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Ion-Specific Effects of Divalent Ions on the Structure of Polyelectrolyte Brushes

Xin Xu^{1,2,*}, Dean Mastropietro^{3,4,*}, Marina Ruths², Matthew Tirrell^{3,4}, Jing Yu¹

Affiliations:

¹School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798.

²Department of Chemistry, University of Massachusetts Lowell, Lowell, MA 01854, USA.

³Pritzker School of Molecular Engineering, University of Chicago, Chicago, IL 60637, USA

⁴Center for Molecular Engineering, Argonne National Laboratory, Lemont, IL 60439, USA.

* Xin Xu and Dean Mastropietro contributed equally to this work.

Abstract:

Polyelectrolyte brushes consist of charged polymer chains attached with one end to a surface at high densities. They are relevant for many practical applications ranging from biosensors to drug delivery to colloidal stability. Their structure and functionality can be dramatically influenced by multivalent counterions in the solution environment. In this work, the surface forces apparatus (SFA) and atomic force microscopy (AFM) were used to investigate the effect

of three alkaline earth divalent cations, Mg^{2+} , Ca^{2+} , and Ba^{2+} , on the structure of polystyrene sulfonate (PSS) brushes tethered to mica and silicon oxide surfaces. While all these ions caused significant shrinkage of the height of the PSS brushes, strong ion-specific effects were observed. Mg^{2+} and Ca^{2+} caused homogeneous shrinkage; Ba^{2+} led to pinned-micelle like inhomogeneous structures. Isothermal titration calorimetry (ITC) demonstrated that this ion specificity was mainly caused by the difference in binding energy between sulfonate groups and the divalent cations. Considering the abundance of divalent cations in industrial processes, natural environments, and biological systems, the understanding of strong ion-specific effects of divalent counterions is of great importance for theoretical studies and various applications involving polyelectrolytes.

1. Introduction

Polyelectrolyte brushes are of great importance for a wide range of fields, including colloidal behavior,¹⁻⁴ lubrication,⁵⁻⁸ drug and therapeutic delivery,⁹ biological interactions,¹⁰⁻¹² and coatings and adhesives.¹³⁻¹⁴ Recently, much attention has been focused on stimuli-responsive polyelectrolyte brushes,¹⁵ whose structure and properties are dramatically influenced by the surrounding environment, e.g., ionic strength, pH, and counterions.¹⁶ Understanding how polyelectrolyte brushes respond to different solution conditions would broaden their application to different environments.

Scaling theory for strong polyelectrolyte brushes with monovalent counterions has been studied extensively.¹⁷⁻¹⁸ In monovalent solutions, the brush height is mainly determined by the balance between the osmotic pressure of the counterions and the polyelectrolyte chain elasticity. There are two important regimes as counterion concentration increases: the “osmotic brush” regime, in which the brush height (thickness) does not change with the salt concentration, and the “salted brush” regime, in which the brush height decreases with increasing salt concentration with a $-1/3$ power law dependence.¹⁷ The existence of ‘osmotic’ and ‘salted brush’ regimes have been confirmed experimentally by various techniques, including surface force measurements and neutron scattering.^{1, 19-20}

The valency of the counterions plays a critical role for the structure of polyelectrolyte brushes. A strong shrinkage in height occurs in the presence of multivalent counterions^{2, 21} because of the replacement of monovalent counterions inside the brush due to an entropically driven ion exchange process and the subsequent electrostatic bridging mediated by the multivalent counterions. The solution concentration of trivalent counterions needed to cause brush collapse is one to three orders of magnitude lower than that of a monovalent salt. In addition to planar polyelectrolyte brush geometries, multivalent counterion effects have been observed on cylindrical and spherical polyelectrolyte brushes, both experimentally^{4, 21-24} and theoretically^{2,}

²⁵. Valency effects, hence, can greatly impact the functionalities of polyelectrolyte brushes. Previous studies have shown that the structure change caused by trivalent counterions can diminish the lubricity and load bearing ability of PSS brushes drastically.²⁶

Much previous research on the effects of valency focused on trivalent counterions such as La^{3+} , Y^{3+} , and $\text{Ru}(\text{NH}_3)_6^{3+}$, where certain effects are more dramatic;^{2, 27-28} less attention has been paid to the effects of divalent counterions despite their common occurrence in natural and biological systems.²⁹ Due to differences in their ion radius,³⁰ hydration,³¹⁻³² and binding energies,³³⁻³⁴ divalent ions can show ion specificities in solution,^{29, 35} which is often ignored in polyelectrolyte models based on mean field theory, such as the Poisson–Boltzmann or Debye–Hückel models. Mean field theories treat ions as point charges and only take into account the electrostatic interactions between them.^{2, 36} A deeper understanding of these phenomena is of importance for theoretical studies,³⁷⁻³⁹ biological systems,⁴⁰⁻⁴⁴ and industrial⁴⁵ applications.

In this work, we explore the effects of alkaline earth metal divalent cations, Mg^{2+} , Ca^{2+} , and Ba^{2+} , on the surface forces and structure of dense polystyrene sulfonate (PSS) brushes synthesized via surface-initiated atom transfer radical polymerization (SI-ATRP).⁴⁶ By combining the surface forces apparatus (SFA), atomic force microscopy (AFM), and isothermal titration calorimetry (ITC) techniques, we demonstrate that Mg^{2+} , Ca^{2+} , and Ba^{2+} show strong ion-specific effects on the structures of PSS brushes in solution.

2. Materials and Experiments

Materials

PSS Synthesis: Sodium 4-vinylbenzenesulfonate (SSNa, technical, $\geq 90\%$), (3-aminopropyl)-triethoxysilane (APTES, 99%), α -bromoisobutyryl bromide (BIBB, 98%), triethylamine (TEA, $\geq 99\%$), 2,2-bipyridyl (bpy, $\geq 99\%$), Cu(I)Br (99.999%), toluene (anhydrous, 99.8%), and

methanol ($\geq 99.9\%$) were purchased from Sigma Aldrich and used without further purification. Deionized water was obtained from a Millipore Milli-Q system with a resistivity of $18.2 \text{ M}\Omega\text{cm}$. The synthesis of PSSNa polymer brush layers on mica and on silicon wafers was performed through a surface-initiated atom transfer radical polymerization (SI-ATRP) procedure reported previously.⁴⁶ The grafting density of the PSS brush is estimated to be 0.025 chain/nm^2 on mica and 0.1 chain/nm^2 on silicon due to the natural differences in initiation site densities between mica and SiO_2 .²⁹

Salts for the solutions: sodium nitrate (NaNO_3 , $\geq 99.0\%$), magnesium nitrate hexahydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99%), calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\geq 99.0\%$), and barium nitrate ($\text{Ba}(\text{NO}_3)_2$, $\geq 99\%$) were purchased from Sigma Aldrich and used without further purification. Poly (sodium 4-styrenesulfonate) (average $M_w \sim 70,000 \text{ g/mol}$) used for ITC measurements was purchased from Sigma Aldrich and used without further purification.

SFA measurements

The force measurements were done using an SFA2000 (SurForce LLC, Santa Barbara, CA). Freshly cleaved mica sheets (thickness, ~ 2 to $5 \text{ }\mu\text{m}$) were glued to cylindrical glass disks ($R = 2 \text{ cm}$) using an UV-curable optical glue (Norland NOA 81). PSS brushes were synthesized on the mica as described previously.⁴⁶ Two disks, each carrying a brush layer, were mounted in the SFA chamber in a crossed-cylinder configuration. This geometry is equivalent to a spherical surface and a flat surface when the two surfaces are at small separation distance (Schematic 1a). In each experiment, the whole chamber of the SFA 2000 was filled with solution (approx. 250 mL). When changing solutions, the old solution was fully drained and the new solution was used to flush the SFA chamber three times. Two to three repeating force measurements were performed for each condition in each of the experiments. The approach and separation speed of the surfaces was about 4 nm/s . The brush height, h , was defined as half

the distance, D , between two PSS covered mica surfaces at $F/R = 1$ mN/m, and assuming the brush heights on both surfaces were the same. $D = 0$ is the distance between two bare mica surfaces without brushes.

AFM measurements

AFM height (topography) and phase images of PSS brushes on silicon wafer (Schematic 1b) in different solutions were measured with a Nanoscope IV Multimode AFM (Bruker) in tapping mode, using a glass liquid cell (Bruker, model MTFML, liquid volume ca. 0.1 mL). The AFM cantilevers (CSC17/Cr-Au, MikroMasch) had a resonance frequency of ca. 12 kHz in air and 4–5 kHz in liquid, with tip radii of 12–20 nm. The image scan rate per line was chosen in the range 0.8–1.5 Hz. The contribution from tip convolution to the size of the features observed in the images was estimated to be 45–70 nm. The waiting time between the PSS brush layer being exposed to solutions in the liquid cell and the start of the imaging was at least 15 min. When changing solutions, the brush sample was first taken out and rinsed with water and air dried, then placed back under the liquid cell and the new solution introduced. The liquid cell was rinsed with a large amount of water and ethanol and air dried between each solution.

Calorimetric Measurements

Calorimetric data were collected on a MicroCal iTC200 isothermal titration calorimeter (GE Healthcare Life Sciences). A series of 20 injections of divalent ion solution (75 mM, 100 mM, and 50 mM for $\text{Mg}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_2$, and $\text{Ba}(\text{NO}_3)_2$, respectively) were delivered into the reaction cell (250 μL) containing 100 μM PSSNa (molecular weight 70,000 g/mol) in 3 mM NaNO_3 solution at 298 K. Each injection was delivered over a 4 s time interval, with a 3 min interval between injections to allow for complete equilibration. The first injection was 0.4 μL while the subsequent nineteen injections were 2 μL each (total volume of divalent salt solution injected is 38.4 μL). The first injection is excluded from the fit as it may contain artifacts due to diffusion effects.⁴⁷ Heat of dilution was determined between each of the divalent ion

solutions (75 mM Mg(NO₃)₂, 100 mM Ca(NO₃)₂, and 50 mM Ba(NO₃)₂) and 3 mM NaNO₃. The integrated heat changes from the heat of dilution were subtracted from the integrated heat changes between the divalent salts and 100 μM PSSNa in 3 mM NaNO₃ for each respective divalent ion solution. This corrected data was used in the fitting.

A model for multiple sites of a single type⁴⁸ was used to fit the integrated heat data:

$$Q = \frac{NM_t\Delta HV_0}{2} \left[1 + \frac{X_t}{NM_t} + \frac{1}{NK_aM_t} - \sqrt{\left(1 + \frac{X_t}{NM_t} + \frac{1}{NK_aM_t}\right)^2 - \frac{4X_t}{NM_t}} \right] \quad (\text{eq. 1})$$

In the above expression, Q is the total heat content of the active cell volume, V_0 . N is the stoichiometry between the divalent ion and the polymer, K_a is the association constant, X_t is the bulk concentration of ligand in the cell, M_t is the bulk concentration of polymer in the cell, and ΔH is the molar heat of binding. The free energy of binding, ΔG , is determined from the equation:

$$\Delta G = -RT \ln K_a \quad (\text{eq. 2})$$

where T is the absolute temperature and R is the gas constant. The binding entropy, ΔS , may then be determined from the Gibbs free energy and binding enthalpy:

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (\text{eq. 3})$$

It is important to note that ITC measures the total heat generation during a binding event, which may include linked equilibria (secondary equilibria or processes that occur as a result of the primary binding event) that can also contribute to the observed enthalpy change.⁴⁹⁻⁵⁰ Likewise, the entropy will include contributions from linked equilibria. For this study we are interested in the thermodynamic trends between the three divalent ions and for this purpose the binding enthalpy need not be isolated from any linked equilibria.

Schematic 1. Surface and PSS brush configurations in (a) SFA and (b) AFM experiments.

3. Results and Discussions

3.1 SFA force curves in pure divalent cation solutions

SFA measurements were done on PSS brush layers grown from mica substrates in aqueous solutions containing Mg^{2+} , Ca^{2+} , or Ba^{2+} . Figure 1a–c shows the SFA force–distance (F – D) curves for these cations at concentrations of 1, 10, and 100 mM. The height (thickness) of the PSS brushes, indicated by the range of repulsion of the force–distance curve, decreased with increasing ionic strength of the solutions. However, the change in brush height showed very different trends for the different cations: In Mg^{2+} and Ca^{2+} solutions, brushes were in a swollen state at concentrations ≤ 1 mM and gradually collapsed as the concentration increased, whereas at 1 mM Ba^{2+} , the brushes were already fully collapsed. A plot of the brush height versus ionic strength (Figure 1d) shows clearly that not only increasing ionic strength has an impact on brush collapse, but the collapse behavior can also be different between different counterions of the same valency.

Figure 1: Force–distance curves for PSS brushes in (a) Mg^{2+} , (b) Ca^{2+} , and (c) Ba^{2+} solutions at concentrations of 1 mM (blue squares), 10 mM (red circles) and 100 mM (green triangles). (d) Height ($h = D/2$) of PSS brushes at $F/R = 1$ mN/m in solutions of different ionic strength (3 mM, 30 mM and 300 mM ionic strength correspond to concentrations of 1 mM, 10 mM, and 100 mM of the divalent counterion). The force curves shown in (a) were measured on a different pair of surfaces than those in (b) and (c).

3.2 AFM images in pure divalent cation solutions

As a complementary technique to the SFA force measurements, which showed the effect of ion specificity on brush height (Figure 1d), AFM tapping mode imaging in solution was used to investigate the effect of ionic strength and ion specificity on brush morphology. In 3 mM Na^+ solution, the PSS brush is in a fully extended state.²⁹ As expected, the AFM image of this

system (Figure 2a) shows a relatively uniform surface morphology with only large lateral scale (~ 500 nm) patterns but small height variations (< 10 nm), which is in agreement with previous work.⁵¹ In the same ionic strength Mg^{2+} and Ca^{2+} solutions (divalent concentration 1 mM), the AFM height image showed a similar morphology as in 3 mM Na^+ (Figure S1 e,f). Despite the brush height decreasing significantly in the SFA measurements with increasing concentration (from 1 to 100 mM) of Mg^{2+} and Ca^{2+} , the AFM images obtained in those solutions are relatively similar and the surface morphology remained uniform (Figure 2 b,c). However, already at the low concentration of 1 mM Ba^{2+} , a very different surface structure of the PSS brush was observed with many small micelle-like features with a width of 20–100 nm. Such a pinned-micelle structure or lateral heterogeneity has recently been reported for collapsed PSS brushes in trivalent Y^{3+} solutions based on AFM measurements in solution and MD simulations.⁵¹ These surface features keep developing as the Ba^{2+} concentration increases (Figure S1 i,m). In summary, the different surface morphologies, along with the different height changes in Figure 1d, show clearly the existence of ion specificity of these three divalent ions when interacting with PSS brushes.

Figure 2: AFM tapping mode height images of PSS brushes on silicon wafer, in aqueous solutions in the presence of (a) 3 mM Na⁺, (b) 100 mM Mg²⁺, (c) 100 mM Ca²⁺, and (d) 1 mM Ba²⁺. All scan (image) sizes are 3 μm × 3 μm, with 500 nm white scale bars.

3.3 SFA force curves in divalent cation solutions of fixed ionic strength

To separate the effects of ion specificity and the ionic strength of the solution, SFA force measurements were performed between two PSS brushes at a constant ionic strength while the concentration of divalent ions was varied. Calculated amounts of monovalent (NaNO₃) and divalent salts (Mg(NO₃)₂, Ca(NO₃)₂, Ba(NO₃)₂) were added to ensure that the solutions had different concentrations of each divalent ion (0.001 mM, 0.01 mM, 0.1 mM, and 1 mM) but the total ionic strength of the solutions was fixed at 3 mM. A previous study²⁹ showed that in 3 mM monovalent solution, the PSS brush is fully extended so any decrease in brush height would be due to divalent counterions in the solution.

For all three divalent cations, the PSS brushes showed two consistent trends: (1) at low concentrations of divalent ions, the range of the repulsive force as well as the shape of the force–distance curves did not change much, indicating that the brush layers stayed in an extended state (Figure 3a-c, and Figure S1); (2) at a particular concentration, 1 mM for Mg²⁺ and 0.1 mM for Ca²⁺ and Ba²⁺, the range of the repulsion started to decrease (Figure 3a-c). Figure 3d shows the absolute PSS brush height, h , as a function of concentration of Mg²⁺, Ca²⁺, and Ba²⁺. It is apparent that at a concentration of 0.1 mM, the different divalent ions cause different behaviors: in Mg²⁺ solution the brush height was the same as at lower concentration, whereas in Ca²⁺ and Ba²⁺ it decreased by 13% and 31%, respectively. Increasing the concentration to 1 mM caused further shrinkage of the brushes while maintaining the same trend in brush height, Mg²⁺ > Ca²⁺ > Ba²⁺ (Figure 3d), despite a smaller difference in height at higher concentration. Taken together, the SFA force curves clearly demonstrate that while all

three ions have the same valency, they can lead to different degrees of shrinkage of the brush layers at the same concentration.

Figure 3: Force–distance curves for PSS brushes in (a) Mg^{2+} , (b) Ca^{2+} , and (c) Ba^{2+} solutions of five different divalent counterion concentrations: 0 mM, 0.001 mM, 0.01 mM, 0.1 mM, and 1 mM with fixed ionic strength, $I_0 = 3$ mM. Filled symbols indicate forces measured on compression and open symbols show forces measured on separation. (d) Height of the PSS brushes at $F/R = 1$ mN/m in different concentrations of divalent ions.

Divalent counterions thus have a strong impact on the brush collapse also in the presence of moderate concentrations of monovalent ions. When the ionic strength of the solution is fixed,

the interaction forces of PSS brushes depend quantitatively on which divalent cation is added to the medium. In addition, the brush surface morphology is sensitive to specific effects of the different ions, which can be expected to be critical for the functionality of polyelectrolyte brushes in the presence of multivalent counterions.

3.4 Reversible uptake of divalent cations by PSS brushes

The divalent ions taken up by the PSS brushes can be fully released in solutions containing high concentration of monovalent salt. Figure 4 shows the results of an experiment in which PSS brushes were fully extended in 3 mM Na⁺. After collapsing the brushes in 1 mM Ba²⁺, the Ba²⁺ solution was replaced by a 3 M Na⁺ solution. The force–distance curve measured in 3 M Na⁺ showed an even shorter range of repulsion than that measured in 1 mM Ba²⁺, and the shape of the force–distance curve also changed significantly. The shorter range of repulsion indicated that structures formed in 1 mM Ba²⁺ were dissolved, and the previous pinned-micelle structures collapsed further. After measuring the interactions in 3 M Na⁺, the monovalent salt concentration was decreased to 3 mM, and then the force–distance curve measured was almost identical to the one measured in the initial 3 mM Na⁺ solution before exposure of the system to any Ba²⁺ ions. The reversible change of the force–distance curves confirmed that the uptake of the divalent cations by the negatively charged PSS brushes was reversible: in low concentration of monovalent salt, the divalent counterions can be taken up by the PSS brushes, causing their collapse; in high concentration of monovalent salt, the divalent counterions in the brush will be replaced by monovalent ones through an ion-exchange process. Similar reversible uptake of multivalent counterions by the PSS brushes was observed for trivalent counterions.²⁸⁻

Figure 4: Force–distance curves of PSS brushes showing that the initial interaction force in 3 mM Na⁺ (▲) can be recovered (★) after brush collapse in Ba²⁺ (◆) by soaking the brushes in 3 M Na⁺ (▼). Filled symbols indicate forces measured on compression and open symbols show forces measured on separation.

AFM images of these systems in solution agreed well with the SFA results and confirmed the release of Ba²⁺ in 3 M Na⁺ solution. The phase images provide additional information, since they reflect stiffness differences of the materials probed by the tip. The micelle-like inhomogeneous features in the height image (Figure 5a) and corresponding phase image (Figure 5d) in 1 mM Ba²⁺ disappeared when the solution was replaced by 3 M Na⁺ (Figure 5b,e). Upon immersing the same brush in 3 mM Na⁺, the surface only showed large-scale (~ 500 nm wide) fluctuations in height (Figure 5c, which is similar to Figure 2a) and a quite uniform phase image (Figure 5f). The phase images showed that the PSS brush recovered to a uniform viscoelastic response, which is strongly suggestive of a return to uniformity. Such

reversible uptake of multivalent counterions by PSS brushes has also been reported with various trivalent counterions, including Y^{3+} and La^{3+} .²⁷⁻²⁸

Figure 5: AFM tapping mode height images of PSS brushes on silicon wafer in the presence of (a) 1 mM Ba^{2+} , (b) 3 M Na^+ , (c) 3 mM Na^+ , and their respective phase images (d–f). All image sizes are $3\ \mu\text{m} \times 3\ \mu\text{m}$, with 500 nm white scale bars.

3.5 ITC measurements on binding energies between PSS and divalent cations

For further investigation on ion specificity, a set of ITC experiments were performed between a 100 μM PSSNa (Mw 70,000 g/mol) homopolymer solution in 3 mM NaNO_3 and 75 mM $\text{Mg}(\text{NO}_3)_2$, 100 mM $\text{Ca}(\text{NO}_3)_2$, and 50 mM $\text{Ba}(\text{NO}_3)_2$ to determine if the binding energies were different. The heat of dilution in the absence of the homopolymer was determined by measuring the heat change between 3 mM NaNO_3 (the background electrolyte) and the divalent solutions.

The thermogram for PSSNa binding with Mg^{2+} is shown in Figure 6. Corresponding thermograms for Ca^{2+} and Ba^{2+} are shown in Figure S2. The top plot is the raw thermal data, shown as heat output of the sample cell heaters, in $\mu\text{cal/s}$, as a function of elapsed time, in minutes. The red line is the baseline after correcting for the reference power ($6 \mu\text{cal/s}$). The blue line represents the heat output during the experiment spanning 20 injections, or approximately 1 injection every 3 minutes. Peaks above the red line correspond to an endothermic response while peaks below the red line correspond to an exothermic response. The bottom plot represents the integrated peaks at each injection as a function of the molar ratio (moles of divalent ion per moles of PSSNa chain) (blue dots) and the resulting fit of equation 1 (red line). Prior to fitting, heats of dilution for each cation were subtracted from each respective data set. The association constants (K_a), enthalpies (ΔH), and stoichiometries (N) shown in Table 1 were determined from fitting a model for multiple sites of a single type to calorimetric data for each separate experiment.⁴⁷⁻⁴⁸

Figure 6: Heat change for a 100 μM solution of PSSNa homopolymer in 3 mM NaNO_3 as 75 mM $\text{Mg}(\text{NO}_3)_2$ was injected. (a) Raw data for a series of injections before subtracting the heat of dilution. The red line represents the baseline after correcting for the reference power (6 $\mu\text{cal/s}$). (b) Integrated heat change data (corrected for heat of dilution) as a function of molar ratio of divalent cation to PSSNa chains (markers) and the resulting fit (red line).

When adding the different divalent solutions into the PSS solutions, the entropy changes are almost the same. This is expected as each divalent cation will displace the same number of sodium ions, resulting in the same entropy change. The entropic term, $T\Delta S$, dominates the Gibbs free energy change, ΔG , of the process, as predicted by theory.¹⁷ The change in binding enthalpy, ΔH , however, is higher for Mg^{2+} and Ca^{2+} than that measured for Ba^{2+} . Note that the binding enthalpy is positive meaning that this interaction is endothermic. We can infer from the values of ΔH that the energy barrier for Ba^{2+} is lower. Previous SFA measurements studying the effects of ion specificity between PSS brushes and divalent counterions have shown that the degree to which the divalent ions cause structural change in the brush follows a similar trend as their radii, $\text{Mg}^{2+} < \text{Ca}^{2+} < \text{Ba}^{2+}$.²⁹ Here we see that the binding enthalpy decreases with increasing ionic radius, which impacts the hydration of the ions.^{31, 52} This implies that increased structural change in the brush is caused by a reduced binding enthalpy and is an enthalpically driven process.

Table 1: Thermodynamic properties and fitting parameters for ITC data on divalent counterions interacting with PSS homopolymer

Species	K_a	ΔG	ΔH	ΔS	$-T\Delta S$	N
	M^{-1}	cal/mol	cal/mol	cal/(mol K)	cal/mol	
Mg^{2+}	444±16	-3610	1965±44	18.7	-5573	41.4±0.7
Mg^{2+}	670±97	-3853	1386±91	17.6	-5245	43.6±2.1
Ca^{2+}	462±12	-3633	1605±23	17.6	-5245	51.4±0.6
Ca^{2+}	612±65	-3800	1432±72	17.6	-5245	47.3±1.8
Ba^{2+}	2670±638	-4672	916±48	18.8	-5602	36.1±1.4
Ba^{2+}	3640±1610	-4855	892±75	19.3	-5751	35.0±2.2

Association constants (K_a), enthalpies (ΔH), and stoichiometries (N), were determined by fitting each independent titration run to a model for multiple sites of a single type using MicroCal Origin software.⁴⁸

Another observation is the low stoichiometry, N , determined from the fits when compared to the chain length of the homopolymer, which is approximately 340 repeat units. There are several possible explanations for the different stoichiometries for Mg^{2+} , Ca^{2+} and Ba^{2+} . First, the experiment continues until saturation which may not necessarily occur when all the sites are occupied by divalent counterions but rather when the displacement of the sodium ions by a divalent ion no longer is thermodynamically favorable. Steric hindrance may also play a role in preventing divalent ions from binding to every sulfonate group. Thus the number of sites determined from the fit likely corresponds to the average number of divalent ions that are site bound, or in direct contact with the sulfonate groups.⁵³

The ITC results provide critical information towards understanding the ion-specific effects of the three divalent cations (Fig 7). ΔG for the binding between Ba^{2+} and PSS is much larger than that of Mg^{2+} and Ca^{2+} , which leads to stronger electrostatic bridging between different PSS

chains. Such strong bridging can lead to the laterally inhomogeneous structure of the collapsed PSS brushes in the presence of Ba^{2+} ,⁵¹ whereas weaker electrostatic bridging with Mg^{2+} or Ca^{2+} results in a more homogeneous collapsed structure. The ITC results also show that the ion exchange process is entropy driven. Increasing the concentration of monovalent ions in the solution can lower the entropy gained during this ion exchange process or even lead to an overall decrease of the entropy of the system.⁵⁴ Therefore the divalent ions taken-up by the polyelectrolyte brushes can be fully released back to the solution in solutions containing high concentrations of monovalent ions.

Figure 7. Illustration of two different PSS collapse mechanisms in the presence of divalent cations: Ba^{2+} leads to a pinned-micelle like inhomogeneous structure while Mg^{2+} and Ca^{2+} give rise to a homogeneous collapsed structure.

4. Conclusion:

We systematically studied the effects of divalent cations, Mg^{2+} , Ca^{2+} , and Ba^{2+} on the structure of PSS brushes by combining SFA, AFM, and ITC techniques. The results highlight the importance of ion specificity. All three divalent cations can lead to collapse of the PSS brushes, however, Ba^{2+} showed a much more profound effect and a distinctly different structure than

Mg^{2+} and Ca^{2+} : homogeneous collapse was identified in the presence of Mg^{2+} and Ca^{2+} , whereas Ba^{2+} gave rise to pinned-micelle like inhomogeneous structures. The ITC results clearly show that such ion-specific effects are mainly caused by the large difference in binding energy between the divalent cations and the sulfonate groups. Such ion specificity is not limited to divalent counterions, but also occurs with trivalent counterions. Previous SFA results have shown that the adhesion measured upon the separation of two PSS brushes saturated with La^{3+} counterions was more than one order of magnitude greater than the adhesion measured with $\text{Ru}(\text{NH}_3)_6^{3+}$ complexes in identical ionic environments.²⁷

The theory of polyelectrolyte brushes has been greatly advanced since the original discussions by Pincus, Zhulina and co-workers.¹⁷⁻¹⁸ However, to our best knowledge, no current model accounts for the ion-specific effects of different counterions on the structures of polyelectrolyte brushes. There is still a great deal to be learned from polyelectrolyte interactions with multivalent ions and complexes. We believe that this work can have a profound impact in many practical applications involving polyelectrolytes, ranging from biomedical sensors to drug delivery to responsive and tunable materials.

Author Information

Corresponding Author

Email: yujing@ntu.edu.sg

ORCID

Xin Xu: 0000-0003-2430-1986

Dean Mastropietro: 0000-0003-4052-3837

Marina Ruths: 0000-0001-9564-2636

Matthew Tirrell: 0000-0001-6185-119X

Jing Yu: 0000-0002-4288-951X

Notes

The authors declare no competing interests.

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