Non-monotonic behavior of weak-polyelectrolytes adsorption on a cationic surface: A Monte Carlo simulation study

Claudio F. Narambuena [a,*], Pablo M. Blanco [b], Adrian Rodriguez [c], Diego E. Rodriguez [c], Sergio Madurga [b], José L. Garcés [d], Francesc Mas [b]

[a] *Facultad Regional San Rafael, Universidad Tecnológica Nacional (UTN-FRSR) & Instituto de Física Aplicada (INFAP), CONICET, San Rafael, 5600, Mendoza, Argentina*

[b] *Physical Chemistry Unit, Materials Science and Physical Chemistry Department & Research Institute of Theoretical and Computational Chemistry (IQTCUB) of Barcelona University (UB), 08028, Barcelona, Catalonia, Spain*

[c] *Facultad Regional Neuquén, Universidad Tecnológica Nacional. Plaza Huincul, 8318, Neuquén, Argentina*

[d] *Chemistry Department, Technical School of Agricultural Engineering & AGROTECNIO of Lleida University (UdL), 25003, Lleida, Catalonia, Spain*

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ABSTRACT

In this work, the weak polyelectrolyte (PE) adsorption on a strong cationic surface is studied with constant pH Monte Carlo simulations using a coarse-grained model. When a large number of PE chains is added to the system, the PE adsorbed amount vs pH curve exhibits a non-monotonic behavior, with the appearance of a maximum close to the intrinsic pK_a^0-value of the PE titratable groups. The apparent pK_a-value of the PE chains shows a non-trivial tendency depending on the pH-value and the surface coverage degree. In increasing the pH-value, the small anions that accompany the cationic surface are replaced by PE chains and small cations. For $pH > pK_a^0 + 1$, an evident charge reversion of surface is observed. These results are explained analyzing the interplay between the attractive and repulsion electrostatic interactions between the different components of the system (inter- and intra-charged monomers of PE chains, the strong cationic surface and small ions) and their effects on the PE chain ionization.

1. Introduction

Polyelectrolytes (PEs) are polymer chains with functional groups capable to ionize in certain conditions [1]. On one hand, when the PE functional groups are fully dissociated independently of bulk condition, the polyelectrolyte is called to be a strong PE. On the other hand, when the dissociation degree is pH-dependent, the polyelectrolyte is considered a weak PE. When PEs are dissolved in a polar solvent (*e.g.* water), they become ionized and they can be adsorbed on charged surfaces. The PE adsorption on a charged substrate can modify the interface properties of substrates, which can be of interest for industrial application on paper technology, water treatment, etc. [2,3].

The strong PE adsorption on charged surfaces has been extensively studied by means of experimental, theoretical and computational studies. One interesting phenomenon experimentally observed is that the amount of charge due to adsorbed polyelectrolyte chains can compensate or even overcompensate the surface charge [4,5]. This phenomenon, known as charge reversion, has been profited in several

applications, being polyelectrolyte multilayer formation the prime example. In this technique, a charged substrate is modified by cyclic adsorption of positive and negative PE chains [6]. This process is possible due the charge reversion taking place on the substrate at every adsorption step [6]. The amount of adsorption of strong polyelectrolytes also depends on the curvature (concave or convex) of charged nanoparticles [7]. On the other hand, the charge of strong polyelectrolytes gives different kinds of interactions between charged surfaces and/or nanoparticles depending on the sign of the charge and the strength of adsorption [8]. Computational studies using Monte Carlo simulations have been undertaken to understand the phenomenon of PE adsorption [9–12]. In these studies, the PE chain is modeled as a set of beads joined by harmonic bonds and the substrate as an uniformly charged surface. Caetano *et al.* demonstrated that the conditions of critical PE adsorption on a charged surface are highly dependent on the number of PE chains in the system [13]. Since, the PE-surface interaction and lateral interaction between adsorbed chains plays key roles in the adsorption process. Narambuena *et al.* have proved that it is possible to observe a

significative charge reversion using simple coarse-grained models [10, 11] and that the adsorption proceeds with a non-trivial counterion condensation degree on the polyelectrolyte chains [12]. However, charge reversion is a topic that even nowadays leads to strong debates on its exact explanation [14].

In the weak PEs case, its adsorption on a charged surface exhibits a more challenging and complex physicochemical process compared to their strong counterpart. This is because the ionization behavior of weak polyelectrolytes in solution is regulated by the binding of small ions (protons, metal ions, etc.) present in solution, and their charge depends on pH, ionic strength, conformational changes and interactions with other polyelectrolytes, surfaces and nanoparticles [15–17]. This mechanism, known as charge regulation (CR), is of great importance in order to understand the physicochemical behavior of polyelectrolytes in a wide range of situations, as for example, in receptor-ligand equilibria in biochemical systems, supramolecular chemistry, wastewater treatment, stability of colloidal systems, etc. [18] On the other hand, this mechanism affects the interactions of weak polyelectrolytes with other polyelectrolytes [19], protein-surface [20–24], protein-protein [25,26], protein-RNA [27], protein-strong polyelectrolyte [28,29], protein-weak polyelectrolyte [30,31], between surfaces [32] and between weak polyelectrolytes and nanoparticles [33–36]. There are few attempts to study theoretically the effect of CR in the interaction of weak polyelectrolytes, mainly focused on rigid and linear polyelectrolytes [37]. Most of the studies on this effect has been performed using constant–pH (or Semi-Grand Canonical) Monte Carlo simulations based on coarse-grained models [34,35,38–41].

In the particular case of a weak PE chain close to a charged flat surface, the proton concentration and the electrostatic environment are significantly different from those in the bulk values. This difference becomes more significative as the charge density of the surface is increased. In turn, these differences become more noticeable as the ionic strength of the medium decreases. Nowadays, weak polyelectrolyte adsorption is still a relatively unexplored topic, with only a small number of experimental and theoretical works on this topic [42–45]. The first theoretical approach to study the adsorption of weak flexible polyelectrolytes on charged surfaces was made in a Self-Consistent Field (SCF) theory by allowing the dielectric constant and the dissociation degree to vary with the distance from the surface [43,44]. These models have been applied to study the adsorption of polyacrylic acid (PAA) adsorption on a positively charged polystyrene latex [45]. The latex particle was strongly charged in the all the pH range studied. At low pH values, the adsorption was found to proceed similarly to the case of a neutral polymer chains interaction with a charged surface, because at those pH-value polyacids have a very low charged monomer fraction. On the opposite case, at high pH-values, the adsorption behavior of strong PE chains is recovered. However, between both limiting pH conditions, the situation becomes more complex and the polyelectrolyte adsorption *versus* pH curve was observed to have a maximum located at pH-values below the pK_a of the weak PE titratable groups [45]. This can be explained by the action of two antagonistic electrostatic phenomena. On one hand, the negatively charged PE chains are electrostatically attracted to the positively charged surface, which promotes the PE adsorption. On the other hand, PE chains are electrostatically repelled to each other, which hinders their adsorption to the charged surface since it reduces their inter-chain distance. At intermediate pH-values, the polyelectrolyte chains are only partially negatively charged which causes them to be absorbed to the charged surface, but it is not enough to cause significative inter-chain repulsion. By increasing the pH-value, the charged monomer fraction accordingly increases, and consequently the amount of PE adsorbed into the surface is lowered. The interplay between the electrostatic interaction and ionization of titratable groups of PE is far from being fully understood.

In this work, we use constant pH Monte Carlo simulations to study the adsorption of weak PE chains on a substrate with positive charges distributed in a square lattice. The adsorbed amount of PE and small ions, the PE degree of dissociation and the electrostatic potential are estimated as a function of pH. The article is organized as follows: in section 2, the computational methods are described in detail whereas the results and discussion are developed in section 3. Finally, the conclusions can be found in section 4.

2. Computational methods

2.1. Coarse grained models

The system is composed by N_T particles in total:

$$N_T = N_{Surf} + N_m + N_c + N_a \tag{1}$$

where N_{Surf} is the number of charged particles in the surface and $N_m = N_p x_p$ is the total number of monomers in the system, distributed in a N_p number of polyelectrolyte chains with x_p monomers per chain. N_c and N_a are the number of small cations and anions of the monovalent salt, respectively. The solvent is modeled as a dielectric continuum with relative dielectric constant ε_r.

The polyelectrolyte is represented as a linear chain of x_p monomers, as can be observed in Fig. 1A. The monomer i is joined with a consecutive monomer $i + 1$ by a bond with a potential energy:

$$U_{Bond}^i = k_{bond} \left(l_{i,i+1} - l_0 \right)^2 \tag{2}$$

where $l_{i,i+1}$ is the distance between the monomers i and $i + 1$ and l_0 is the equilibrium bond length. The potential energy is characterized by a spring constant $k_{bond} = 10^5 k_B T$, where k_B is the Boltzmann's constant and $T = 300\ K$ is the absolute temperature. The k_{bond} value is chosen high enough to avoid significant fluctuation in the distance between neighbor monomers. Each monomer is modeled as a rigid sphere with a diameter $d = 0.2$ nm centered in the position of the monomer. In turn, each monomer i has a charge Z_i, located in its center, that can be either 0 or -1 elementary charge, e, for a neutral or ionized monomer, respectively. Since the polyelectrolyte is a weak polyacid, the charge of the monomers is considered a fluctuating property and it varies within the simulation.

The simulation box (Fig. 1B) is a rectangular parallelepiped with volume $V = W \times W \times L$, and sides W and L. Two solid walls are localized at $z = 0$ and $z = L$. Charged spheres are centered at $z = 0$, in order to mimic the strong basic groups of the substrate. Those charged particles are distributed forming a square lattice so that the total number of surface particles is $N_{Surf} = 13 \times 13 = 169$. Within the simulation, the particles position is fixed and thus the square lattice is preserved. The particles are solid spheres with a diameter $d = 0.2$ nm with a punctual positive elementary charge, e, located in its center. Since the particles enclose strong basic groups, its charge is kept constant and it is always positive, independently of the pH conditions of the media. The charge of the surface particles generates a positive surface charge density

$$\sigma_{Surf} = \frac{N_{Surf}\ e}{W^2} \tag{3}$$

which is settled to $\sigma_{Surf} = 0.2\ e/\text{nm}^2$ (around to 32 mC/m²). Consequently, the simulation box length is $W^2 = 845$ nm² with $W \approx 29.069$ nm and a distance between neighbor surface particles of $d_S = \sqrt{e/\sigma_{Surf}} \approx 2.2$ nm.

The electrostatic interaction between two charged particles i and j, whose centers are separated a distance r_{ij}, is calculated with a coulombic potential with an excluded volume correction

$$U_{El}(r_{ij}) = \begin{cases} l_B \dfrac{q_i q_j}{r_{ij}} & \text{if} \quad r_{ij} > \dfrac{d_i}{2} + \dfrac{d_j}{2} \\[2mm] \infty & \text{if} \quad r_{ij} \leq \dfrac{d_i}{2} + \dfrac{d_j}{2} \end{cases} \tag{4}$$

where q_i and q_j are the charge valence of particles i and j, respectively
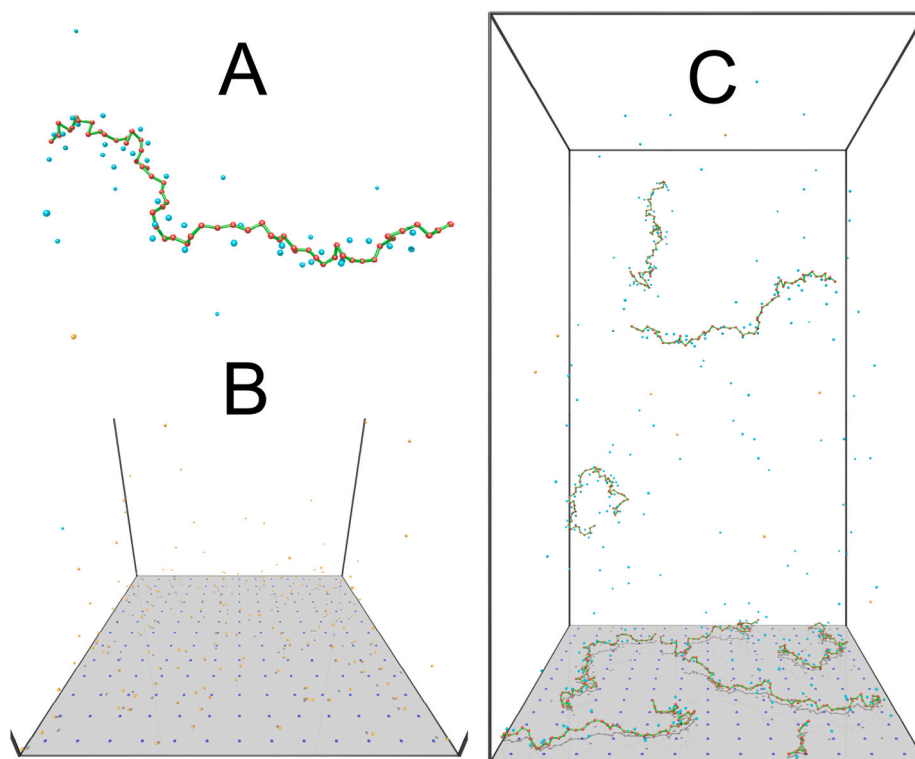
Fig. 1. Simulation box and coarse-grained model for the weak acid polyelectrolyte chain. A) Coarse grained model that represents the weak polyelectrolyte. B) Positively charged square lattice that represents the strong base substrate. C) Simulation box with dimensions $W \times W \times L$ with $W^2 = 845$ nm^2 and $L = 50$ nm.

and l_{B} is the Bjerrum length:

$$l_{\mathrm{B}} = \frac{e^2}{4\pi\varepsilon_0\varepsilon_r k_B T} \tag{5}$$

where ε_0 is the permittivity of the vacuum and $\varepsilon_r = 78$ is the dielectric constant for water at room temperature. l_{B} represents the separation between two elementary charges that have an electrostatic energy equal to the thermal energy. For two interacting particles located at a smaller distance than l_{B}, their electrostatic interaction is greater than the thermal energy. For water at room temperature, its value is $l_{\mathrm{B}} \approx 0.71$ nm. The long-range electrostatic interactions are treated with the external potential method (EPM), which was firstly proposed by Torrie and Valleau [46] and subsequently modified by Boda [47].

Since the modeled chain represents a weak polyelectrolyte, the number of charged monomers is governed by the ionization process, which depends on several variables such as the pH-value, the salt concentration, etc. This process is classically described using the weak acid-base chemical equilibrium, which for a protonated acid group of the chain $-HA$ reads

$$-\mathrm{HA} \; \leftrightarrows \; -\mathrm{A}^- + \mathrm{H}^+ \tag{6}$$

where $-\mathrm{A}^-$ is the ionized deprotonated weak acid of the chain and H^+ is a proton. This equation describes the deprotonation process of the weak acid and it is governed by its acid equilibrium constant K_{a}°, defined as a function of the chemical activities a_i of the species involved

$$K_{\mathrm{a}}^{\circ} = \frac{a_{-\mathrm{A}^-} \cdot a_{\mathrm{H}^+}}{a_{-\mathrm{HA}}}. \tag{7}$$

K_{a}° measures the weak acid tendency to dissociate. Each chemical activity is connected with the molar concentration c_i by $a_i = c_i \, \gamma_i$, where γ_i is the activity coefficient. Additionally, the pK_a° is defined as

$$pK_{\mathrm{a}}^{\circ} = -\log_{10} K_{\mathrm{a}}^{\circ}. \tag{8}$$

For ideal complexation/protonation process, when all the acid-base

groups have the same value of the acidity equilibrium constant, K_{a}°, and in infinite dilution ($\gamma_{-\mathrm{A}}$, $\gamma_{-\mathrm{AH}} \to 1$), the ideal dissociation degree of the polyelectrolyte, $\alpha_{\mathrm{PE}}^{\mathrm{id}}$ can be calculated as a function of the pH $= -\log_{10} a_{\mathrm{H}^+}$, from the well-known Henderson-Hasselbalch equation, as

$$\alpha_{\mathrm{PE}}^{\mathrm{id}} = \frac{c_{\mathrm{A}^-}}{c_{\mathrm{A}^-} + c_{\mathrm{HA}}} = \frac{1}{1 + 10^{\left(pK_{\mathrm{a}}^{\circ} - pH\right)}}. \tag{9}$$

Far from ideal conditions, the protonation equilibrium is governed by the PE apparent dissociation constant $K_{\mathrm{a}}^{\mathrm{app}}$, which provides information about the average affinity of the macromolecular sites for the protons [18,48–50]. The $K_{\mathrm{a}}^{\mathrm{app}}$-value, in general, depends on the charge of the macromolecule, different at each pH and ionic strength value, and can be calculated using a generalization of the Henderson- Hasselbalch equation [51].

$$pK_{\mathrm{a}}^{\mathrm{app}} = pH - \log\left(\frac{\alpha_{\mathrm{PE}}}{1 - \alpha_{\mathrm{PE}}}\right) = f(\mathrm{pH}, \ I, c_{\mathrm{PE}}, \dots), \tag{10}$$

where α_{PE} is the average dissociation degree of the titratable groups of the polyelectrolyte in non-ideal situations, which in this work will be measured by constant pH Monte Carlo simulations. We consider all the PE titratable monomers to be identical with the same intrinsic dissociation acid constant value $pK_{\mathrm{a}}^{\circ} = 4.25$, which is a value typically found in polycarboxylic acids.

2.2. Monte Carlo method

The Monte Carlo (MC) simulations were performed using the Metropolis algorithm [52,53].

In order to effectively sample the configurational space and equilibrate the system, the following trial movements are done: (i) translational motion of small ions and monomer particles, (ii) translational motion of the PE chain as a whole, (iii) pivot rotation of the PE chain and (iv) flip rotation of the PE chain [54]. The trial movements were accepted according to the probability:

$$\min\{1, \exp(-\beta\Delta U)\} \tag{11}$$

where ΔU is the total energy difference between the initial and trial states.

The ionization of the titratable groups was changed performing a MC semi-grand canonical procedure [55,56]. Every hundred MC steps, the charge of each titratable monomer is increased or decreased by 1 unit due to proton binding/unbinding to the group. In order to maintain the system electroneutrality, the creation (deletion) of a small anion was therefore required. Those trial protonation/deprotonation movements are accepted according to the semi-grand canonical probability

$$\min\left(1, e^{-\beta\Delta U_{El}\pm\ln 10(pH-pK_a)}\right) \tag{12}$$

where ΔU_{El} is the total change in electrostatic energy and the sign $\pm$ can be either - or + corresponding to the protonation or deprotonation, respectively [55,56].

For all the simulations performed, the total number of MC steps was 2×10^6. Every simulation was equilibrated in the first 10^6 steps, necessary to stabilize the ionization process, and the remaining 10^6 steps were used to calculate the ensemble averages. The control variables, which are fixed throughout the simulation, are: the number of poly-electrolyte chains, N_p; the proton chemical potential (so that the number of protonated/unprotonated PE groups is not fixed); and, finally, the chemical potential of the salt (the number of small ions is thus variable). The chemical potentials of the proton and the small ions are supposed to be fixed by the presence of an external reservoir. The salt concentration is fixed to $c_{Salt} = 1$ mM in the reservoir using an algorithm of insertion/deletion of neutral pairs of salt particles. This procedure as well as its trial movement probability are explained in detail in Ref. [57] and it was applied to the computational study of the diffuse double layer in an ionic system next to a uniformly charged plane surface [46].

2.3. Measured quantities

The local density of monomers, $c_m(z)$ (in nm^{-3}) is measured as a function of the distance to the charged surface at $z = 0$ using a histogram methodology. The simulation box is divided in parallel bins with area W^2 and thickness $\Delta z = 0.1$ nm, so $c_m(z)$ can be calculated as

$$c_m(z) \approx c_m(z_i) = \frac{n_m(z_i)}{V_b}, \tag{13}$$

where $n_m(z_i)$ is the average number of monomers localized at a distance from the surface between z_i and $z_i + \Delta z$ and the bin volume is $V_b = W^2\Delta z$. The total number of monomers can be calculated as $N_m = N_p x_p = \sum_{i=1}^{i=500} n_m(z_i)$. The local density of small cations and anions, $c_c(z)$ and $c_a(z)$ can be defined of analogous way.

The PE adsorbed amount Γ_m is measured counting the total number of monomers adsorbed on the volume compress between the surface ($z = 0$) and a parallel plane located at distance $z = 2.5$ nm

$$\Gamma_m = \int_{z=0}^{z=2.5 \text{ nm}} c_m(z)dz \approx \sum_{i=1}^{25} c_m(z_i)\Delta z. \tag{14}$$

The distance $z = 2.5$ nm, taken as the superior limit in the integral, is chosen considering the concentration profiles. In turn, the ionization degree of adsorbed monomers is calculated as:

$$\alpha_{PE} = \frac{\left|\int_{z=0}^{z=2.5 \text{ nm}} \rho_m(z)dz\right|}{\int_{z=0}^{z=2.5 \text{ nm}} c_m(z)dz} \tag{15}$$

where $\rho_m(z)$ (in nm^{-3}) is the local charge density due to the charged monomers of the PE

$$\rho_m(z) \approx \rho_m(z_i) = \frac{Q_m(z_i)}{V_b} \tag{16}$$

and $Q_m(z_i) = \sum_{j=1}^{n_m(z_i)} q_j(z_i)$ is the total local charge due to the n_m monomers located between z_i and $z_i + \Delta z$. $q_j(z_i)$ is the electrical charge of monomer j.

The electrostatic potential at a distance z from the charged surface $\psi(z)$ is calculated as follows [47,58,59]:

$$\psi(z) = -\frac{e}{\epsilon_0\epsilon_r}\int_z^L \rho(z')(z' - z)dz' \tag{17}$$

where the $\rho(z)$ is the total charge density at a distance z from the charged surface, and it is calculated as

$$\rho(z) = \rho_m(z) + \rho_c(z) + \rho_a(z) \tag{18}$$

where $\rho_c(z)$ and $\rho_a(z)$ are the local charge density at z due to the small cations and anions respectively, and it is calculated in the same way as the monomer charge density (Eq. (16)). The deduction of Eq. (17) can be found briefly explained in the Supplementary Material (Section S1).

3. Results and discussion

The system studied is the adsorption of weak PE chains with $x_p = 60$ (60 monomers per PE chain) and $l_0 = 0.50$ nm. The weak PE adsorb on a strong charged surface represented by a square lattice of 13×13 positive charges. This lattice with $N_{Surf} = 13 \times 13 = 169$ charges is placed on a surface with $A = 845$ nm^2 in order to set the charge density of surface to the value $\sigma_{Surf} = 0.2$ e/nm^2.

Fig. 2 shows the concentration of monomers as a function of the distance z from the charged surface at different pH-values ranging from 2 to 8, when four PE chains (Fig. 2A) and ten PE chains (Fig. 2B) are added. In the first case, four PE chains are added to the system, $N_p = 4$, so there is a total of $N_m = x_p \cdot N_p = 240$ monomers inside the simulation box. At pH $= 2$, the monomer concentration is well distributed with a maximum value close to $z \approx 1$ nm. As the pH-value increases the position of the concentration maximum shifts to the surface (located at $z = 0$) and it increases in intensity, which suggests that the polyelectrolyte chains are more attracted to the surface. At pH $= 4$, the concentration profile has a maximum located at $z \approx 0.5$ nm and most of the monomers are located at a distance less than 2 nm from the surface. This concentration distribution reflects a statistical average of a set of conformations that the polyelectrolyte takes throughout the Monte Carlo simulation. Let us compare the z distance of maximum adsorption with the dimensions of the polyelectrolyte chain. Two limiting values can be considered: the diameter of a monomer ($d = 0.2$ nm) and the end-to-end distance of the fully stretched conformation of PE chain, which is approximated by the chain contour length $L_C = (x_p - 1)l_0 = 29.5$ nm. The maximum localization ($z \approx 0.5$ nm) is much smaller than the size of the stretched chain and just a couple of times the diameter of the monomer. This fact indicates that the PE chains adopt a conformation with the most of monomers close to the surface, so they are placed co-planarly to the surface. At pH $= 6$ and pH $= 8$, the maximum of adsorption is closer to the surface, but the intensity of concentration maximum slightly decreases as the pH increases. Let us now see how this picture changes if ten chains of chains PE are added to the system (i.e. $N_m = x_p N_p = 600$ monomers in total), which is shown in Fig. 2B. At pH $= 2$, the concentration profile of the PE chains shows a maximum at a distance $z \approx 1$ nm from the surface. It can be also observed that as the pH-value increases the concentration of PE accordingly increases. At pH $= 4$, it can be observed an increase in the intensity of the peak located at $z \approx 0.6$ nm. However, it can be noted that, for pH $= 6$ and pH $= 8$, the concentration of monomers close to the surface abruptly
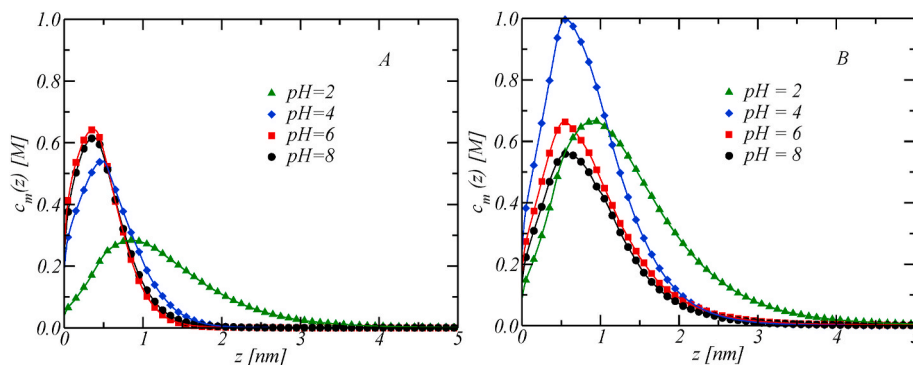
Fig. 2. Concentration of monomers as a function of distance z from the surface at different pH-values ranging from 2 to 8 and for two different numbers of PE chains N_p added to the system: A) $N_p = 4$ and B) $N_p = 10$.

decreases.

In order to better understand the latter observations and to quantify the weak PE - surface interaction, we calculate the PE adsorbed amount Γ_m (Eq. (14)) as a function of pH. In Fig. 3, Γ_m is shown as a function of the pH-value for different N_p values ranging from 4 to 12. When four chains are added to system ($N_p = 4$, orange triangles), the adsorption is moderate at low pH-values. The amount of PE adsorbed increases as the pH-values increases, until a plateau is reached at pH = 3. The adsorption plateau value is close to $\Gamma_m \approx 0.28$ monomers/nm^2, which is close to the maximum possible $N_m/W^2 \approx 0.284$ nm^{-2}, which suggests that the chains are fully adsorbed on the surface.

When six chains are added to the system ($N_p = 6$), the adsorption curves show a high plateau for pH-values ranging from 3 to 5 with a value $\Gamma_m \approx 0.42$ monomers/nm^2 which is close to maximum possible $N_m/W^2 \approx 0.426$ nm^{-2}. At high pH values, the adsorption decreases to a low valley of $\Gamma_m \approx 0.35$ monomers/nm^2. The appearance of a maximum adsorption is more evident in increasing the N_p value. The systems with $N_p = 8$, $N_p = 10$ and $N_p = 12$ have maximum of adsorption values equal to $\Gamma_m \approx 0.56$, $\Gamma_m \approx 0.7$ and $\Gamma_m \approx 0.82$ nm^{-2}, respectively, which are close to the corresponding maximum value possible N_m/W^2 namely $\approx$ 0.57, ≈ 0.71 and ≈ 0.85 nm^{-2} respectively. This fact indicates that the chains are fully adsorbed in the maximum in the pH range between pH = 3 and pH = 5. However, at high pH values the adsorption has a similar magnitude ($\Gamma_m \approx 0.41$ monomers/nm^2) for the three cases, which

suggests that the surface is saturated of PE. The presence of a maximum in the adsorption of weak PE on strong charged surface was first observed experimentally by Tanaka et al. four decades ago [42]. In turn, several theoretical studies using mean field approach was performed in order to explain these phenomenon [43–45]. Up to our knowledge, this is the first time that the maximum of weak PE adsorption has been reported by means of computational simulation, allowing a molecular analysis of this phenomenon.

In Fig. 4, two snapshots of equilibrium configurations obtained by
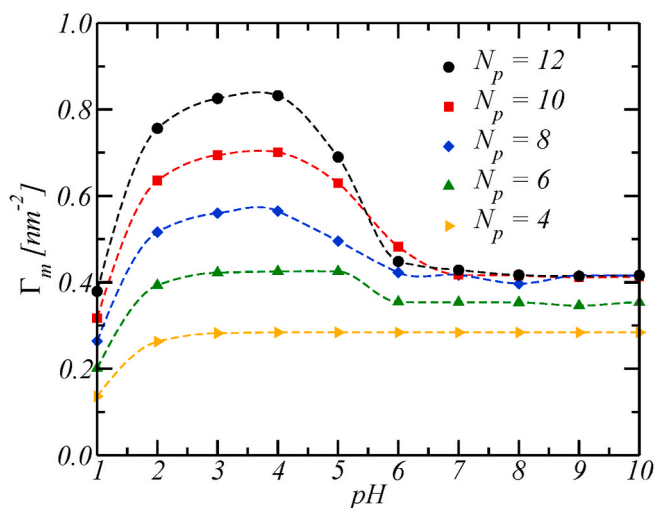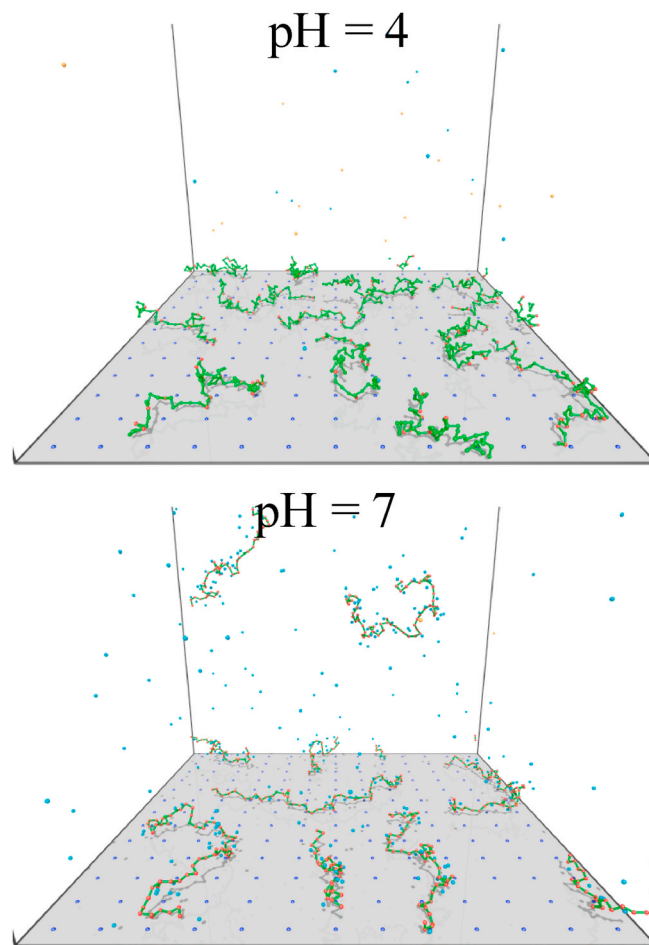

Fig. 3. PE adsorption on the charged surface as a function of pH at different number of PE chains added to the system. The PE chains have $x_p = 60$ monomers and $l_0 = 0.50$ nm. The solution has a salt concentration equal to $c_{Salt} = 1$ mM.

Fig. 4. Snapshots of equilibrium configurations obtained by Monte Carlo simulation at pH = 4 (top) and pH = 7 (bottom) of a system with twelve PE chains ($N_p = 12$). The PE chains have $x_p = 60$ monomers and $l_0 = 0.50$ nm and the reservoir has a salt concentration equal to 1 mM.

Monte Carlo simulation of twelve chains ($N_p = 12$) at pH values of pH = 4 (Fig. 4 top) and of pH = 7 (Fig. 4 bottom) are shown. The titratable groups are depicted as green and red spheres, depending if they are neutral o negatively charged, respectively. On one hand, it can be observed at pH = 4 that all the PE chains are adsorbed, adopting a fairly extended conformation. Analyzing the ionic presence close to the surface, it can be noted that there is not an obvious predominance of small anions or cations, which suggests that the adsorbed chains neutralize the positive charge of the substrate. On the other hand, at pH = 7 the number of adsorbed chains decreases compared with those at pH = 4 and it can be also observed that in this case the chains are a very and almost totally ionized. The chains desorption at pH = 7 can be explained by the repulsion between chains which pulls them back to the bulk solution. It is interesting to note that the high amount of negative charge of the adsorbed PE chains causes an accumulation of small cation counterions close to the surface, which suggests a possible charge reversion in these conditions.

In order, to quantitatively study this phenomenon the adsorbed amount of total and charged monomers are estimated, as well as the number of small cations and anions close to the charged surface. In Fig. 5, the local densities and adsorbed amount of species are depicted. Local density of monomers, $c_m(z)$, local charge density of charged monomer, $\rho_m(z)$ are plotted as a function of the distance z to the charged surface in Fig. 5A, showing the results obtained when the case with two chains ($N_p = 2$) and pH = 4 is considered. It can be noted that the charged monomers are a half part approximately of total amount of monomers, which suggests that the monomers degree of ionization is close to 0.5. It can also be observed that is significant the quantity of small anions close to the charged surface. The concentration curves can be used to calculate the adsorbed amount by means of Eq. (13), which is depicted as a function of the pH-value for the cases with $N_p = 2$ and $N_p = 10$ in Fig. 5B and in Fig. 5C, respectively. The adsorbed amount is calculated for PE monomers (black circles), PE charged monomers (red squares), small anions (orange diamonds) and cations (cyan triangles). For $N_p = 2$ (Fig. 5B), at low pH-values only a small amount of chains is adsorbed to $\Gamma \approx 0.07$ nm^{-2} and only a minima fraction of monomers is charged.

We can note that there are a significant number of small anions close to the charged substrate, because they are necessary to neutralize the positive charge of the substrate. It can be also observed that the adsorbed amount of total and charged monomers monotonically increases as the pH value increase until a plateau is reached. As a natural consequence of the increase of charged monomer adsorbed, the anion surface concentration accordingly decreases as the pH-value increases. However, it is important to note that the PE negative charge is not enough to counter the surface positive charge and there are adsorbed anions even at high pH-values. Those results can be compared with the ones obtained when the case with ten PE chains ($N_p = 10$) is considered, which is shown in Fig. 5C. Interestingly, the charged monomer surface concentration does not show a maximum but it increases as the pH-value increases until a plateau is reached, which equals the adsorbed amount of monomers. This fact suggests that the PE chains adsorbed are fully ionized at pH-values larger than 8. In turn, the number of small anions close to the surface quickly decreases as pH increases. Around $pH = 4.25$, the concentration of anions close to the surface interface vanish, and it is replaced by a cationic one. Furthermore, the amount of charge due to adsorbed polyelectrolyte chains $\Gamma_{cm} \approx 0.2$ nm^{-2} (red filled squares) is equivalent to the surface charge density, $e\Gamma_{cm} \approx \sigma_{Surf}$. In other words, at this pH value the PE charge neutralizes the charge on the surface. Intuitively one would think that this is the natural limit of adsorption. However, as the pH value increases, the amount of polyelectrolyte increases until it reaches a plateau after pH = 8, where the amount of adsorbed charge is a little more than the surface charge $e\Gamma_{cm} \approx 2\sigma_{Surf}$. In turn, the cation adsorbed amount increases until a constant value at pH values larger than 7.
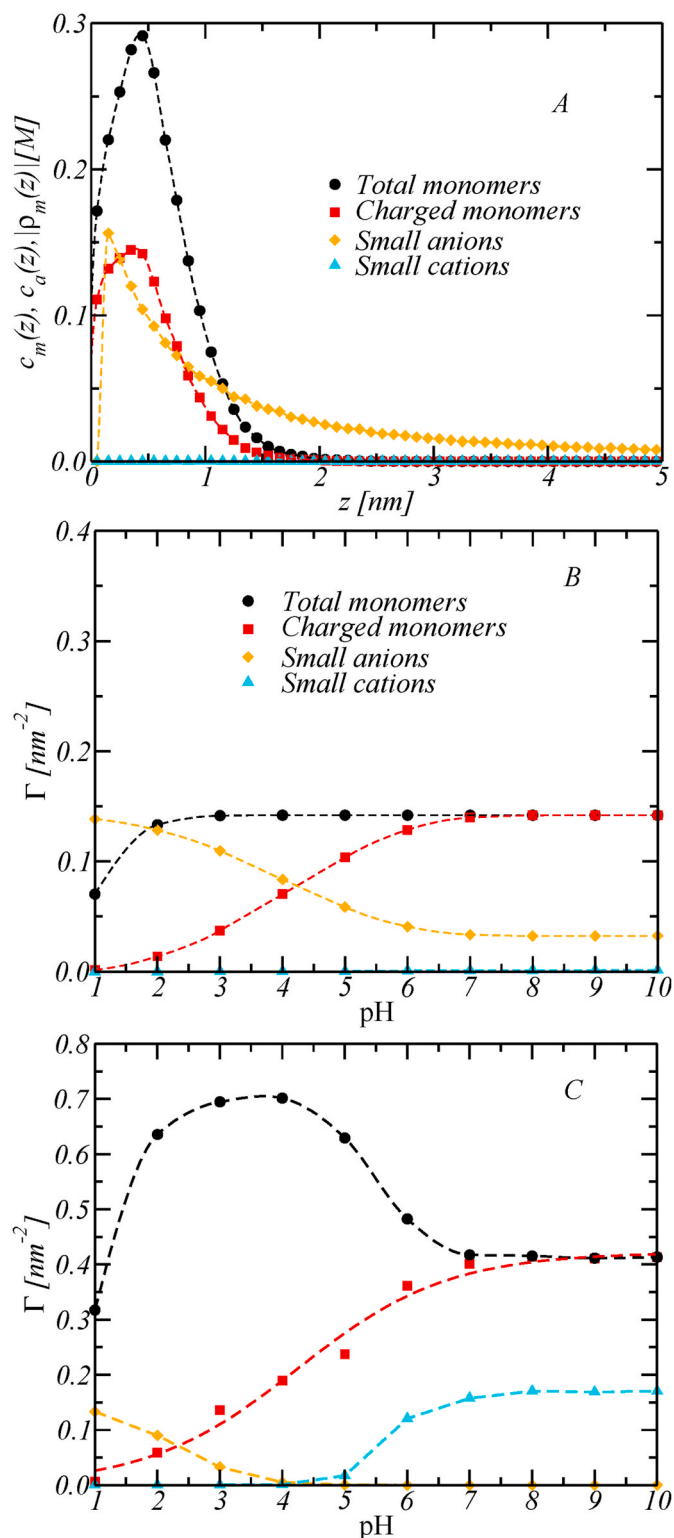
Fig. 5. A) Local density of monomers, $c_m(z)$, local charge density of charged monomer, $\rho_m(z)$ as a function of distance z to the charged surface, as well as the small anions concentration, $c_A(z)$, at pH = 4. B) Adsorbed amount of total and charged monomers, and small ions close to the charged surface as function of *pH* when $N_p = 2$. C) The same that B but with $N_p = 10$. The PE chains have $x_p = 60$ monomers and $l_0 = 0.50$ nm. The reservoir has a salt concentration equal to 1 mM.

At this point, these observations arise two natural questions:

A) How does the titration curves of the weak acid PE chains change when they are adsorbed?

B) The composition of the ionic environment close to the surface changes from small anionic to cationic when the pH-value is increased. This fact suggests a change in the surface-PE charge density. Does this ionic exchange indicate a charge reversal?

In order to answer the first question, we calculate the PE degree of ionization (Eq. (15)), α_{PE} *vs.* pH curves obtained by MC simulation varying the number of PE chains N_p from 1 to 10, see Fig. 6. For comparative reasons, we also plot in Fig. 6 the ideal titration curve of the PE (black dashed line), and the titration curve of an isolated PE chain in the bulk (black downwards triangles), obtained by MC simulation of a single chain without the charged surface. Note that for the ideal titration curve (Eq. (9)) half of the groups are dissociated when the pH-value is pH $= pK_a^{\circ} = 4.25$. However, for the case with a single PE chain in the bulk, the titration curve is shifted to the right and half of the groups are dissociated at a pH-value of 5.6, which could be considered a half-ionization pK_a-value so that $pK_a^{\alpha_{PE}=0.5} \approx 5.6$.

This is because in the ideal case the ionization of each monomer is independent of the ionization state of the others and it depends exclusively on the pH-value (Eq. (9)). However, in the Monte Carlo simulation the probability of acceptation of ionization or deionization depends on both pH (in fact it depends on the difference pH $- pK_a$) and the electrostatic energetic change involved in the process ΔU_{El} (Eq. (12)). The shifting of the Monte Carlo results compared to ideal case can be explained because of the electrostatic repulsion between the negatively charged monomers of the PE chain, which decreases the probability of ionization. As a result, higher pH-values are necessary to find similar degree of ionization values than in the ideal case. It is interesting to compare these results with the ones obtained in MC simulation of one PE chain in the presence of the charged surface (violet circles in Fig. 6B). It is important to note that in the following cases the α_{PE} is calculated only of the PE chains adsorbed on the surface (see equation (15)). The PE degree of ionization of one adsorbed chain shifts to the left compared to the results obtained in the case of the PE chain in the bulk. It is observed a half-ionization pK_a value of $pK_a^{\alpha_{PE}=0.5} \approx 4$, which indicates that the chain has an more acid ionization behavior than the ideal case ($pK_a^{\circ} = 4.25$). Now let us investigate what happens when more PE chains are added to the system with the charged surface. For $N_p = 2$ (red squares in Fig. 6B), the ionization curve is very similar to the case with $N_p = 1$ which suggests that the two adsorbed chains behave independently. However, when N_p is increased to 4 (blue diamonds in Fig. 6B), the degree of ionization shifts to the right again. This fact can be explained because the adsorbed chains interact with each other in increasing the surface coverage. Interestingly, when ten chains are added (green

triangles in Fig. 6B) the ionization behavior gets more and more interesting. At low pH-values, the ionization is similar to the cases with fewer chains because the chains are only slightly charged. However, in increasing the pH-value, the $N_p = 10$ have two different ionizations. First, its ionization is close to the behavior of the cases with low N_p values but for pH-values larger than 5 the ionization is closer to the ionization of the isolated chain in the bulk. In other words, when the degree of ionization is greater than 0.3, the repulsive electrostatic interaction between the adsorbed chains is stronger than the electrostatic interaction with the positively charged surface.

To deepen the study of the acid behavior of the polyelectrolyte, we will estimate the apparent pK_a-value, pK_a^{app}, as a function of pH using Eq. (10). Fig. 7 shows the pK_a^{app}-values at different conditions. The ideal value is shown in a dotted line, which has a constant value $pK_a^{app} = pK_a^{\circ}$ since this value is independent of pH-value. Also, it is shown the acid-base behavior of an isolated chain in bulk as a continuous line. In this case, the chain shows a pK_a^{app}-value close to the intrinsic pK_a° value at low pH-values.

However, as the pH-value increases, the pK_a^{app}-value increases indicating that the PE chain has lower capacity to ionize its acid groups (higher affinity to bind protons). This is because as the pH increases the amount of negative charges on the PE chain also increases, which increases in turn the electrostatic repulsion on possible new ionized groups. At high pH-values, the pK_a^{app}-value reaches a plateau at
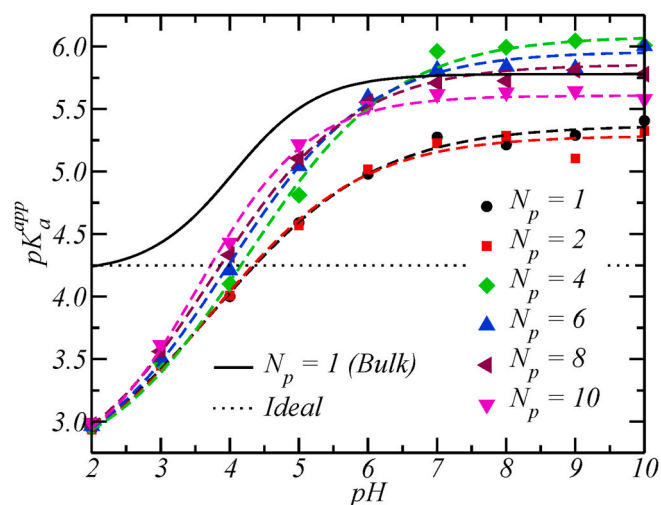
Fig. 7. Apparent pK_a^{app} as a function of pH for different amounts of PE chains. The simulated PE chains have $x_p = 60$ monomers and $l_0 = 0.50$ nm. The ideal case and MC simulation of an isolated PE chain ($N_p = 1$) are depicted for comparison. The reservoir has a salt concentration equal to 1 mM.
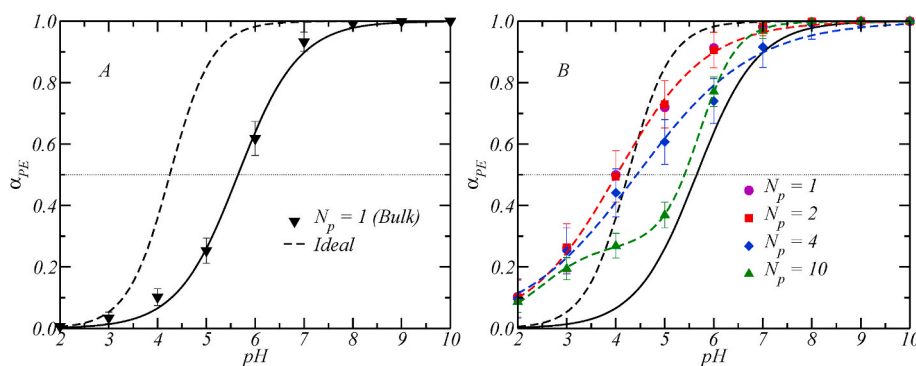
Fig. 6. Degree of ionization of PE chains as a function of pH. A) Ideal case (Eq. (9)) and MC simulation of an isolated PE chain ($N_p = 1$). B) Different amounts of chains and conditions. The simulated PE chains have $x_p = 60$ monomers and $l_0 = 0.50$ nm. The reservoir has a salt concentration equal to 1 mM.

$pK_a^{app} \approx 5.75$. All adsorbed PE chains (filled symbols) show a similar pK_a^{app}-value of $pK_a^{app} \approx 3$ at low pH values, since only a small fraction of monomers are charged. For all systems under these conditions, the interaction between the surface and the PE chains predominates. As the pH increases, these systems show different behaviors and can be ordered in two groups: 1–2 PE chains in solution and 4–10 PE chains in solution.

The behavior of one chain adsorbed is shown as black filled circles. The positive charges of the substrate have two effects: (1) they exert an attractive electrostatic interaction with the negatively charged groups of the PE chain and (2) they promote the titratable groups ionization, generating a higher fraction of charged monomers. Therefore, the profile starts with a $pK_a^{app} -$ value around 3, which is below the intrinsic pK_a-value. For pH values larger than 4.3, the situation is reversed, and the pK_a^{app}-value has a less acid behavior that the ideal one ($pK_a^{app} > pK_a$). This is because in increasing the pH-value the PE monomers are ionized and the intra-molecular electrostatic repulsion difficult the formation of new ionized monomers. At high pH-values, the adsorbed PE chain reach a higher value close to $pK_a^{app} \approx 5.3$. It can be also observed that the case with two PE chains adsorbed (red filled squares in Fig. 7) behaves in a very similar way of very similar form to the case with one adsorbed chain. This result suggests that the two PE chains do not interact significantly with each other. Then each chain (of the two) is adsorbed independently on the surface.

When larger numbers of chains are adsorbed ($N_p = 4$, 6, 8 and 10 with diamonds and up, left and down triangles respectively, in Fig. 7) the pK_a^{app}-values are significantly larger than those obtained with less PE chains adsorbed, which means that in the first case the PE chain has a higher affinity for protons so that the titratable groups are neutral. This is due to the increasing inter-molecular electrostatic repulsion between adsorbed chains. For pH-values ranging from 2 to 6, the pK_a^{app} increases as the amount of PE chains increases. This is because, in this pH range, the amount of adsorbed PE increases as the amount of chains are added to the simulated system (See Fig. 5C). Then, the amount of negative charges in the surface increases and consequently so it does the inter-chain repulsion, which favors the proton binding affinity increasing the pK_a^{app}-values. At pH = 6, these four profiles have a similar value of $pK_a^{app} \approx 5.5$. This is because at this pH-value coincides with the lower pH-value in the PE adsorbed amount plateau (See Fig. 5C). Thus, at this point the surface is saturated of PE chains and some start to desorb. However, at higher pH-values, the trend is reversed and the pK_a^{app} decreases as the amount of PE chains increases. This is because for pH > 6 the amount of PE chains adsorbed is almost constant as a function of pH and the amount of chains added. This trend can be explained by the increase in the anionic atmosphere in the surface, which screens the inter-chain repulsion stabilizing the formation of ionized monomers.

Let us now answer the second question and analyze if the small ions exchange observed in (Fig. 5C at pH > 5) is due to a charge reversion phenomenon. This will be analyzed by estimating the electrostatic potential (Eq. (17)) as a function of the distance to the surface z and can be found in Fig. 8.

Fig. 8 presents the electrostatic potential for the system with $N_p = 10$ at different pH values ranging from 2 to 8. Each chain has $x_p = 60$ and $l_0 = 0.50$ nm. It can be observed that for pH = 2 the electrostatic potential at the surface is around $\psi(z = 0) \approx 140$ mV due to the positive charge of the surface. The potential tends to zero in increasing the distance to the surface. In this case, the electrostatic potential profile is mainly due to the positively charged surface and the small anions, since the PE chains are almost neutral. However, at pH = 3 the presence of adsorbed PE chains on the surface cause a relevant decrease of 25 mV in $\psi(z)$ respect the profile at pH = 2. This can be explained since the charged monomer fraction goes from 10% to 20% when the pH value is changed from 2 to 3, respectively (See Fig. 6). In turn, the negative charge of the PE chains displaces a large quantity of anions, as can be observed in Fig. 5C. Since in these conditions the PE chains are fully adsorbed (see Fig. 3), the charge contribution from the PE chain can be
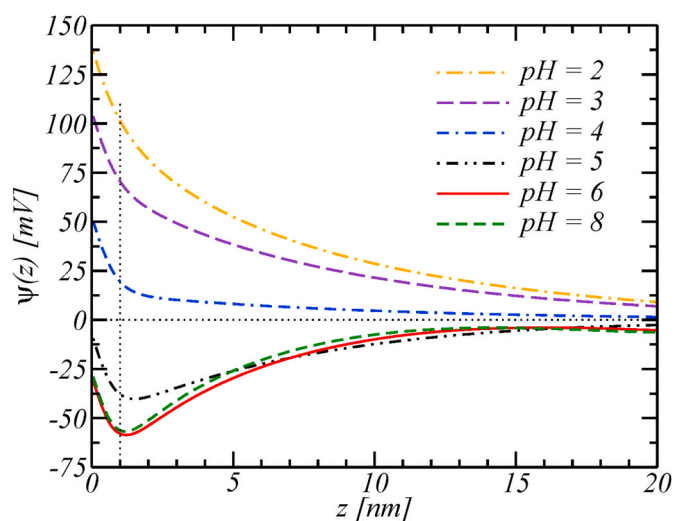

Fig. 8. Electrostatic potential as a function of distance to the charged surface. The system has ten PE chains ($N_p = 10$) with $x_p = 60$ monomers and $l_0 = 0.50$ nm. The reservoir has a salt concentration equal to 1 mM.

quickly estimated as $N_m \alpha_{PE} \approx 120$ negative charges, which is a similar value to the total number of positive charges on the surface. At pH = 4, the electrostatic potential has a drastic decay because almost all the positive charge of the surface is countered by the PE chains and only a few anions are located close to the surface, as can be observed in Fig. 5C. At pH = 5, the electrostatic potential switches its sign and it reaches a minimum value of $\psi \approx -40$ mV at $z \approx 1$ nm, closely located to the surface. The change of sign of the potential proves that the adsorbed PE negative charge is enough to revert the surface charge, which explains why the small cation concentration increases at this pH values as can be observed in Fig. 5C. At higher pH values, the electrostatic potential shows similar tendencies with a more pronounced minimum around $\psi \approx -60$ mV. This fact explains why for pH values larger than 6 the PE and small cation concentrations reach a plateau; it is because for pH values larger than 6 the surface change becomes almost pH-independent.

In order to better analyze the latter point, the electrostatic potential at $z = 1$ nm ($\psi_{Ads} = \psi(z = 1$ nm $)$) as a function of the pH-value for systems with a different number of PE chains N_p ranging from 2 to 10 is depicted in Fig. 9. In the system with $N_p = 2$ (green squares) the
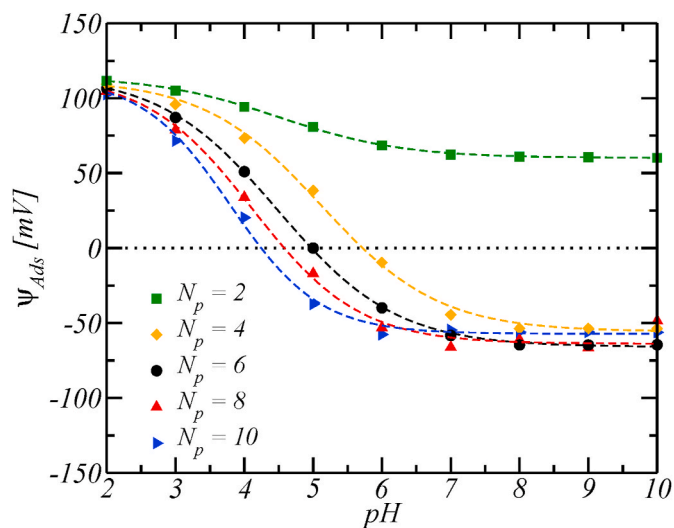

Fig. 9. Effect of pH on the electrostatic potential at $z = 1$ nm, ψ_{Ads}. The PE chains have $x_p = 60$ monomers and $l_0 = 0.50$ nm. The solution has a salt concentration equal to 1 mM.

electrostatic potential decreases until a plateau is reached, which has a positive value. In consequence, charge reversion is not observed in these conditions. In the case $N_p = 4$ (orange diamonds), ψ_{Ads} strongly decreases as the pH-value increases and becomes zero at pH $\approx$ 5.7. At larger pH-values, ψ_{Ads} switches its sign and it reaches a constant value around $\psi_{Ads} \approx -50$ mV. The pH-value where the system substrate + PE has a neutral electrostatic potential can be understood as the isoelectric point of the system, *pI*. When six PE chains are added to the system (black circles), ψ_{Ads} has a strong decay, the pI is shifted to the left to pI $\approx$ 5 and the potential minimum value is $\psi_{Ads} \approx -65$ mV. In adding extra PE chains to the system, the isoelectric point of system shifts to lower values.

4. Conclusions

We carried out a Monte Carlo simulation study on the adsorption of weak polyelectrolyte on strong charged substrate. Both the polyelectrolyte and the substrate are represented by simple models, which focus in the electrostatic interaction between the charged monomers and charged particles in the substrate.

In our Monte Carlo simulations, we observe the appearance of a maximum value in the adsorbed amount of chains *vs.* pH curves in certain conditions. The adsorption maximum is localized at a pH-value close to the intrinsic $pK_a^0 = 4.25$ value of the PE titratable groups, and $\tilde{}$ 1.5 pH units below of the half-ionization pK_a-value of chains $pK_a^{\alpha_{PE}=0.5} \approx$ 5.6. This maximum was experimentally reported and theoretically previously studied, and it was found to be located at $\tilde{}$1 pH unit below the intrinsic dissociation constant of the carboxylic groups of the macromolecules [45]. Regardless the maximum exact location (which may be given by the definition of the intrinsic pK_a^0), it is important to note that the charged monomer adsorbed amount does not exhibit any maximum in any circumstance.

In addition, we observe a complex behavior in the PE degree of dissociation of the chains adsorbed on the surface. The PE degree of dissociation has been found to change depending on the coverage degree of PE chains on the surface. Those changes are analyzed in detail calculating the apparent dissociation constant pK_a^{app}, which show interesting trends depending on the pH-value and the number of PE chains. This is because for high coverage degrees the inter-chain lateral interaction becomes significant. These novel results for the adsorbed weak PE chains on planar charged surface show that the apparent dissociation pK_a^{app} of the adsorbed chains is significantly affected by the inter-chain lateral interaction.

We also observed that the PE amount of negative charge increase caused in increasing the pH-value is accompanied by a decrease in the small anion adsorbed amount and an increase in the small cation adsorbed amount. This ionic exchange at high pH-values allows us to observe the charge reversion phenomenon in surface caused by the PE chains adsorption.

Up to our knowledge, this is the first time that this phenomenon is reproduced by means of computational simulation. We want to highlight that we do not include non-electrostatic interaction between the system particles in our simulations. This means that the abovementioned conclusions are a natural consequence of the columbic interaction of the system species and the acid/base equilibria. The immediate perspective of this work is to study the effect of 1:1 monovalent salt concentration. In turn, it would be very interesting to study the adsorption of weak polyelectrolytes in the presence of salt with a divalent cation or a divalent anion, that is, the effect of using type 1:2 and 2:1 salts. Another interesting perspective is to study the effect of charge discreteness on the adsorption of polyelectrolytes, which have been found to be relevant on finite-area adsorbing surfaces like Janus particles [60]. In turn, it would be also relevant to study the effect of different charge distributions on the surface.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.polymer.2020.123170.

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