be seen from the table that the affinity sequence for different cations to PSS is $Ba^{2+} > Pb^{2+} > Sr^{2+} > Ca^{2+} > Cu^{2+} > Mg^{2+} > H^+ > K^+ > Na^+ > Li^+$. The selectivity order of alkali metals ($K^+ > Na^+ > Li^+$) is the same as that on some titanosilicate adsorbents [47]. The relative affinity of $Pb^{2+}$ and $Cu^{2+}$ to PSS is similar to that reported for sodium dodecyl sulfate (SDS) surfactant micelles[17], a natural macroalga absorbent[36], and a synthesized zeolite[48]. The order observed here is also same as the sequence of ion exchange selectivity on PSS obtained by Li *et al.*[38], of $Mg^{2+}$, $Ca^{2+} >> K^+ > Na^+$, except for $Cu^{2+}$, which they reported as having a higher affinity than $Ca^{2+}$. It is somewhat contrary to the research on PAA reported on by Sabbagh and Delsanti[39], which found $Cu^{2+} >> Ca^{2+} > Mg^{2+} > Ba^{2+}$, likely due to the considerable difference between the active functional groups of the two polymers (PSS: sulfonate group, PAA: carboxylate group).

Based on Pauley's model[49] for predicting cation-exchange equilibria, selectivity is a function of the ionic radius for an outer-sphere ionic complexation. **Figure 4** shows the relationship between $K_{sel}$ and the cation hydrated radii based on data from **Table 3**. Typically, for cations with the same valence, the selectivity coefficients of the cations are proportionally related to their ionic radii, as smaller cations associate with more water molecules[50]. This leads to a larger hydrated radius, which in turn reduces the electrostatic interaction between the cation and PSS. A similar trend for the affinity of anions for cationic ion exchange materials (surfactant micelles) was observed for a similar UF separation process[16]. Although the hydrated radii of $Ca^{2+}$ and $Sr^{2+}$ are the same and the hydrated radius of $Pb^{2+}$ is larger than that of $Ba^{2+}$ based on Nightingale Jr's report[51], the water shells of $Sr^{2+}$ and $Ba^{2+}$ are smaller than those of $Ca^{2+}$ and $Pb^{2+}$ respectively, leading to their higher affinities for PSS.

Precipitates were observed to form when the concentrations of $Ba^{2+}$ and $Pb^{2+}$ were high, due to their strong affinity for PSS. No precipitate was observed for the other cations. Previous studies also observed Ba forming a precipitate with PSS (Pb was not reported)[39, 52].

**Table 3**. Selectivity coefficients of cations and their ionic radii

| Cations | $K_{sel}$† | $R^2$ | ionic radii[51, 53] (nm)‡ | Width of hydration shell [53] (nm) | hydrated radii[51] (nm) |
|---|---|---|---|---|---|
| $Li^+$ | 0.80 | 0.98 | 0.060<br>0.069 | 0.172 | 0.382 |
| $Na^+$ | 1 | - | 0.095<br>0.102 | 0.116 | 0.358 |
| $K^+$ | 1.20 | 0.99 | 0.133<br>0.138 | 0.074 | 0.331 |
| $H^+$ | 1.73 | 0.94 | 0.028<br>0.030 | 0.300 | 0.282 |
| $Mg^{2+}$ | 0.23 | 0.99 | 0.065<br>0.072 | 0.227 | 0.428 |
| $Cu^{2+}$ | 0.27 | 0.98 | 0.072<br>0.073 | 0.224 | 0.419 |
| $Ca^{2+}$ | 0.30 | 0.99 | 0.099<br>0.100 | 0.171 | 0.412 |
| $Sr^{2+}$ | 0.32 | 0.98 | 0.113<br>0.113 | 0.150 | 0.412 |
| $Pb^{2+}$ | 0.37 | 0.98 | 0.132<br>0.118 | 0.143 | 0.401 |
| $Ba^{2+}$ | 0.45 | 0.98 | 0.135<br>0.136 | 0.118 | 0.404 |
| $Co^{2+}$ | - | - | 0.072 | 0.220 | 0.423 |

| | | | | | |
|---|---|---|---|---|---|
| | | | 0.075 | | |
| $Ni^{2+}$ | - | - | 0.070<br>0.069 | 0.233 | 0.404 |

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[†] For monovalent cations, $K_{sel}$ is unitless; for divalent cations, the units are mole/L.

[‡]The upper value for each cation is from [51], and the lower one is from [53].

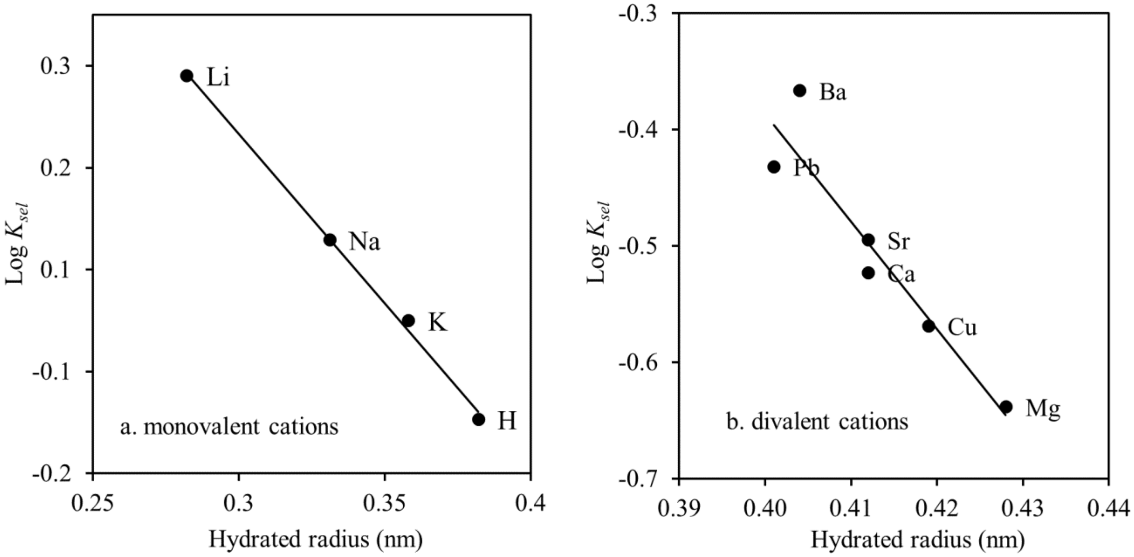

**Figure 4**. Relationship between cation selectivity coefficients and cationic radii

### 3.2 Competitive Association of Cations with PSS in Multi-Cation Systems

The selectivity coefficients of cations obtained from binary systems during UF separation indicate the affinity order of different cations to PSS. However, competition from other cations in a multi-cation system may change the affinity of cations for PSS. The distribution of different cations between the aqueous and the polymer phases (defined by **equations 9** and **10**) was used to compare their affinity for PSS in a water environment with competing ions. **Figure 5** shows the measured distribution of cations in the aqueous and the polymer phases for a solution with 1 mM $Mg^{2+}$, $Cu^{2+}$, $Ca^{2+}$, and $Sr^{2+}$, 2 mM $Na^+$ and $K^+$, and 5 - 10 mM PSS. The $Mg^{2+}$ distribution data can be taken as an example (**Figure 5a**): when the equivalent fraction of $Mg^{2+}$ in the aqueous phase is 0.10 ($x = 0.10$), its equivalent fraction on PSS is 0.154 ($y = 0.154 > 0.10$), meaning $Mg^{2+}$ has a higher affinity for PSS than it has for water in the presence of these other cations. As can be seen, all four divalent cations associate more strongly with PSS than with water in this condition, and the strength of this affinity follows the same order as that of their selectivity coefficients in a binary system with $Na^+$ ($Sr^{2+} > Ca^{2+} > Cu^{2+} > Mg^{2+}$). Conversely, $Na^+$ (**Figure 5b**) and $K^+$ (not shown in the figure) are associated more weakly with PSS than with the aqueous phase ($x > y$, e.g., for $Na^+$, $x = 0.4$, $y = 0.1$), due to the competition from the divalent cations. **Figure 5c** illustrates the distribution of $Sr^{2+}$, $Pb^{2+}$ and $Ba^{2+}$ (1 mM, respectively, 2mM $Na^+$ and $K^+$, and 3-8 mM PSS) between water and PSS. The affinities also follow the same order as that obtained from binary systems ($Ba^{2+} > Pb^{2+} > Sr^{2+}$).

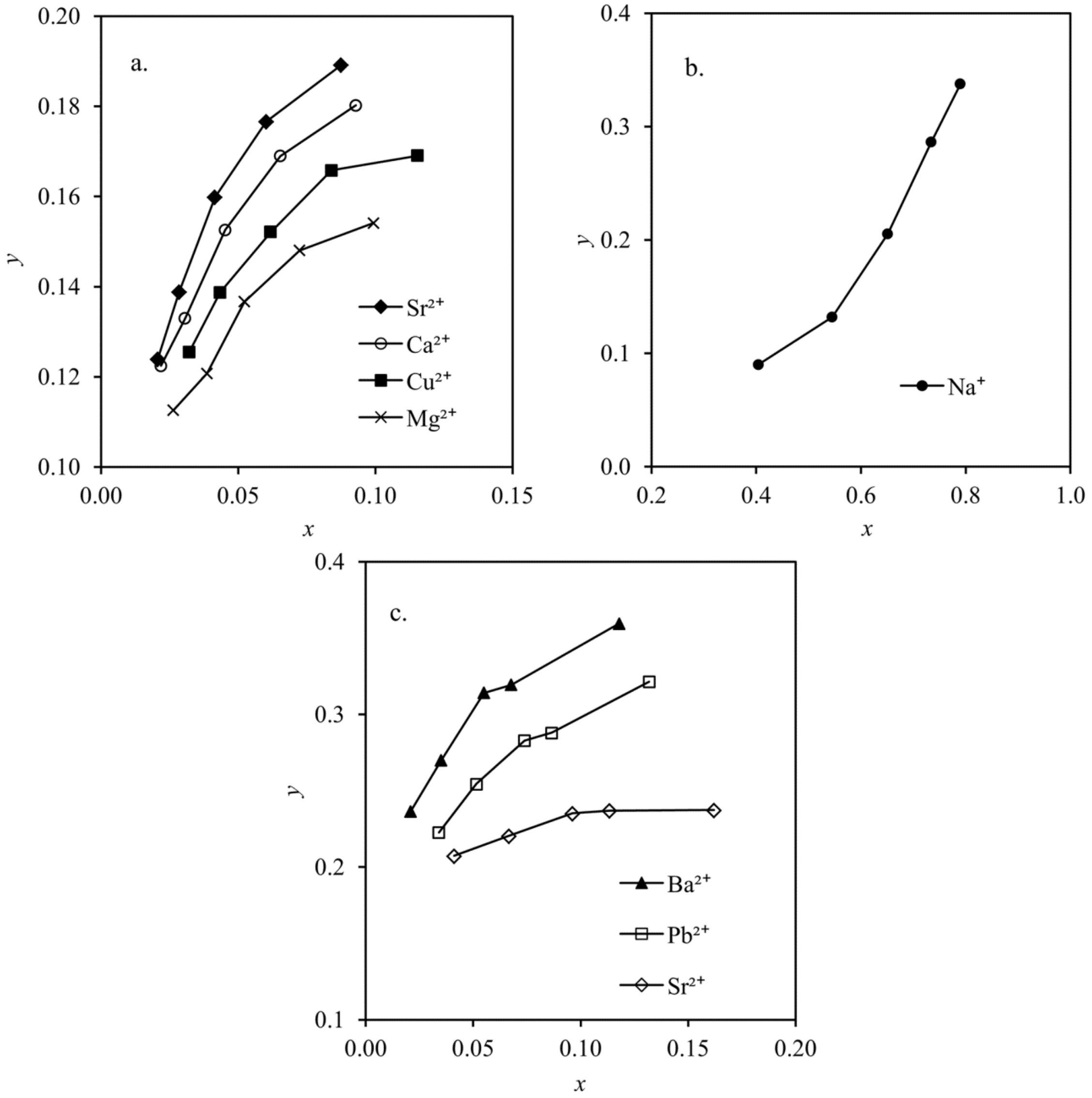

**Figure 5.** Distribution of cations (equivalent fractions) in the aqueous (x) and the polymer phases (y) in multi-cation solutions a: divalent cations in a multi-cation system containing $Mg^{2+}$, $Ca^{2+}$, $Cu^{2+}$, $Sr^{2+}$, $K^+$, and $Na^+$; b: $Na^+$ in the same system as for plot a; c: divalent cations in a multi-cation system containing $Ba^{2+}$, $Pb^{2+}$, $Sr^{2+}$, $K^+$, and $Na^+$.

Because the cation affinity sequence is the same in multi-cation systems as it is in binary systems, and cation selectivity has a proportional relationship with ionic radius, the affinity of other cations in a binary system can be predicted based on their radii. **Table 3** shows that $Co^{2+}$

and $Ni^{2+}$ have similar ionic radii and hydrated radii as $Cu^{2+}$ and $Mg^{2+}$, so similar selectivity for PSS is expected. **Figure 6** shows the measured distributions of divalent cations including $Ca^{2+}$, $Cu^{2+}$, $Co^{2+}$, $Ni^{2+}$, and $Mg^{2+}$ in a multi-cation system (1 mM each, with 5-15 mM PSS). The distribution results indicate that the selectivity coefficients of $Co^{2+}$ and $Ni^{2+}$ are between $Cu^{2+}$ (0.27 mole/L) and $Mg^{2+}$ (0.23 mole/L), and the affinity of PSS for $Co^{2+}$ is slightly higher than for $Ni^{2+}$. While $Co^{2+}$ follows the expected pattern, $Ni^{2+}$ reportedly[51] has a hydrated ionic radius comparable to that of $Ba^{2+}$, but has a much lower affinity for PSS. Marcus' research, however, showed similar hydrated ionic radii for Co(II) and Ni(II)[54], which is more consistent with these results. Indeed, based on comparisons of ionic radius and hydration shell width among $Ni^{2+}$, $Mg^{2+}$, and $Cu^{2+}$, the selectivity of $Ni^{2+}$ is likely to be close to those of $Mg^{2+}$, $Co^{2+}$ and $Cu^{2+}$, and less than that of $Ba^{2+}$. The research of Akita *et al.*[55] also showed selectivity for Co(II) over Ni(II) using a micellar enhanced UF method, similar to the polyelectrolyte-UF process used here.

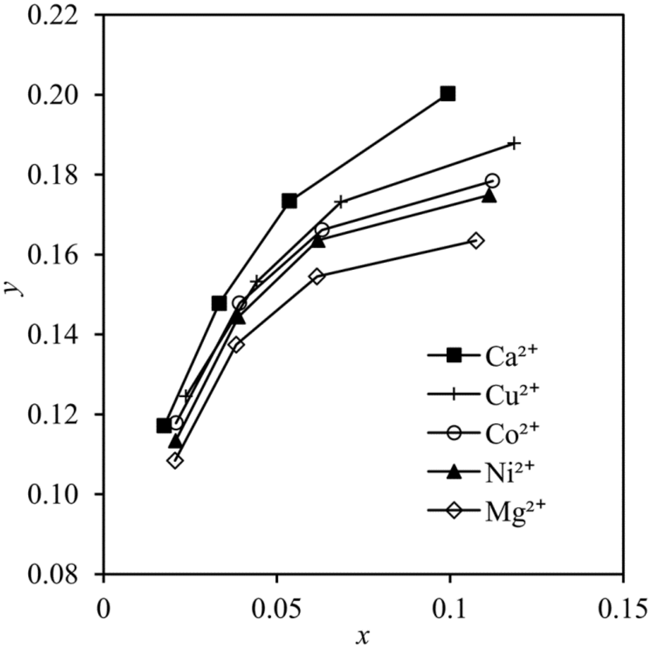

**Figure 6.** Distribution of $Co^{2+}$ and $Ni^{2+}$ (equivalent fractions) in the aqueous (x) and the polymer (y) phases in a multi-cation solution

### 3.3 A Speciation Model for Cation Distribution in Different Phases

As shown above, the sequence of cation affinities for PSS in a competitive water environment proved to be the same as the sequence derived from a series of binary systems. The next step was to determine, using the model shown in **Table 1**, whether the selectivity coefficients of cations in a multi-cation system are also same as those in binary systems. The distribution fraction of cations on purified PSS was used to compare the test results and model calculations. As shown in **Figure 7**, both divalent and monovalent cations show a good agreement between experimental and calculated values. For both divalent and monovalent cations in these water samples, the calculated values were not significantly different from the experimental results at the 0.05 confidence level using a paired samples t-test. These results demonstrate that the model based on selectivity coefficients and mass balances can be used to predict the distribution of cations into different phases in multi-cation systems.

While this approach should be broadly applicable, several factors not considered here may affect specific model predictions. Varying the water temperature and ionic strength may affect the selectivity coefficient values and the ion exchange kinetics[6], although the relative selectivity is expected to remain unaffected. The presence of organic molecules (e.g., humic substances) in natural waters or wastewaters may also result in cation complexation that would affect ion equilibrium with PSS [56]. Therefore, additional research is needed to investigate the use of this model under different water compositions and for use with other polyelectrolytes.

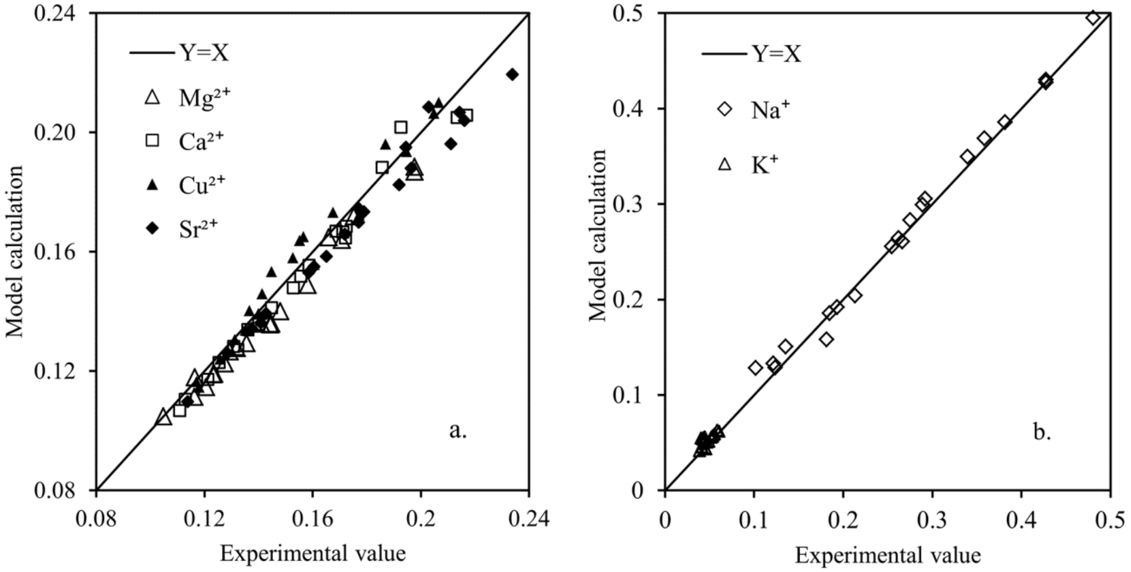

**Figure 7.** Comparison of experimental and model calculated values for cation distribution between the aqueous and PSS polymer phases. a: divalent cations; b: monovalent cations

### 3.4 Heavy Metal Removal from Water

Simulated metal-contaminated water samples were prepared to test the model's ability to predict heavy metal removal during UF separation, using $Cu^{2+}$ and $Pb^{2+}$ as contaminant metal examples. **Figure 8** shows $Cu^{2+}$ (50 mg/L) removal from pH 5.5 water samples by PSS-assisted ultrafiltration using varying concentrations of unpurified 200 kDa PSS, with or without other cations present. Without adding other cations (aside from the $Na^+$ added in the form of Na-PSS), the $Cu^{2+}$ rejection fraction (*R*) by a 10 kDa UF membrane reached 0.91 (i.e., 91% $Cu^{2+}$ was removed) when adding 0.6 g/L PSS (≈ 2.3 mM effective ion exchange sites), and *R* increased to 0.98 as the concentration of PSS increased to 1.2 g/L. Rivas *et al.*[32, 33] observed a similarly high removal of heavy metals, including $Cu^{2+}$, from water using PSS and poly(styrene sulfonic acid-*co*-maleic acid) (PSSM) without other cations present. Chou *et al.*[57] also reported 75% - 80% removal of $Cu^{2+}$ by UF (MWCO: 10 kDa) at a Cu/PSS (70 kDa) molar ratio of 1:5. This is because $Cu^{2+}$ has a much higher affinity for PSS than does $Na^+$. In a competitive, multi-cation water environment (**Table 2**), $Cu^{2+}$ rejection decreased to 0.36 when the concentration of PSS was 1.2 g/L, while $R$ reached 0.82 when PSS increased to 4.8 g/L (**Figure 8**). The decrease in rejection was mainly caused by competition from $Ca^{2+}$ and $Mg^{2+}$ in the artificial water samples, which have a selectivity for PSS comparable to that of $Cu^{2+}$. Sasaki *et al.*[34] also showed a decreased rejection of $Cu^{2+}$ during PSS-assisted UF as the $Na^{+}$ concentration increased from 0 to 80 mM.

When comparing $Cu^{2+}$ removal during the 10 kDa UF experiments to the model calculations (using $\alpha = 0.8$), the calculated values based on mass balances and selectivity coefficients obtained from binary systems demonstrated good agreement with experimental data in both Cu-only and multi-cation waters. Note that any complexation of Cu with small molecules or oligomers that may have passed through the membrane was neglected.

Experiments using a 1 kDa UF membrane resulted in an increase in $Cu^{2+}$ rejection of approximately 5-10% compared to the 10 kDa membrane (**Figure 8**). This could be due to rejection of smaller PSS molecules with the smaller MWCO filter, increasing the effective ion-exchange sites available to associate with $Cu^{2+}$ (which corresponds to an increase in the model parameter "$\alpha$"), or to clogging of the membrane pores by the PSS molecules, which might also enhance $Cu^{2+}$ rejection. A previous study[46] also showed higher rejection of a bio-polymer with a higher ratio of the biopolymer's MW to the MWCO of the UF membrane, and 99% rejection when the ratio was greater than 150. Therefore, PSS with a higher MW was expected to have a higher rejection of $Cu^{2+}$. Indeed, removal of $Cu^{2+}$ by UF using 3 g/L PSS was 3% higher using 1,000 kDa PSS than when using 200 kDa PSS under the same conditions, at 73.0% ± 1.4% versus 70.3% ± 1.0% respectively (**Figure 9** for $Cu^{2+}$ removal; **Figure S2** in the **Supporting Information** for rejection of 1000 kDa PSS).

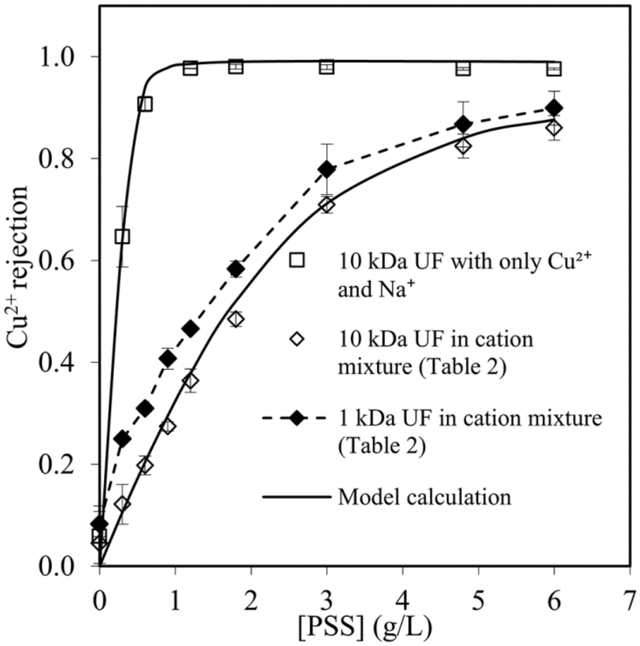

**Figure 8.** $Cu^{2+}$ removal by PSS-assisted UF using 1 and 10 kDa membranes

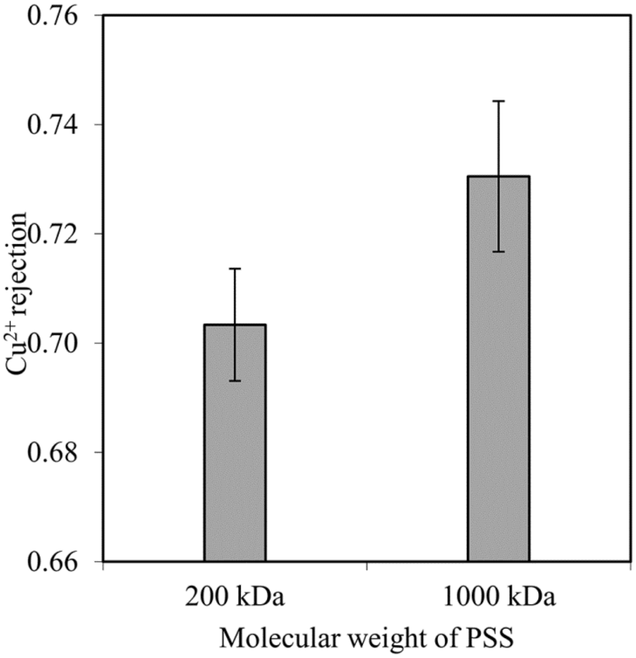

**Figure 9.** Rejection of $Cu^{2+}$ by 3g/L PSS with 10 kDa UF membrane using PSS of two different molecular weights

Based on the selectivity values of cations from **Table 3**, $Pb^{2+}$ should have a higher affinity than $Cu^{2+}$ for PSS; thus, higher removal of $Pb^{2+}$ was expected by PSS-assisted UF under the same conditions (**Table 2**). **Figure 10** shows the rejection of $Pb^{2+}$ and $Cu^{2+}$ (both with an initial concentration of 50 mg/L) using PSS-assisted UF with a 10 kDa UF membrane. Eighty percent of the $Pb^{2+}$ was rejected by adding 3 g/L PSS, 9% higher than for $Cu^{2+}$ removal under the same conditions. The higher $Pb^{2+}$ rejection, relative to $Cu^{2+}$, resulted both from its higher affinity for PSS and also from a higher molar ratio of PSS to cation in the solution.

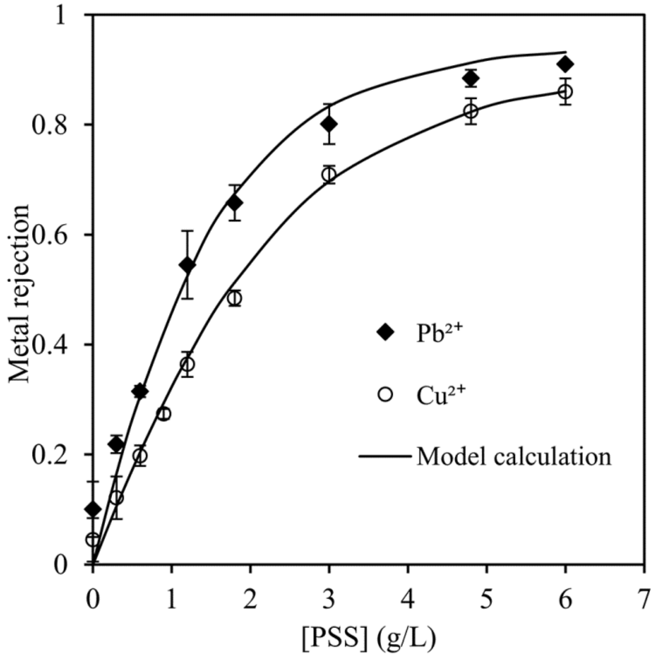

**Figure 10.** $Pb^{2+}$ and $Cu^{2+}$ (50 mg/L) rejection by 200 kDa PSS with 10 kDa UF

The influence of pH on $Cu^{2+}$ removal in the multi-cation solution is illustrated in **Figure 11**. At 3 g/L PSS, removal of $Cu^{2+}$ was very similar at pH 3 and 5.5 (71.0% and 71.7%, respectively), and close to the removal observed by Chou *et al.*[57] The affinity of $H^+$ for PSS is much lower than that of divalent cations, and consequently $H^+$ competition is low except at high concentrations (very low pH values). At pH 2.2, a $Cu^{2+}$ removal efficiency of 64.7 ± 0.8% was still achieved with PSS. These results differ from those using polyelectrolytes with carboxylic functional groups, which become less effective at cation removal under low pH conditions[58, 59]. Removal of $Cu^{2+}$ increased to 96.6% at pH 7, greater than expected based on model predictions. As this pH, however, Cu removal was affected by Cu precipitation as $Cu(OH)_2$. By comparison, 76.6% removal of $Cu^{2+}$ was observed without PSS addition when the solution was adjusted to pH 7 with NaOH. These values indicate that PSS addition did impact Cu removal at this pH, but it is not clear whether complexation or precipitation was the dominant mechanism. Huang *et al*.[17] also reported additional heavy metal removal due to precipitation during micellar-enhanced ultrafiltration at high pH.

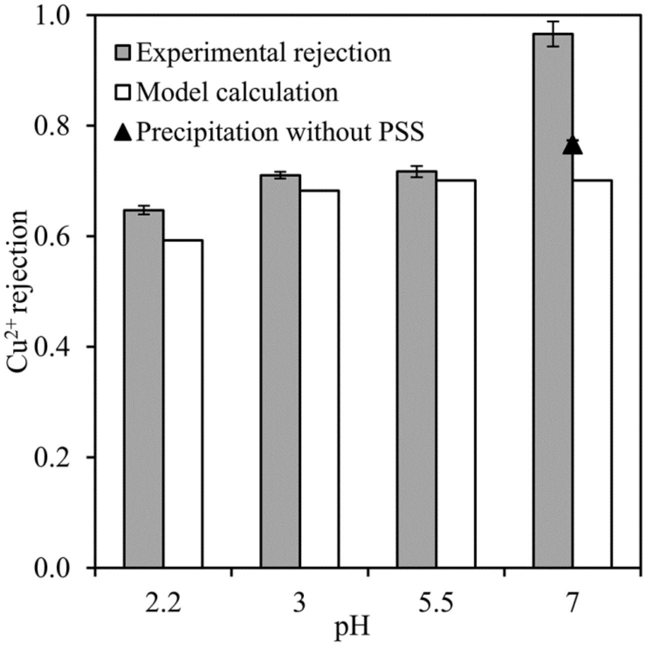

**Figure 11.** $Cu^{2+}$ rejection by 3 g/L PSS with 10 kDa UF at different pH values

## 4. Conclusions

Selectivity coefficients ($K_{sel}$) for cation complexation with a soluble anionic polyelectrolyte, poly(sodium 4-styrenesulfonate) (PSS), were measured for cations commonly found in natural waters ($H^+$, $Li^+$, $Na^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$, $Sr^{2+}$, and $Ba^{2+}$), and for selected toxic cationic metals ($Pb^{2+}$, $Cu^{2+}$, $Co^{2+}$ and $Ni^{2+}$), using an ion exchange model and experimental results from binary PSS-assisted ultrafiltration systems. The selectivity sequence of cation affinity for PSS was found to be $Ba^{2+} > Pb^{2+} > Sr^{2+} > Ca^{2+} > Cu^{2+} > Co^{2+} > Ni^{2+} > Mg^{2+} > H^+ > K^+ > Na^+ > Li^+$. Divalent cations have higher affinity for PSS than do monovalent ions, since their higher charge leads to stronger electrostatic attraction, while for cations with the same charge, $K_{sel}$ correlates negatively with the hydrated radius. In experiments on multi-cation solutions, measured removals of cations by PSS-assisted UF were found to agree well with removals calculated using a simple model based on measured binary-system $K_{sel}$ values and mass balances. Thus, binary selectivity coefficients can be used to predict cation distribution for PSS in multi-cation systems with good agreement to the experimental data. Removal of $Cu^{2+}$ and $Pb^{2+}$ from solutions containing multiple divalent and monovalent cations was evaluated to assess the potential for PSS-assisted UF to remove heavy metals from water in a competitive environment. Results show that this approach can be used for heavy metal removal, even in a very low pH environment. Results also indicate that a greater ratio of PSS MW/MWCO during UF separation leads to a greater removal of heavy metals.

## Supporting Information

Supporting information available includes a sample model calculation; the retention of PSS during UF separation ("$\alpha$" values in the model); distribution of $Mg^{2+}$ and $Na^+$ in the aqueous phase (x) and the polymer phase (y) in a binary-system; and $Ba^{2+}$ selectivity coefficient to PSS with different molecular weights.

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