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Polyelectrolyte Brush Interaction with Multivalent Ions

E. B. Zhulina,*,†,‡ O. V. Borisov,‡ and T. M. Birshtein‡

University of Pittsburgh, Department of Chemical Engineering, Pittsburgh Pennsylvania 15261, and Institute of Macromolecular Compounds, Russian Academy of Sciences, St. Petersburg 199004, Russia

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ABSTRACT: We present a scaling theory to describe the equilibrium structure of an annealed polyelectrolyte brush interacting with multivalent salt ions. We demonstrate that at low ionic strengths of the solution the polyelectrolyte brush swells with increases in the bulk concentration of salt, Φ_s. When multivalent counterions are added to the solution, the scaling exponents describing the dependences of the brush thickness H on Φ_s become a function of the valency q of the counterion. We also find that, when such a brush is compressed, the shape of the force versus deformation profile depends on q. In the case of multivalent coions, the characteristics of the brush depend on the net concentration of charge, $q\Phi_s$, of the added ions. As a result, the force versus deformation profile obeys a single scaling law as a function of $q\Phi_s$. At high concentrations of salt, the features of the salt ions affect the properties of the annealed brush through the net ionic strength of the solution.

1. Introduction

Dispersions of colloid particles are widely used in applications such as papermaking, food technologies, cosmetics, and so on. In the majority of colloidal systems, the dispersed particles experience attractive forces that can cause flocculation of the colloids. To prevent or regulate the flocculation, colloidal dispersions are often stabilized by polymers, which form protective coatings around the particles. When the polymers are charged, a combined effect of steric and electrostatic stabilization takes place.[1] A steric force arises due to the short-range repulsions between the uncharged polymer units, whereas an electrostatic force results from the charges on the chains. Because of the strong repulsions between these charges, such coatings are more efficient in protecting the dispersion than are their neutral counterparts. In addition, the stabilizing properties of the charged layers can be tuned by such factors as pH and the ionic strength of the solution.[1]

Formation of polyelectrolyte layers on dispersed colloidal particles can be achieved in various ways. A conventional scheme is adsorption of polyelectrolytes on oppositely charged surfaces. In cases of similarly charged or neutral substrates in water solution, hydrophobic attractions between the uncharged monomers and the surface can serve as a driving force for adsorption. In this study, we focus on polyelectrolytes in a water system that have a relatively short hydrophobic anchoring block, which attaches the macromolecule to the surface of the substrate, while the rest of the charged chain is dangling in the solution. (Such polymers are often referred to as hydrophobically modified polyelectrolytes.) At a sufficient density of polymer on the particle, the dangling ends of the adsorbed chains form a polyelectrolyte brush.

The properties of polyelectrolyte brushes have been the subject of intensive investigation during the past decade.[2−16] These studies have focused mainly on the so-called quenched or strong polyelectrolytes (that is, polymers with fixed charge distributions, which do not change with variations in the external conditions). Fewer studies[3d,6,13−16] have dealt with the so-called annealed polyelectrolytes where the charge distribution is not fixed but can vary with pH. (Typical examples of such polyelectrolytes are weak polyacids and polybases.) The predictions of the theoretical models of quenched polyelectrolyte brushes have been found to be in reasonable agreement with experimental observations.[17−22] Theory[2a,3a,12] predicts that at relatively high ionic strengths, the concentrations of mobile ions in a quenched brush approach their bulk solution values. Under these conditions, the screening effect of the salt can be described[3c] in terms of an effective second virial coefficient of polymer−polymer interactions, $v_{\text{eff}} \sim l_B r_D^2$, where r_D is the Debye screening length in the bulk solution defined as

$$r_D = \frac{1}{\sqrt{4\pi\ l_B \Sigma_i z_i^2 \Phi_i}} = \frac{1}{\sqrt{4\pi l_B I}} \tag{1}$$

Here, $l_B = e^2/\epsilon kT$ is the Bijerrum length, z_i and Φ_i are the valency and the bulk concentration of ion of type i, and $I = \Sigma_i z_i 2\Phi_i$ is the ionic strength of the bulk solution. (As usual, e is the elementary charge, ϵ is the dielectric constant of the solvent, and kT is the thermal energy.) In terms of this model, the effect of ion valency is reduced to the variation in the net ionic strength I according to eq 1, and this regime is referred to as the "salt-dominance" regime.[3c]

However, at low ionic strengths, the local concentrations of ions inside the brush become noticeably different from their bulk values, and screening of the electrostatic repulsion between the polyions is carried out by the counterions trapped inside the brush.[2a,3a] Here, the electrostatic interactions are effectively described in terms of the osmotic pressure of the trapped counterions, and this regime is referred to as the "osmotic" regime. For quenched polyelectrolytes, the addition of salt leads to only slight changes in the distribution of the ions in the system, and the thickness of the brush is virtually unaffected by variations in the ionic strength of the bulk solution. Recently, a theoretical prediction for polyelectrolyte brush thickness as a function of the

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† University of Pittsburgh.
‡ Russian Academy of Sciences.

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ionic strength was confirmed experimentally.[19,20] However, only monovalent (sodium chloride) ions were involved in these studies, whereas the theory[12] covers a wider range of valencies.

The effect of salt ions on the annealed polyelectrolyte brushes have less thoroughly been investigated. Here, theoretical studies of the influence of salt have focused mainly on monovalent ions. As demonstrated in refs 3d and 13−15, the addition of monovalent salt can lead to a so-called "abnormal" behavior of an annealed polyelectrolyte brush. In contrast to the quenched systems, the thickness of an annealed brush *increases* with an increase in the ionic strength. This is due to a shift in the ionization equilibrium as the salt ions substitute their own counterions in the brush. As a result, the degree of ionization of the tethered polyelectrolytes increases, and the brush swells additionally. Some results on the effect of multivalent salt ions on annealed brushes were presented earlier.[16] However, this analysis was limited by the case of multivalent counterions only.

A goal of the present study is to analyze a general case when multivalent ions of arbitrary sign and valency are present in the bulk solution and interact with an annealed polyelectrolyte brush. We assume that the salt ions *do not bind* to the charged groups on the chains and that the mobile ions and the polyions interact through a self-consistent electrostatic field associated with the tethered layer. We investigate how the valency and sign of the added ions affect the thickness of the polymer coating and the stabilizing force that appears when the two brushes are put into close contact. To reach this goal, we employ a simple scaling model through which we obtain the power-law dependences for the characteristics of the system. We focus on the exponents in these dependences and ignore all numerical coefficients. As we demonstrate below, the sign and the valency of the salt ions can play an important role at low ionic strengths. We show, in particular, that salts with multivalent counterions are more efficient in screening than salts with multivalent coions. A surprising result is that in the case of multivalent counterions the scaling exponents become sensitive to the valency of the salt ion. In particular, when an annealed polyelectrolyte brush is compressed, the force versus deformation profile is expected to be different in dilute solutions of salts with mono- and divalent counterions.

The paper is organized as follows. In section 2, we formulate the theoretical model and describe the mathematical formalism. In sections 3 and 4, we consider how the presence of multivalent salt ions in the solution affects the ionization of an annealed polyelectrolyte brush and its thickness, and in section 5, we analyze the force that appears when the brush is compressed. Finally, in section 6, we summarize our results and conclusions.

2. Model and Formalism

We consider a brush composed of long flexible polymer chains tethered onto an impermeable planar surface with the grafting density $1/s$ (s is the area per chain). Each chain contains $N \gg 1$ symmetric units of size $a \simeq l_B$. (The latter condition holds for flexible polyelectrolytes in water.) The polymer is assumed to be a weak polyacid. That is, each unit can dissociate into a negatively charged group, A^-, and a positively charged, mobile counterion (in our case, hydrogen ion H^+). We refer to such polymers as annealed polyelectrolytes.

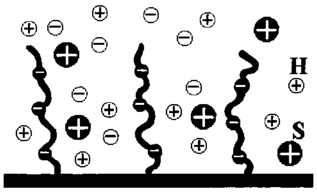

Figure 1. Schematic of an annealed polyelectrolyte brush immersed in a salt solution with multivalent ions.

The brush is assumed to be immersed in a water solution of salt (see Figure 1). The salt is totally dissociated into counterions S^+ and coions S^- which can have different valencies. We focus on salt, which dissociates into multivalent counterions and monovalent coions or multivalent coions and monovalent counterions. In both cases, we denote by $q > 1$ the valency of the multivalent ion. We let Φ_s be the concentration of the multivalent ions in the bulk solution. Then, the concentration of the monovalent salt ions is given by $q\Phi_s$.

In addition to salt ions, the solution contains also hydrogen ions, $H+$. Their concentration Φ_H determines the pH of the bulk solution as $\mathrm{pH} = -\log(a_H) \approx -\log(\Phi_H)$ where a_H is the activity of hydrogen ions and Φ_H is measured in moles per liter. (Replacement of the activity of hydrogen ions, a_H, by Φ_H is a conventional approximation valid at low H^+ concentrations.) Variation in the bulk value of pH is attained by addition of a low-molecular-weight acid, HX. We thus restrict the range of pH from above, that is $\mathrm{pH} < \mathrm{pH}^o = 7$. (The value of $\mathrm{pH}^o = 7$ corresponds to pure water. The range of $\mathrm{pH} > \mathrm{pH}^o$ can be covered by addition of a base which will increase the pH of the solution due to the shift in the ionization equilibrium of water. The generalization of our model for this case is straightforward.)

Assuming the total dissociation of the acid, $HX = X^- + H^+$, and ignoring the dissociation of water molecules, we have $\Phi_H \approx \Phi_x$ where Φ_x is the bulk concentration of the added acid ($\Phi_x > 10^{-7}$). We now introduce the degree of dissociation of the AH group, α_o, in the bulk solution as or

$$\alpha_o/(1-\alpha_o) = K/\Phi_H \tag{2a}$$

$$\alpha_o = K/(\Phi_H + K) \approx K/\Phi_H \tag{2b}$$

Here, K is the dissociation constant which determines the $\mathrm{p}K = -\log(K)$ of the tethered polyacid, and K is measured in the units of concentration. The right hand side of eq 2b implies that $\alpha_o \ll 1$. This assumption is not crucial. It allows us to derive simple scaling laws for the brush thickness as a function of K and Φ_H in sections 3−5. The larger values of $\alpha_o < 1$ are incorporated by the replacement of α_o by $\alpha_o/(1-\alpha_o)$ in the corresponding expressions in sections 3−5.

The repulsive interactions between the ionized groups on the tethered polyions force the chains to stretch in the direction normal to the surface. In this study, we assume that the electrostatic interactions dominate over the short-range forces that act between the noncharged units. These short-range forces are often attractive and can cause the collapse of the brush. The conditions for such a stretched-to-collapsed transition have been investigated earlier.[3a,2b,15] We do not discuss these conditions here but assume that our system is always found in the swollen state. (We will address the issue of the stretched-to-collapsed transition in the brushes interacting with multivalent ions elsewhere).

We employ a box model to describe the equilibrium properties of our system. In particular, we neglect concentration gradients in the direction normal to the surface and assume that all of the free ends of the chains are located at the outer edge of the brush. We define H as the thickness of the coating, and $c = N/sH$ is the average concentration of the polymer inside the brush. Our previous investigations[3b,11,15] indicated that, as in the case of neutral systems, gradients in the polymer concentration do not change the scaling laws for averaged characteristics of charged brushes.

Ionization of the tethered polyions affects the distributions of the mobile ions in the system. Namely, the concentrations of positively charged counterions in the brush exceed their bulk values, whereas the concentrations of negatively charged coions in the brush become less than the bulk values. However, on average the brush remains electrically neutral. This assumption is referred to as the local electroneutrality approximation,[3a,b,11,14] and we shall use it throughout this study. We introduce the respective local concentrations c_H, c_X^-, c_S^+ and c_S^- of the H^+, X^-, S^+, and S^- ions inside the brush. The differences in the local brush concentrations of the ions with respect to their bulk values give rise to an excess osmotic pressure, π, which has the approximate form

$$\pi/kT = c_H + c_X^- + c_S^+ + c_S^- - 2\Phi_X - (q+1)\Phi_s \quad (3)$$

In terms of the model, this osmotic pressure determines the value of the stretching force, $f_{str} = \pi s$, which acts on a tethered polyion. The equilibrium end-to-end distance (or, equivalently, the brush thickness H) is determined by the balance of the electrostatic force, f_{str}, and the elastic force, f_{el}, which is due to entropy losses caused by chain stretching. Assuming the Gaussian elasticity for the tethered polyions (that is, $f_{el} = kTH/a^2N$), we can write the balance of these forces as

$$\pi/kT = \frac{1}{a^2cs^2} \quad (4)$$

(Note that here and below, all numerical coefficients are omitted in all equations.)

Equations 3 and 4 relate the polymer concentration in the brush, c, to the local concentrations of mobile ions. To find additional relationships between those concentrations, we employ the condition of local electroneutrality and the Donnan rule. Because the specific implementation of those arguments depends on the sign of multivalent ions, we will now consider the cases of positively and negatively charged multivalent ions separately.

Multivalent Coions. We start with the negatively charged multivalent salt coions. The condition of local electroneutrality in the brush yields

$$\alpha c + qc_S^- + c_X^- = c_H + c_S^+ \quad (5)$$

where α is the degree of ionization of tethered polyions (and αc is the corresponding concentration of the immobilized charge in the brush).

The Donnan rule relates the local concentrations of mobile ions in the brush to their bulk values

$$\frac{c_S^-}{\Phi_s} = \left(\frac{c_X^-}{\Phi_X}\right)^q = \left(\frac{\Phi_H}{c_H}\right)^q = \left(\frac{q\Phi_s}{c_S^+}\right)^q \quad (6)$$

Let us recollect that the Donnan equilibrium implies the distribution of all mobile charged species according to their Boltzmann factors. In other words, the probability of finding an ion of a given valency z_i inside the brush is proportional to $\exp(-z_ie\Psi/kT)$, where Ψ is the excess electrostatic potential in the brush with respect to the bulk solution. Applying this argument to the charged ions of all types (i.e., to multivalent coions and all other monovalent ions), we arrive at eq 6.

Equations 3−6 can reduce to the following two equations:

$$\alpha c + q\Phi_s\left(\frac{\Phi_H}{c_H}\right)^q + \Phi_H\left(\frac{\Phi_H}{c_H}\right) = c_H + q\Phi_s\left(\frac{c_H}{\Phi_H}\right) \quad (7)$$

and

$$c_H + \Phi_s\left(\frac{\Phi_H}{c_H}\right) + \Phi_H\left(\frac{\Phi_H}{c_H}\right) + q\Phi_s\left(\frac{c_H}{\Phi_H}\right) - 2\Phi_H - (1+q)\Phi_s = \frac{1}{a^2s^2c} \quad (8)$$

Equations 7 and 8 describe both the quenched and the annealed systems. However, for annealed polyelectrolytes, the degree of ionization, α, depends on the local pH inside the brush as

$$\alpha \approx \frac{K}{c_H} \quad (9)$$

Thus, we will always take into account eq 9 in our analysis of annealed polyelectrolytes.

Multivalent Counterions. We now formulate the conditions of brush electroneutrality and of the Donnan equilibrium for the case of positively charged multivalent salt counterions. The electroneutrality of the brush yields

$$\alpha c + c_S^- + c_X^- = c_H + qc_S^+ \quad (10)$$

whereas the Donnan rule gives

$$\frac{c_S^+}{\Phi_s} = \left(\frac{c_H}{\Phi_H}\right)^q = \left(\frac{q\Phi_s}{c_S^-}\right)^q = \left(\frac{\Phi_X}{c_X^-}\right)^q \quad (11)$$

Here, the degree of ionization α is again determined by eq 9. After some transformations, we have

$$\alpha c + q\Phi_s\left(\frac{\Phi_H}{c_H}\right) + \Phi_H\left(\frac{\Phi_H}{c_H}\right) = c_H + q\Phi_s\left(\frac{c_H}{\Phi_H}\right)^q \quad (12)$$

$$c_H + q\Phi_s\left(\frac{\Phi_H}{c_H}\right) + \Phi_H\left(\frac{\Phi_H}{c_H}\right) + \Phi_s\left(\frac{c_H}{\Phi_H}\right)^q - (1+q)\Phi_s - 2\Phi_H = \frac{1}{a^2s^2c} \quad (13)$$

Again, eq 12 ensures the electroneutrality of the brush, whereas eq 13 provides the balance of forces in the tethered polyions.

3. Salt-Free Solution

We start our analysis from the salt-free solution. Here, $\Phi_s = 0$ and assuming that $c_H/\Phi_H \gg 1$, we obtain from eqs 7 and 8 (or eqs 12 and 13)

$$\alpha c \approx c_H \tag{14}$$

and

$$c_H \approx \frac{1}{a^2 s^2 c} \approx \frac{\alpha^{1/2}}{as} \tag{15}$$

In other words, we find here that the charge on the tethered chains is neutralized by hydrogen ions, H^+, and these ions provide the osmotic swelling of the brush. Applying eq 9 for the degree of ionization α, we arrive at the known results for an annealed osmotic brush,[3d]

$$\alpha = (Ksa)^{2/3} = (\alpha_o \Phi_H as)^{2/3} \tag{16}$$

The corresponding concentration of hydrogen ions in the brush is given by

$$c_H = c_H^* = \frac{(\alpha_o \Phi_H)^{1/3}}{(as)^{2/3}} \tag{17}$$

whereas the average brush thickness H yields

$$H = a\alpha^{1/2} N = a^{4/3} N (\alpha_o s \Phi_H)^{1/3} \tag{18}$$

By comparing c_H (eq 17) with the bulk concentration of H^+ ions, Φ_H, we find that $c_H/\Phi_H \gg 1$ when $s \ll \alpha_o^{3/4}(a\Phi_H)^{-1}$. We assume below that this inequality is always fulfilled.

4. Salt Solution

Addition of salt to the bulk solution leads to the redistribution of all mobile ions in the system. The brush "responds" to the variations in the ionic atmosphere by adjusting the degree of chains ionization. We focus first on the case of relatively low ionic strengths in the bulk solution.

Low Salt Concentrations. At low salt contents, the average concentrations of co- and counterions in the brush remain essentially different from the values in the bulk solution. This is due to excess electrostatic potential in the tethered layer. As a result, the local pH in the brush is lower than the bulk value ($c_H \gg \Phi_H$). We refer to this regime as the osmotic regime. Depending on the sign of the multivalent salt ion, qualitatively different behavior of the system is observed in this range of ionic strengths. Below, we consider separately the cases of multivalent coions and counterions. To simplify the analysis, we assume that $q \gg 1$. This approximation will allow us to establish asymptotical laws for ions distributions.

Multivalent Coions. The concentrations of the immobilized charge on the chains, αc, and those of mobile hydrogen ions, c_H, are given in this case by eqs 7 and 8. By substituting αc from eq 7 into eq 8 and using the inequality $c_H/\Phi_H \gg 1$, we obtain the following approximate equation for concentration of hydrogen ions, c_H:

$$\left(\frac{c_H}{\Phi_H} + \frac{c_H}{q\Phi_s}\right)\left(\frac{c_H}{\Phi_H} + \frac{c_H}{q\Phi_s} - \frac{1+q}{q}\right) = \frac{\alpha}{q^2 \Phi_s^2 a^2 s^2} \tag{19}$$

By solving this equation with respect to c_H, we find that when $\alpha/(q^2\Phi_s^2a^2s^2) \gg 1$, we have

$$\alpha c \approx c_H \left(\frac{q\Phi_s + \Phi_H}{\Phi_H}\right) \approx \frac{\alpha^{1/2}}{as} \tag{20}$$

whereas when $q^{-1} < \alpha/(q^2\Phi_s^2a^2s^2) < 1$, we obtain

$$\alpha c \approx q\Phi_s \left(\frac{c_H}{\Phi_H}\right) \approx \frac{1+q}{q}\sqrt{q\Phi_s} \approx q\Phi_s \tag{21}$$

Note that all numerical coefficients are omitted. The degree of ionization, α, is determined by eqs 9 and 20 as

$$\alpha = \alpha_o \frac{(as)^{2/3}\Phi_H^{1/3}(\Phi_H + q\Phi_s)^{2/3}}{K^{1/3}} \tag{22}$$

As follows from eq 22, the increase in Φ_s leads to the corresponding increase in α. The effect of the coion valency is manifested by the numerical factor, q, in eq 22.

Equation 22 indicates that α attains its bulk value (that is, $\alpha = \alpha_o$) when $q\Phi_s \approx K^{1/2}\Phi_H^{-1/2}(as)^{-1} = (c_H^*)^{3/2}\Phi_H^{-1/2}$. In terms of the scaling model, at this salt concentration, $\alpha/(q^2\Phi_s^2a^2s^2)$ is equal to unity. At larger values of Φ_s, α remains unaffected by variations in bulk ionic strength. Thus, dependence 21 implies that $\alpha \approx \alpha_o$.

Under the conditions when $\alpha/(q^2\Phi_s^2a^2s^2 \gg 1$, the average thickness of the brush, H, is determined by eqs 20 and 22 as

$$H = \frac{N}{cs} = a\alpha^{1/2}N = a^{4/3}\alpha_o^{1/2}\frac{\Phi_H^{1/6}(\Phi_H + q\Phi_s)^{1/3}s^{1/3}}{K^{1/6}} N \tag{23}$$

At larger salt concentrations (corresponding to $\alpha/(q^2 \Phi_s^2a^2s^2 < 1)$, we obtain from eq 21,

$$H \approx \frac{\alpha_o N}{q\Phi_s s} \tag{24}$$

We note that a similar dependence for H was obtained by Zhulina et al.[12] for the case of quenched brush immersed in a salt solution with multivalent coions. As discussed by Zhulina et al.,[12] this regime becomes possible at moderate salt concentrations. Here, the electrostatic potential within the brush provides already almost uniform distribution for monovalent counterions but is still sufficiently high to prevent the penetration of multivalent coions into the brush. Under these conditions, the charge balance in the brush, $\alpha c \approx q\Phi_s$, leads to the dependence in eq 24.

The crossover of dependences 23 and 24 yields $q\Phi_s = (c_H^*)^{3/2}\Phi_H^{-1/2} = \alpha_o^{1/2}/(as)$. At this salt concentration, H attains the value of $H = a\alpha_o^{1/2}N$. We thus find that in the range of relatively low ionic strengths of the solution the brush thickness H increases as $H \sim q\Phi_s^{1/3}$ (eq 23), passes through a maximum at $q\Phi_s \approx (c_H^*)^{3/2}\Phi_H^{-1/2}$, and then decreases as $H \sim q\Phi_S^{-1}$ (eq 24).

We emphasize that although the valency of coion, q, appears in eqs 23 and 24 in this concentration range the coions are excluded from the brush and the actual screening of electrostatic interactions between tethered polyions is performed by monovalent salt counterions. In other words, the effect of coion valency, q, reduces to the variation in the bulk concentration $q\Phi_s$ of salt counterions.

Multivalent Counterions. In the case of multivalent salt counterions, we use eqs 12 and 13 to determine αc and c_H. By taking advantage of the inequality $c_H/\Phi_H \gg 1$, we obtain from eq 12

$$\alpha c \approx c_H + q\Phi_s\left(\frac{c_H}{\Phi_H}\right)^q \tag{25}$$

By substituting eq 25 into eq 13 we have

$$\left[\frac{c_H}{q\Phi_s} + \left(\frac{c_H}{\Phi_H}\right)^q\right]\left[\frac{c_H}{q\Phi_s} + \frac{1}{q}\left(\frac{c_H}{\Phi_H}\right)^q\right] \approx \frac{\alpha}{q^2\Phi_S^2a^2s^2} \tag{26}$$

At extremely low salt concentrations, $\Phi_s \to 0$, the first terms in both brackets on the left hand side of eq 26 remain dominant, and the system exhibits "salt-free" behavior. Namely, the neutralization of the brush charge and osmotic swelling are carried out by hydrogen ions. Here, the characteristics of the brush are given by eqs 16−18. The end of the salt-free regime occurs when $c_H/q\Phi_s = (c_H/\Phi_H)^q$ or when salt counterions start to participate in the neutralization of the brush charge. In scaling terms, this happens when the salt concentration attains the value of

$$q\Phi_s = q\Phi_S^* = c_H^*\left(\frac{\Phi_H}{c_H^*}\right)^q \tag{27}$$

At larger salt concentrations, we can single out a narrow range of ionic strengths where $q^{-1}(c_H/\Phi_s)^q < c_H/q\Phi_s < (c_H/\Phi_s)^q$. (Note that in our analysis $q \gg 1$.) Here, the charge on polyions is neutralized by salt counterions (i.e., $\alpha c \approx qc_S^+ = q\Phi_s(c_H/\Phi_H)^q$), whereas the osmotic pressure is still determined by hydrogen ions (that is, $c_H \gg c_S^+ = \Phi_s(c_H/\Phi_H)^q$). In this case, eq 26 reduces to

$$\left(\frac{c_H}{\Phi_H}\right)^{q+1} = \frac{\alpha}{\Phi_H q\Phi_s s^2a^2} \tag{28}$$

Applying eqs 9 and 17, we obtain from eq 28 the following expression for the degree of ionization α:

$$\alpha = \alpha_o\left(\frac{\Phi_H}{c_H^*}\right)^{2/(q+2)}\left(\frac{q\Phi_s}{c_H^*}\right)^{1/(q+2)} \tag{29}$$

whereas the brush thickness H scales here as

$$H = a^{4/3}(\alpha_o s\Phi_H)^{1/3}N\left(\frac{\Phi_H}{c_H^*}\right)^{q/(q+2)}\left(\frac{q\Phi_s}{c_H^*}\right)^{-1/(q+2)} \tag{30}$$

The end of this regime is determined by the condition $c_H = c_S^+$ or when

$$q\Phi_s = q\Phi_S^{**} = c_H^*\left(\frac{\Phi_H}{c_H^*}\right)^q q^{(q+2)/3} = q\Phi_S^*q^{(q+2)/3} \tag{31}$$

At larger salt concentrations, salt counterions ensure both the charge neutralization and the osmotic swelling of the brush. Here, eq 26 reduces to

$$\left(\frac{c_H}{\Phi_H}\right)^{2q} = \frac{\alpha}{q\Phi_S^2s^2a^2} \tag{32}$$

and eq 9 provides the following dependence for the degree of ionization α:

$$\alpha = \alpha_o\left(\frac{\Phi_H}{c_H^*}\right)^{1/(2q+1)}\left(\frac{q\Phi_s}{c_H^*}\right)^{2/(2q+1)}q^{-1/(2q+1)} \tag{33}$$

Correspondingly, the brush thickness H scales here as

$$H = a\alpha^{1/2}Nq^{-1/2} = a\alpha_o^{1/2}N\left(\frac{\Phi_H}{c_H^*}\right)^{1/2(2q+1)}\left(\frac{q\Phi_s}{c_H^*}\right)^{1/(2q+1)}q^{-(1+q)/(1+2q)} \tag{34}$$

We thus find that the valency of the salt counterion (value of q) affects the exponents in the scaling dependences for α and H. In contrast to the case of multivalent salt coions, mono-, di-, and trivalent counterions provide different scaling laws for the characteristics of the brush. More specifically, our findings indicate that salt counterions with higher valency provide weaker dependences of brush thickness on salt concentration, $H \simeq \Phi_s^{1/(1+2q)}$. In addition, the range of the "salt-free" behavior of the system decreases exponentially with increasing q (see eq 27).

High Salt Concentrations. At large concentrations of salt in the bulk solution, excess electrostatic potential in the tethered layer diminishes, and the concentrations of mobile ions inside and outside the brush become almost equal. In this range of ionic strengths, we have $\alpha/(q\Phi_S^2a^2s^2) \ll 1/q$ and $c_H/\Phi_H \approx 1$. Here, we search for the solution of eqs 7 and 8 by applying the following expansion:

$$\frac{c_H}{\Phi_H} = 1 + b\left(\frac{\alpha}{q\Phi_S^2a^2s^2}\right)^{1/3} \tag{35}$$

where $b(q)$ is the unknown coefficient. By substituting eq 35 into eqs 7 and 8, we obtain after some transformations,

$$b = \left[\frac{2}{q(q+1)^2}\right]^{1/3} \tag{36}$$

(The same result for b is obtained if we use eqs 12 and 13 instead of eqs 7 and 8.) By substituting expressions 35 and 36 into eq 7, we find

$$\alpha c \approx 2^{1/3}q^{1/3}(1+q)^{1/3}\alpha^{1/3}\Phi_s^{1/3}(as)^{-2/3} \tag{37}$$

Taking into account the fact that at high salt concentrations in the bulk solution $\alpha = \alpha_o$, we find from eq 37 that the brush thickness H scales here as

$$H = a^{2/3}\alpha_o^{2/3}N[q(q+1)\Phi_s s]^{-1/3} = a^{2/3}\alpha_o^{2/3}N[sI]^{-1/3} \tag{38}$$

where $I = q^2\Phi_s + q\Phi_s$ is the ionic strength of the solution. In other words, at high salt concentrations (or, in the salt-dominance regime), the effect of ion valency is manifested by variations in the net ionic strength of

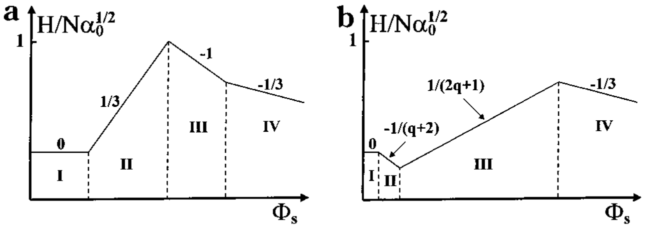

Figure 2. Reduced brush thickness $H/\alpha_o^{1/2}N$ vs Φ_s for the cases of (a) multivalent salt coions and (b) counterions. The numbers at the curves are the values of the exponents, d(log H)/d(log Φ_s). Regions I–IV and the boundaries between different regions are discussed in the text.

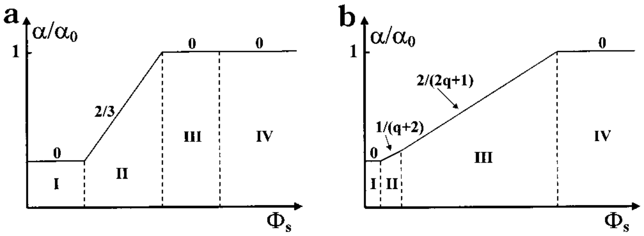

Figure 3. Reduced degree of ionization α/α_o vs Φ_s for the cases of (a) multivalent salt coions and (b) counterions. The numbers at the curves are the values of the exponents, d(log α)/d(log Φ_s). Regions I–IV and the boundaries between different regions are discussed in the text.

the bulk solution. Here, the sign of the multivalent ion is of no importance.

The condition of crossover of dependences 24 and 34 with dependence 38 indicates that the transition into the salt-dominance regime occurs when salt concentration attains the value of $q\Phi_s = q\Phi_S^{***} = q^{1/2}(c_H^*)^{3/2}\Phi_H^{-1/2}$. At $\Phi_s < \Phi_S^{***}$, the brush exhibits the osmotic regimes, whereas at $\Phi_s > \Phi_S^{***}$, the system is found in the salt-dominance regime. Increases in the ion valency q shift the transition concentration to lower values of Φ_s.

Figures 2 and 3 demonstrate schematics for the reduced brush thickness, $H/aN\alpha_o^{1/2}$, and the degree of ionization, α/α_o, as functions of salt concentration Φ_s. In the case of multivalent coions (Figures 2a and 3a), we distinguish four regions of salt concentrations where the characteristics of the brush obey different scaling laws. That is, at low Φ_s (region I corresponding to $q\Phi_s \ll \Phi_H$), H and α are given by eqs 16 and 18 (or, equivalently by eqs 23 and 22 at $\Phi_s = 0$). At higher values of Φ_s [region II corresponding to $\Phi_H < q\Phi_s < (c_H^*)^{3/2}\Phi_H^{-1/2}$], the scaling dependences for H and α are given by eqs 23 and 22 at $\Phi_H = 0$. In region III [located at $(c_H^*)^{3/2}\Phi_H^{-1/2} < q\Phi_s < q^{1/2}(c_H^*)^{3/2}\Phi_H^{-1/2}$], α equals α_o, whereas H is determined by eq 24. Finally, in the salt-dominance regime IV [or at $q\Phi_s > q^{1/2}(c_H^*)^{3/2}\Phi_H^{-1/2}$], H is given by eq 38. (Numbers at the curves indicate the values of the corresponding exponents.)

In the case of multivalent counterions (Figures 2b and 3b), we also distinguish four different regions. The first two regions (I and II, corresponding to $\Phi_s < \Phi_S^*$ and $\Phi_s^* < \Phi_s < \Phi_S^{**}$; see eqs 27 and 31) are located at extremely small salt concentrations. Here, the brush characteristics are determined by eqs 16 and 18 and 29 and 30 in regions I and II, respectively. In region III (i.e., at $\Phi_s^{**} < \Phi_S < \Phi_S^{***}$), H and α are given by eqs 33 and 34, whereas in the salt-dominance region IV ($\Phi_s > \Phi_S^{***}$), $\alpha = \alpha_o$ and H is determined by eq 38. We emphasize that these figures are schematic and serve to illustrate the scaling laws derived in this section, rather than provide a precise description of the system.

5. Stabilizing Force

The results of previous sections apply to a single brush that is in thermodynamic equilibrium with the bulk solution. Here, the elastic force due to the stretching of polyions is balanced by the osmotic pressure of all mobile ions. Compression of this brush causes a decrease in the elastic force (chains are less stretched) and an increase in the osmotic pressure of ions owing to the redistribution in the ionic atmosphere. As a result, we find a restoring (or stabilizing) force, f, that opposes the compression. The value of this force (per unit area) is given by

$$f/kT = f_{\mathrm{str}}/kT - f_{\mathrm{el}}/kT = a^2\pi/kT - \frac{1}{s^2c} \quad (39)$$

where π is given by eq 3.

The polyions are tethered irreversibly, and therefore, layer deformation leads to an increase in polymer concentration in the brush as $c = N/sD$, where $D < H$ is the thickness of the compressed layer. Below, c is used as a measure of compression, and the force versus deformation profile is examined in various ranges of salt concentration in the bulk solution.

When $D = H$, the brush is not deformed, $f_{\mathrm{el}} = f_{\mathrm{str}}$, and correspondingly, $f = 0$. At relatively strong compression, the contribution due to f_{el} in eq 39 can be neglected, and the value of the restoring force, f, is then solely determined by f_{str} (or the osmotic pressure of the mobile ions, π). We now derive the scaling laws for f in this range of deformations. As in the previous section, we consider the cases of multivalent co- and counterions separately.

Multivalent Coions. In the case of multivalent salt coions, the condition of electroneutrality of the brush and the Donnan rule are given by eqs 5 and 6, respectively. These relationships hold for both nondeformed and compressed layers. We employ them now to derive the expressions for the restoring force, $f \approx a^2\pi$.

Low Φ_s. At low salt concentrations in the bulk solution (regions I and II in Figure 2a), the brush charge is neutralized by H^+ ions and salt counterions, and we have from eq 5

$$\alpha c \approx c_H + c_S^+ \quad (40)$$

These ions are also responsible for the osmotic swelling of the brush. By retaining the dominant terms, we find from eq 3,

$$\pi/kT \approx c_H + c_S^+ \quad (41)$$

We thus obtain

$$\pi = \alpha c \quad (42)$$

The degree of ionization α is determined by the local pH in the brush as $\alpha = K/c_H$. By employing the Donnan rule (eq 6) and using the definition of α_o (eq 2), we obtain from eq 40,

$$\alpha = \sqrt{\frac{\alpha_o(\Phi_H + q\Phi_s)}{c}} \quad (43)$$

We thus arrive at the expression for the stabilizing (restoring) force

$$f/kT \approx a^2\sqrt{\alpha_o c(\Phi_H + q\Phi_s)} \qquad (44)$$

Moderate Φ_s. In the range of salt concentrations corresponding to region III in Figure 2a, π is still given by eq 42. However, in terms of the scaling model, here α is already close to its bulk value, $\alpha = \alpha_o$. Correspondingly, the restoring force f scales here as

$$f/kT = a^2\alpha_o c \qquad (45)$$

We note, however, that region III is rather narrow for experimentally accessible values of $q = 1-3$. Hence, it is expected that dependence 45 will be hardly detectable for conventional low-molecular-weight salts.

High Φ_s. In the limit of high salt contents (region IV in Figure 2a), the concentrations of all mobile ions inside and outside the layer are almost equal, and $c_H/\Phi_H \approx 1$. Here, the degree of ionization α equals α_o, and $\alpha c \ll q\Phi_s$. We now employ the following expansion:

$$\frac{c_H}{\Phi_H} = 1 + b_1\left(\frac{\alpha c}{q\Phi_s}\right) + b_2\left(\frac{\alpha c}{q\Phi_s}\right)^2 + ... \qquad (46)$$

where $b_1(q)$ and $b_2(q)$ are the unknown coefficients. By substituting eq 46 into eq 5 and retaining the relevant terms, we find $b_1 = 1/(q + 1)$ and $b_2 = q/2(q + 1)^2$. By substituting the expansion for c_H/Φ_H in the expression for π (eq 3), we arrive at the following result for the restoring force,

$$f/kT = \frac{a^2\alpha_o^2c^2}{2q(q+1)\Phi_s} \sim \frac{\alpha_o^2a^2c^2}{I} \qquad (47)$$

Equation 47 indicates that at high ionic strengths of the solution (i.e., in the salt-dominance regime) electrostatic interactions in the brush can be expressed through binary contacts between polymer units ($f \sim c^2$) with an effective virial coefficient $v_{\mathrm{eff}} \simeq l_B\alpha_o^2r_D^2$. In other words, the force profile has the same shape as in neutral polymer brushes immersed in a good solvent.

We therefore find that in the case of multivalent coions the force versus deformation profiles are determined by different scaling laws at low and high ionic strengths of the solution. Namely, at low ionic strengths, $f \sim c^{1/2}$, whereas at high ionic strengths, $f \sim c^2$. At low ionic strengths, the effect of coion valency, q, is manifested by the variation in the bulk concentration of salt counterions, $q\Phi_s$ (here, f depends on $q\Phi_s$, according to eq 44), whereas at high ionic strengths, $f \sim 1/I$ (i.e., the restoring force is determined by the net ionic strength of the bulk solution according to eq 47).

Multivalent Counterions. We now consider the case of multivalent salt counterions. In this case, the condition of electroneutrality and the Donnan rule are given by eqs 10 and 11, respectively. We will not consider here very small salt concentrations corresponding to regions I and II but will focus on the range of relatively small salt concentrations, $q\Phi_s > q\Phi_S^{**}$, corresponding to region III in Figure 2b.

Low Φ_s. In the range of salt concentrations $q\Phi_s > q\Phi_s^{**}$, neutralization and swelling of the brush are carried out by salt counterions. Here, eqs 4 and 10 give

$$\alpha c \approx qc_S^+ \qquad (48)$$

and

$$\pi/kT \approx c_S^+ \qquad (49)$$

As a result, the osmotic pressure yields

$$\pi/kT = \alpha c/q \qquad (50)$$

where $\alpha = K/c_H$. By employing the Donnan rule (eq 11) and using the definition of α_o (eq 2), we obtain

$$\alpha = \alpha_o\left(\frac{c_S^+}{\Phi_s}\right)^{-1/q} = \alpha_o\frac{\Phi_s^{1/q}}{\pi^{1/q}}(kT)^{1/q} \qquad (51)$$

By substituting eq 51 into eq 50, we arrive at the scaling expression for the restoring force

$$f/kT = a^2\left(\frac{\alpha_o c}{q}\right)^{q/(q+1)}\Phi_s^{1/(q+1)} \qquad (52)$$

Hence, the valency q of the salt counterion affects the shape of the force versus deformation profile at small ionic strengths of the solution: $f \sim c^{q/(q+1)}$.

High Φ_s. At high salt concentrations in the bulk solution (region IV in Figure 2b), we arrive at eqs 46 and 47. Here, the sign of the multivalent ions does not play any role, and the force versus deformation profile is determined by the net ionic strength of the solution I according to eq 47.

6. Discussion

Our findings indicate that the sign and the valency of salt ions can considerably affect the properties of the annealed polylectrolyte layers. At high salt concentrations, the features of salt ions are manifested by the net ionic strength of the solution, $I = (q^2 + q)\Phi_s$. In contrast, at low salt contents, a polyelectrolyte brush becomes sensitive not only to the valency but also to the sign of the multivalent salt ion. We find a markedly different behavior of a polyelectrolyte brush in dilute salt solutions with multivalent co- and counterions.

Figures 2 demonstrate the brush thickness H as a function of salt concentration Φ_s for the two types of multivalent salt ions (co- and counterions). As seen from these figures, in both cases, H passes through a maximum at moderate salt concentrations. However, in the case of multivalent counterions (Figure 2b), the maximal value, $H_{\max}$, is smaller by a factor of $q^{1/2}$ than that in the case of multivalent coions (Figure 2a). Hence, salts with multivalent counterions are more effective in screening the electrostatic interactions in tethered polyelectrolytes at low ionic strengths of the solution.

Moreover, in the case of multivalent salt counterions, the scaling exponents become sensitive to the counterion valency. In other words, the slopes of the curves in Figures 2 and 3 are determined by the value of q. Note that the slopes change most in the experimentally accessible range of q (that is, at $q = 1-3$). It is, therefore, expected that the difference in the behavior of polyelectrolyte brushes immersed in dilute solutions of salts with $q = 1-3$ can be detected experimentally. Recent experimental studies of Zhang et al.[21] on hydrophobically modified polyelectrolytes demonstrated a considerable effect of salt valency on the threshold of adsorption in these systems. Namely, in the case of the divalent salt $CaCl_2$, adsorption of charged chains with short anchoring blocks was detected at salt contents lower than those in the case of NaCl. These observations are consistent with our prediction on the stronger screening in polyelectrolyte brushes by multivalent salt ions.

The dependence of scaling exponents on q is also expected in deformed brushes. We predict, in particular, that the valency of salt counterion affects the shape of the force versus deformation profile when two brushes are put into close contact or the brush is compressed by a bare surface. Equation 52 indicates that in the case of multivalent counterions and at low ionic strengths of the solution $f \sim c^{q/(q+1)}$. In the case of multivalent coins, eq 44 gives $f \sim c^{1/2}$ under similar conditions. (For monovalent salts with $q = 1$, eqs 52 and 44 give the same result, $f \sim c^{1/2}$.) Hence, at low ionic strengths of the solution, the dependence of force f on deformation (or, equivalently, on $c \sim 1/D$) is weaker than that at high ionic strengths when $f \sim c^2$ (eq 47).

Our findings indicate that variation in the degree of ionization of annealed polyelectrolytes at low ionic strengths of the solution is manifested by an "abnormal" dependence of f on Φ_s. In other words, owing to the shift in ionization equilibrium, the value of force f *increases* with increases in Φ_s. This effect is predicted for both types of the multivalent salt ions. However, specific scaling laws are different for the counterions and the coions. Namely, eqs 52 and 44 give $f \sim (\Phi_s)^{1/(q+1)}$ and $f \sim (\Phi_s)^{1/2}$, respectively. In addition, the range of deformations in which this force acts becomes more extended (as a result of an increase in the thickness of the undeformed brush, H, according to eqs 34 and 23). On the other hand, at high ionic strengths, both H and f decrease with increases in Φ_s. According to eqs 38 and 47, we have here $H \sim \Phi_s^{-1/3}$ and $f \sim \Phi_s^{-1}$. Thus, the compression of a polyelectrolyte layer in solution with increasing ionic strength will lead to a rather complicated behavior of the force versus deformation profile. Initially, increases in Φ_s will lead to the corresponding increases in both the distance at which the force becomes detectable and the net value of force. (In terms of the model, this distance is associated with the thickness of an undeformed layer, H). However, at high ionic strengths (i.e., in the salt-dominance regime), the effect will be reversed: both H and f will diminish with further increases in Φ_s. The shape of the profile will also change according to eq 47.

A similar behavior of deformed polyelectrolyte layers has recently been observed experimentally by Shorr and Tirrell,[22] who measured the force between two compressed annealed brushes formed by PS−PAA copolymers. They found a nonmonotonic shift in the force versus deformation profiles as the bulk concentration of a low-molecular-weight salt (NaCl) was varied. The shapes of the profile were also different at high and low contents of the salt. These experimental observations are in agreement with our predictions and highlight the effect of charge annealing on the stabilizing properties of polyelectrolyte layers. Further experiments are in progress that will facilitate a more precise comparison between the theory and the experiment.

In conclusion, we emphasize that though the force versus deformation profiles obtained in this paper were derived for a compressed annealed brush, they hold for a wider class of polymer layers, in particular for the layers where the polyelectrolyte chains are annealed and the density of polymer per unit area is fixed. We, therefore, expect the same scaling laws for the restoring force caused by compression of the irreversibly adsorbed polyelectrolyte layer (typical protective coatings on colloid particles). The results of our study demonstrate that the stabilizing force can effectively be varied by additions of multivalent ions. Thus, low-molecular-weight salts with proper valencies of the ions could serve for mediating the interactions between charged layers and tailoring the stabilizing properties of polymer coatings for desired applications.

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