

Numerical Study of the Interplay of Monomer-Surface Electrostatic and Non-electrostatic Interactions in the Adsorption of Weak Polyelectrolytes on Oppositely Charged Surfaces*

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Abstract The adsorption of weak polybase on oppositely charged planar surfaces has been investigated numerically by using the self-consistent field theory (SCFT). Particular attention was paid to the interplay of monomer-surface electrostatic and non-electrostatic interactions in the adsorption behaviors of weak polybase. In this study, the strength of monomer-surface non-electrostatic interactions was set to be no more than the thermal energy $k_B T$. It was found from the numerical study that in the regime of low surface charge density of the substrate and low pH or high bulk degree of ionization, both the screening-enhanced and screening-reduced salt effects emerge. On the contrary, in the opposite regime, only the screening-reduced salt effect was observed. Moreover, the overall charge neutrality inside the adsorption layer was analyzed. The underlying mechanism governing the adsorption behaviors of weak polybase on oppositely charged surfaces was elucidated.

Keywords: Polyelectrolyte adsorption; Self-consistent field theory; Non-electrostatic interaction.

INTRODUCTION

The adsorption of polyelectrolytes (PEs) on oppositely charged surfaces is of great importance from both fundamental and technological perspectives. The phenomenon of PE adsorption has drawn intense theoretical and experimental research efforts^[1–7]. In spite of significant advance in our understanding of PE adsorption, many conceptual questions remain open. This is mainly due to the complex interplay and competition among different interactions over a wide range of length scales, as well as very large parameter space involved in the problem.

From the studies of PE adsorption on charged surfaces, it has become apparent that electrostatic interaction is not the sole governing force. Non-electrostatic interactions play an important role in PEs adsorption and can even dominate over electrostatic interaction in certain situations^[8–16]. The experimental finding that the adsorbed amount of PE increases with increasing salt concentration, which corresponds to the so-called screening-enhanced salt effect, unequivocally shows the important role played by non-electrostatic monomer-surface interactions in PE adsorption^[13]. In the atomic force microscope (AFM) experiment of peeling single polyacrylic acid and polyallylamine molecules from solid substrates, it was found that the non-electrostatic contribution to the adsorption energy is $3k_B T$ to $6k_B T$ per monomer and non-electrostatic interactions dominate even for highly charged substrates^[9].

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Previous theoretical and computational studies of PE adsorption taking into account the non-electrostatic monomer-surface interaction mainly focused on strong polyelectrolytes whose ionizable functional groups fully dissociate in aqueous solutions^[17–19]. However, most of the experiments concerning PE adsorption involve weak polyelectrolytes whose ionizable functional groups participate in acid-base chemical equilibrium^[20–24]. Thus, the physiochemical conditions of the aqueous solution such as pH can significantly affect the adsorption behaviors of weak PEs on oppositely charged surfaces. Moreover, in the vicinity of oppositely charged surfaces, the local degree of ionization of weak PEs will deviate strongly from the bulk value. Therefore, the adsorption of weak polyelectrolytes on oppositely charged surfaces taking into account non-electrostatic monomer-surface interactions warrant further theoretical and computational investigations.

In this work, the continuum self-consistent field theory (SCFT) was employed to numerically study the adsorption of weak polybase on oppositely charged planar surfaces, taking into account the short-range monomer-surface non-electrostatic interaction. Compared with the adsorption behaviors of strong polyelectrolytes, new and interesting features arise for weak polyelectrolytes, as will be presented and discussed in subsequent sections.

MODEL AND METHODS

The system considered in this work comprises an aqueous solution of weak polybase in contact with an infinitely large planar and negatively charged solid surface. A Cartesian coordinate system was set up such that the x axis is normal to the planar substrate and the coordinate of the substrate is $x = 0$. The surface charge density of the uniformly charged planar substrate is denoted as σ_e (in units of number of elementary charges per unit area and $\sigma_e < 0$). Assuming lateral homogeneity for all of the relevant physical quantities along the surface of the uniformly charged substrate, *i.e.*, the y - z plane, the problem is reduced from three-dimensional (3D) to one-dimensional (1D), and each 3D physical quantity can be viewed as a 1D property on a per unit area in the x direction basis. To model the short-range attractive monomer-surface non-electrostatic interaction, a short-range field $U(x)$ in the unit of thermal energy $k_B T$ is invoked, which has the following form:

$$U(x) = \begin{cases} 0 & \text{for } x > x_s \\ -u_0 & \text{for } 0 < x \leq x_s \end{cases} \quad (1)$$

where x_s denotes the range of the attractive surface-monomer interaction^[17, 18]. It should be pointed out that, there are two kinds of non-electrostatic interactions. The first kind is the dispersion forces. The second one is the hydrophobic interaction, which is mostly an entropic effect originating from the disruption of the hydrogen bond network and the formation of hydration shell around the non-polar solute. Eq. (1) is a simple and phenomenological approach to modeling monomer-surface attractive non-electrostatic interaction.

In this work, the standard SCFT was employed to numerically study the adsorption of weak polybase on oppositely charged planar surface in the presence of short-range monomer-surface non-electrostatic interaction. As a well-established mean-field theory, SCFT is complimentary to molecular simulations and density functional theory (DFT) in studying multicomponent polymeric systems. The essence of SCFT is that the many-chain problem is transformed into one of an effective single flexible chain in a mean-field, which is determined self-consistently^[25, 26].

For brevity, the dimensionless 1D SCF equations in terms of the volume fraction of each species in the solution are listed in the following. The detail of the derivation of the equations can be found in reference [27].

$$\omega_p(x) = \chi_{ps} N \phi_s(x) + \eta(x) + N U(x) - N \cdot \ln \{1 - f_b + f_b \exp[-\psi(x)]\} \quad (2)$$

$$\omega_s(x) = \chi_{ps} N \phi_p(x) + \eta(x) \quad (3)$$

$$\omega_{ion}(x) = z_{ion} \psi(x) \quad (4)$$

$$\phi_p(x) = \phi_p^b \int_0^1 ds q(x, s) q(x, 1-s) / \int_0^1 ds q(x \rightarrow +\infty, s) q(x \rightarrow +\infty, 1-s) \quad (5)$$

$$\phi_s(x) = \phi_s^b \exp[\omega_s(x \rightarrow +\infty) / N - \omega_s(x) / N] \quad (6)$$

$$\phi_{ion}(x) = \phi_{ion}^b \exp[\omega_{ion}(x \rightarrow +\infty) - \omega_{ion}(x)] \quad (7)$$

$$\phi_p(x) + \phi_s(x) = 1 \quad (8)$$

$$\varepsilon \frac{d^2 \psi(x)}{dx^2} = -N \sum_{ion} z_{ion} \phi_{ion}(x) - N \phi_p(x) f_b \exp[-\psi(x)] / \{1 - f_b + f_b \exp[-\psi(x)]\} \quad (9)$$

where N is the number of monomers per polyelectrolyte chain, ϕ_j and ϕ_j^b with $j = P, S$, and ion are the dimensionless local and bulk volume fractions of PE chains, solvent molecules, and point-like mobile ions (Na^+ , Cl^- , H^+ , OH^-), χ_{ps} denotes the Flory-Huggins interaction parameter between monomers and solvent molecules, f_b is the bulk charge fraction or bulk degree of ionization of weak polybase chains, $\eta(x)$ is the Lagrange multiplier to enforce the incompressible condition, ω_j denotes the conjugate interaction field within the SCFT formalism, $\psi(x)$ denotes the electric potential field, z_{ion} are for the charge valences of the mobile ions. Moreover, ε stands for the dielectric permittivity of the medium, and for simplicity, it is assumed to be the same as pure water at the room temperature. Note that as $x \rightarrow +\infty$, $\psi \rightarrow 0$.

The propagator $q(x, s)$ in Eq. (5) corresponding to the probability of finding the (Ns) th segment of a polymer chain at x satisfies the following modified diffusion equation:

$$\frac{\partial q(x, s)}{\partial s} = \frac{d^2 q(x, s)}{dx^2} - \omega_p(x) q(x, s) \quad (10)$$

For the weak base type PEs studied here, it is easy to show that

$$pK_w - pH = pK_b + \lg[f_b / (1 - f_b)] \quad (11)$$

where $pK_w \equiv -\lg([H^+][OH^-])$ and $pK_b \equiv -\lg(K_b)$ with K_b the equilibrium constant. Thus, by adding a strong base, *e.g.*, NaOH or a strong acid, *e.g.*, HCl to the bulk solution, the pH of the bulk solution can be adjusted to afford the desired bulk charge fraction f_b .

The local charge fraction of PE chains $f(x)$ is defined as

$$f(x) = f_b \exp[-\psi(x)] / \{1 - f_b + f_b \exp[-\psi(x)]\} \quad (12)$$

To study the charge inversion phenomenon, the parameter of degree of charge compensation is introduced as follows:

$$\Xi = \int_0^\infty f(x) [\phi_p(x) - \phi_f(x)] dx / |\sigma_e| \quad (13)$$

where $\phi_f(x)$ denotes the volume fraction of the free chains in the system. The surface charges are only partially compensated when $\Xi < 1$, exactly compensated when $\Xi = 1$, and over-compensated (charge reversal) when $\Xi > 1$. Charge over-compensation ($\Xi > 1$) is an important and commonly observed feature in polyelectrolyte adsorption on oppositely charged surfaces and polyelectrolyte layer-by-layer (LbL) assembly. Charge over-compensation is the basis for the electrostatically driven layer-by-layer assembly of polyelectrolytes^[28, 29]. To calculate Ξ , the region between the charged surface and the second inflection point of the monomer density profile away from the charged surface is defined as the boundary layer. The thickness of the boundary layer is denoted by L_B . A free chain has no monomer falling inside the boundary layer.

To examine the overall charge neutrality inside the boundary layer, the parameter of degree of charge neutrality inside the boundary layer is invoked as follows

$$\begin{aligned}\Sigma &= \frac{\int_{L_B} [\phi_{Na^+}(x) + \phi_{H^+}(x) - \phi_{Cl^-}(x) - \phi_{OH^-}(x)] dx + \int_0^\infty f(x) [\phi_p(x) - \phi_f(x)] dx - |\sigma_e|}{|\sigma_e|} \\ &= \frac{\int_{L_B} [\phi_{Na^+}(x) + \phi_{H^+}(x) - \phi_{Cl^-}(x) - \phi_{OH^-}(x)] dx}{|\sigma_e|} + \Xi^*\end{aligned}\quad (14)$$

where $\Xi^* = \Xi - 1$. If $\Sigma = 0$, an exact charge neutrality inside the boundary layer is achieved.

In the present study, the chain length of weak polybase was fixed as $N = 50$ with monomer size of $a = 0.7$ nm. The range of the non-electrostatic interaction x_s was set to $1.08a$. Following previous numerical SCFT studies done by us and others^[26, 27], the radius of gyration of a neutral Gaussian chain R_g ($R_g = a\sqrt{N/6}$) was chosen as the length unit to scale all of the relevant physical quantities except for the surface charge density. The product of the surface charge density σ_e and a^2 , which is defined as the dimensionless surface charge density, was varied from 0 to -1.90×10^{-1} , which corresponds to a maximum charge density of $\sigma_e = 3.89 \times 10^{-1}$ nm⁻². The pK_b of the weak polybase was chosen to be 5. The bulk degree of ionization f_b is in the range of 0.06 to 0.4, which corresponds to a range of pH from 10.19 to 9.18. χ_{ps} was set to zero. The dimensionless electric potential is defined as $\psi_{\text{dimensionless}} = e\psi/k_B T$ with e denoting the charge of an electron. The strength of monomer-surface interaction u_0 in units of $k_B T$ was varied from 0.1 to 1.0. The maximum bulk concentration of added salt ions is 0.21, which corresponds to a bulk salt molar concentration of 1.0 mol/L.

The modified diffusion equation and Poisson-Boltzmann type equation were numerically solved by using the standard linear and non-linear multigrid methods^[27]. The boundary condition for the Poisson-Boltzmann type equation is $d\psi(x)/dx|_{x=0} = -\sigma_e/\epsilon$. The grid size of the computational domain is $\Delta x = 1/32R_g$ and the pseudo-time step size is $\Delta x = 1/100$.

RESULTS AND DISCUSSION

The Effects of Surface Charge Density and Bulk pH on the Degree of Charge Compensation

For strong polyelectrolytes, when the monomer-surface non-electrostatic interaction is very weak, the electrostatic attraction between oppositely charged polymer chains and the substrate is the dominant driving force for polyelectrolyte adsorption. With increasing amount of added salt ions, fewer polyelectrolyte chains will be adsorbed on the substrate due to the electrostatic screening from salt ions. This corresponds to the so-called screening-reduced regime. For strong polyelectrolytes at very high strength of monomer-surface non-electrostatic attractive interaction, the non-electrostatic attraction becomes the main driving force for polyelectrolyte adsorption. In this case, the electrostatic repulsion between adsorbed polyelectrolyte chains is the opposing force to polyelectrolyte adsorption. Adding salt ions can alleviate or reduce the electrostatic repulsion between adsorbed polyelectrolyte chains due to the electrostatic screening from salt ions. Therefore, more polyelectrolyte chains will be adsorbed on the substrate with increasing amount of salt ions. This corresponds to the so-called screening-enhanced regime.

It was found from our previous study of the adsorption of strong polyelectrolytes on oppositely charged surfaces that, the desorption-adsorption transition induced by monomer-surface interaction is located around $u_0 \sim 0.3$ ^[18]. In the case of the strength of monomer-surface interaction being lower than this value, the electrostatic screening effect from the added salt ions leads to the eventual desorption of charged polymer chains from the oppositely charged surfaces. For the case of weak polyelectrolytes studied in this paper as shown in Figs. 1 to 3, the transition takes place at $u_0 \sim 0.3-0.4$, which is about the same as that for the case of strong polyelectrolytes. At such a value of u_0 , the boundary layer thickness coincides with the range of surface-monomer non-electrostatic interaction ($1.08a$ or equivalently $0.375 R_g$) (see Fig. 4). As shown in Fig. 1, in the regime of low surface charge density and high bulk degree of ionization or low pH, both screening-reduced and screening-enhanced effects of added salt ions emerge at relatively low and high strengths of monomer-surface non-electrostatic interactions,

Fig. 2 Degree of charge compensation as a function of salt concentration at different strengths of monomer-surface non-electrostatic interaction (The system parameters are $\sigma_e = -0.0476$, $f_b = 0.06$.)

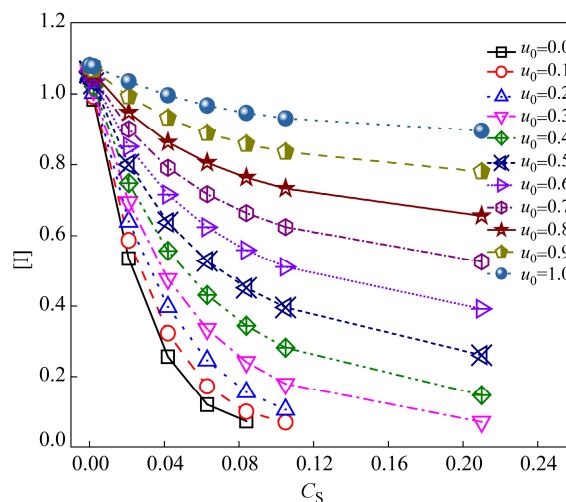


Fig. 3 Degree of charge compensation as a function of salt concentration at different strengths of monomer-surface non-electrostatic interaction (The system parameters are $\sigma_e = -0.190, f_b = 0.4$.)

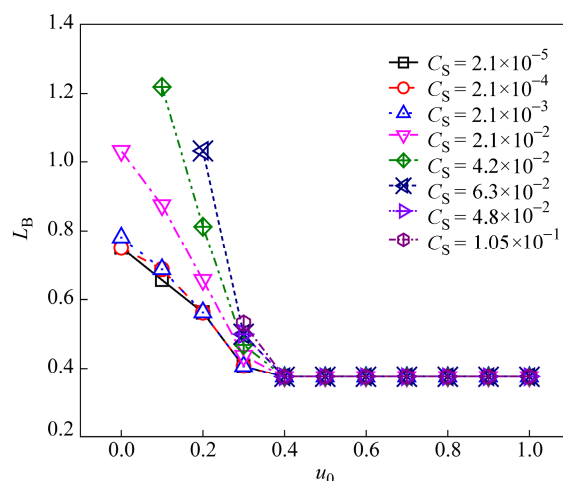


Fig. 4 Boundary layer thickness as a function of strength of monomer-surface interaction at different salt concentrations (The system parameters are $\sigma_e = -0.0476, f_b = 0.4$.)

The Local Degree of Ionization of Weak Polybase

In the absence of monomer-surface non-electrostatic interaction, as shown in Figs. 5 and 6, the local degree of ionization is enhanced for weak polyelectrolytes near an oppositely charged surface, irrespective of surface charge density and bulk degree of ionization. This is because the acid-base ionization equilibrium of the charged monomers shifts toward the right of the equation, *i.e.*, $P + H_2O \rightleftharpoons PH^+ + OH^-$, due to the decrease in the concentration of OH^- near a negatively charged surface. With increasing the strength of monomer-surface non-electrostatic attractive interaction, more polyelectrolyte chains will be adsorbed on the charged substrate, which would lead to stronger electrostatic repulsion between adsorbed polyelectrolyte chains. As a consequence, as shown in Figs. 5 and 6, the local degree of ionization or charge density of weak polybase chains will be reduced in order to alleviate the electrostatic repulsion between adsorbed polyelectrolyte chains. In general, higher concentration of salt ions leads to stronger electrostatic screening effect. As a result, the local degree of ionization or charge density of weak polybase chains near the oppositely charge substrate will be reduced.

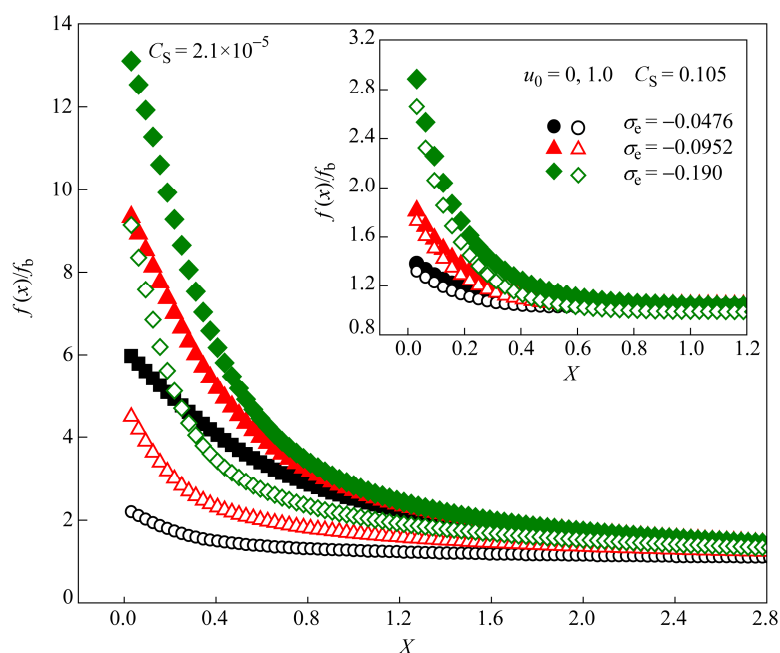


Fig. 5 The local degrees of ionization of weak polybase as a function of the distance from the charged surface with different surface charge densities at a salt concentration of 2.1×10^{-5} and bulk pH = 10.19 corresponding to $f_b = 0.06$. In the figure, the filled and open symbols correspond to $u_0 = 0$ and 1.0, respectively. In the inset, the corresponding profiles of the local degree of ionization at a salt concentration of 0.105 are displayed.

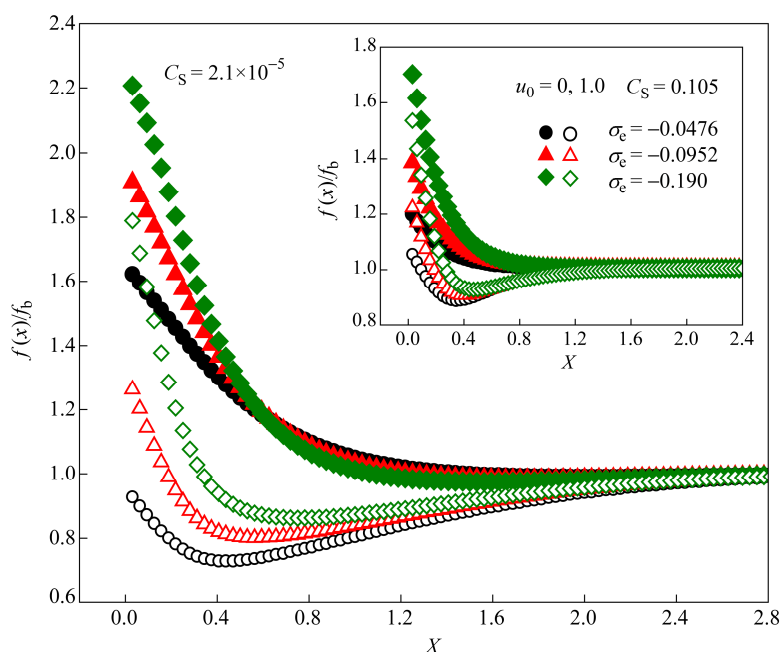


Fig. 6 The local degrees of ionization of weak polybase as a function of the distance from the charged surface with different surface charge densities at a salt concentration of 2.1×10^{-5} and bulk pH = 9.18 corresponding to $f_b = 0.4$. In the figure, the filled and open symbols correspond to $u_0 = 0$ and 1.0, respectively. In the inset, the corresponding profiles of the local degree of ionization at a salt concentration of 0.105 are displayed.

However, in the regime of high bulk degree of ionization in the presence of strong monomer-surface non-electrostatic interaction as shown in Fig. 6, the local degree of ionization of weak polybase varies non-monotonically away from the oppositely charged surface. The position of the local minimum approximately coincides with the range of the attractive monomer-surface non-electrostatic interaction ($0.375 R_g$). It can be further seen from Fig. 6 and its inset that, the depth of the local minimum decreases with increasing magnitude of the surface charge density and salt concentration. The suppression of local degree of ionization as shown in Fig. 6 and its inset stems from the fact that, in the regime of high bulk degree of ionization in the presence of strong monomer-surface non-electrostatic interaction, the electrostatic repulsion among highly concentrated and strongly charged monomers is very strong. Therefore, the acid-base ionization equilibrium shifts toward the left of the equation in order to alleviate the electrostatic repulsion among charged monomers.

It can be further clearly seen by comparing Figs. 5 and 6 with their respective insets that, compared with the regime of high bulk degree of ionization, in the regime of low bulk degree of ionization or equivalently high bulk pH (see Fig. 5 and its inset), the relative increase in the local degree of ionization near the oppositely charged surface is more significantly suppressed with the addition of large amount of salt ions. This is the main reason why the screening-reduced effect of added salt ions is predominant in the regime of low bulk degree of ionization as revealed from Fig. 2.

Degree of Charge Neutrality Inside the Boundary Layer

In the regime of low degree of charge compensation, which corresponds to high surface charge density and/or low bulk degree of ionization as exemplified by Figs. 7 and 8, the degree of charge neutrality inside the boundary layer Σ is higher than the corresponding value of Ξ^* . Σ being larger than Ξ^* means that the positively charged mobile ions besides the positively charged monomers are the dominant charge species inside the boundary layer. For the present study of weak polybase at $\text{pH} > 7$, Na^+ is the dominant mobile ion species inside the boundary layer. Moreover, Figs. 7 and 8 show that, in the regime of low degree of charge compensation, the deviation from overall charge neutrality is not strong with the degree of charge neutrality in the range of -0.2 to $+0.2$. On the other hand, in the regime of high degree of charge compensation, Fig. 9 shows that the deviation from overall charge neutrality inside the boundary layer is severe in the presence of strong monomer-surface non-electrostatic interaction. Figure 9 further reveals that, at the strongest non-electrostatic interaction, *i.e.*, $u_0 = 1.0$, Σ is smaller than Ξ^* , which is in sharp contrast to the case shown in Figs. 7 and 8. Because the surface charge density of the negatively charged surface is low and the bulk degree of ionization is high, coupled with large amount of adsorbed positively charged monomers due to the strong monomer-surface non-electrostatic

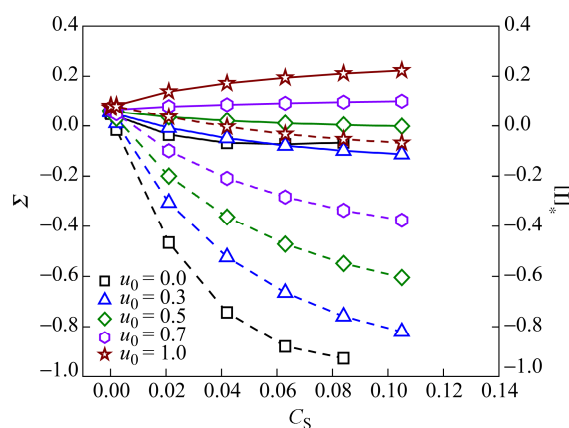


Fig. 7 The degrees of charge neutrality inside the boundary layer as a function of salt concentration at different strengths of monomer-surface non-electrostatic interaction at $\sigma_e = -0.190$, $f_b = 0.4$ (solid curves); and the relative differences between the charges on the adsorbed chains and the surface charges at different strengths of non-electrostatic interaction plotted against the salt concentration (broken curves)

interaction, negatively charged mobile ions are enriched inside the boundary layer in order to reduce the electrostatic repulsion between highly charged and concentrated monomers. Our numerical result shows that Cl^- is the dominant ion species inside the boundary layer.

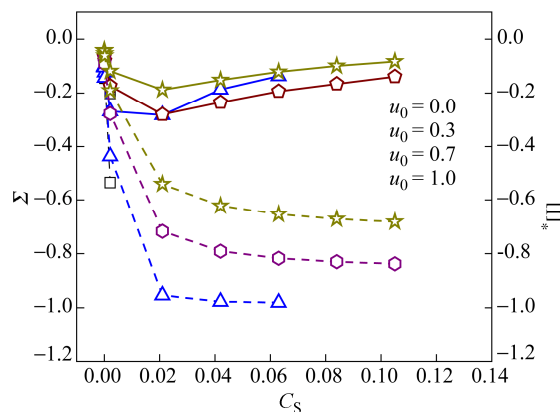


Fig. 8 The degrees of charge neutrality inside the boundary layer as a function of salt concentration at different strengths of monomer-surface non-electrostatic interaction at $\sigma_e = -0.0952$, $f_b = 0.06$ (solid curves); and the relative difference between the charges on the adsorbed chains and the surface charges plotted against the salt concentration (broken curves)

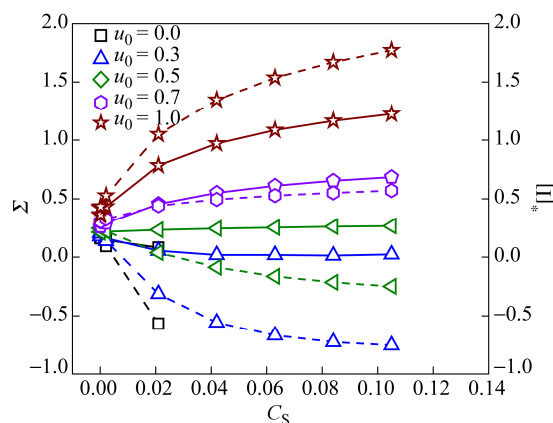


Fig. 9 The degree of charge neutrality inside the boundary layer as a function of salt concentration at different strengths of monomer-surface non-electrostatic interaction at $\sigma_e = -0.0476$, $f_b = 0.4$ (solid curves); and the relative difference between the charges on the adsorbed chains and the surface charges plotted against the salt concentration (broken curves)

CONCLUSIONS

In this work, the interplay of monomer-surface electrostatic and non-electrostatic interactions in the adsorption of weak polybase on negatively charged planar surface was numerically investigated by SCFT. The effects of the strength of the short range monomer-surface non-electrostatic interaction and added salt ions on the degree of charge compensation and overall charge neutrality inside the boundary layer were examined.

Numerical results reveal that in the regime of low surface charge density and high bulk charge fraction of weak polyelectrolytes, the local degree of ionization of monomers near the charged surface deviates not much from its bulk value. In such a regime, both screening-reduced and screening-enhanced effects of added salt ions emerge at relatively low and high strengths of monomer-surface non-electrostatic interactions, respectively. Such a feature is identical to that for the case of strong polyelectrolytes. Outside this regime, especially in the opposite regime, only the screening-reduced effect of added salt ions can be observed for the adsorption of weak polybase on oppositely charged planar surface. The reason for this is that in the opposite regime of high surface charge

density and low bulk degree of ionization, the relative increase in the local degree of ionization near the oppositely charged surface is more significantly suppressed by the addition of large amount of salt ions.

It was found in this study that in the regime of high bulk degree of ionization in the presence of strong monomer-surface non-electrostatic interaction, the local degree of ionization of weak polybase varies non-monotonically away from the oppositely charged surface. The emergence of a local minimum in the profile of local degree of ionization stems from the fact that, in this regime of high bulk degree of ionization in the presence of strong monomer-surface non-electrostatic interaction, the electrostatic repulsion among highly concentrated and strongly charged monomers is very strong. Therefore, the acid-base ionization equilibrium shifts toward the left of the equation in order to alleviate the electrostatic repulsion between charged monomers.

In the regime of low degree of charge compensation, which corresponds to high surface charge density and/or low bulk degree of ionization, numerical results indicate that Na^+ is the dominant mobile ion species inside the boundary layer. Moreover, in this regime, the deviation from overall charge neutrality is not strong inside the boundary layer. On the contrary, in the regime of high degree of charge compensation, the deviation from overall charge neutrality inside the boundary layer was found to be severe in the presence of strong monomer-surface non-electrostatic interaction. In this regime of high degree of charge compensation with the presence of strong monomer-surface non-electrostatic interaction, negatively charged mobile ions with Cl^- being the dominant species are enriched inside the boundary layer in order to reduce the strong electrostatic repulsion between highly charged and concentrated monomers.

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