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Polyelectrolyte Adsorption on a Charged Surface. A Study by Monte Carlo Simulations

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ABSTRACT: In the present work, we develop a grand canonical Monte Carlo study of polyelectrolyte (PE) adsorption on a charged surface by means of a primitive model for the PE and the ions. Charge reversal upon PE adsorption was obtained by using a model that only retains the electrostatic interactions. Free energy changes for the adsorption process were calculated and different contributions to this quantity were analyzed. Among them, the entropic gain due to ion release, the conformational changes of the PE, and enthalpic changes were considered. The results suggest that the entropic contribution is the driving force of this phenomenon, stemming from the release of counterions from the double layers of the PE and the charged surface. The positive enthalpy value obtained is rationalized in terms of the decrease of the number of ionic pairs upon adsorption.

1. Introduction

Polyelectrolytes (PEs) are linear chain polymers that in solution may have a charge on their monomers. Aqueous PEs solutions, in the presence or not of other small ions, show a number of remarkable physicochemical properties.[1] Furthermore, many molecules playing key roles in biology like DNA exhibit this type of behavior and can be considered to be PEs.[1] For this reason, the understanding of the molecular mechanisms that lead to these properties are of primarily importance for generating knowledge on polyelectrolyte behavior and for their potential application for practical and technological purposes.

The property that we want to address in the present work is the adsorption of PEs on charged surfaces. An important number of experimental studies have focused on the structural characteristics of the adsorbed polyelectrolyte and its stability upon changes in its environmental conditions like temperature and ionic strength of the solution.[2] From a simplistic electrostatic analysis, it could be concluded that PE adsorption on an oppositely charged surface should have a natural limit when the original surface charge is exactly compensated by the charge density of the adsorbed chains (charge compensation). However, under certain circumstances, it is experimentally observed that the amount of PE adsorbed is larger than that required to compensate the surface charge[2] so that a charge density with an opposite charge to that of the original surface is generated. This phenomenon is called charge reversal, which may be of such an extent that the magnitude of the final charge density is equal to the original one. Then, the adsorbed layer of PE could be placed in the presence of another PE of opposite charge to yield again a surface with charge overcompensation. This process, performed cyclically, is the one employed to generate PE multilayers.[2] The structure and properties of these multilayers and their technological applications are multiple[2] and depend on the conditions under which they are generated, like charge density of the substrate, ionic strength, etc. A special case is the generation of self-assembled polyelectrolyte nanorings formed by polyelectrolytes observed for the first time in the work of Perez et al.[3] They are formed by poly(ethylenimine) (PEI) and poly(sodium 4-styrenesulfonate) (PSS) during the first two steps of the formation of the self-assembled polyelectrolyte films (SAPFs).

Overcharging is a general phenomenon, occurring, for example, with inorganic colloids and macromolecules, in the presence of multivalent counterions. A discussion on the “chemical” and “physical” interaction giving place to overcharging can found in Lyklema.[4]

In contrast with the numerous studies on the relationship between the structure and functionality of adsorbed PEs, the thermodynamic aspects of their adsorption have received far less attention. Therefore, it is necessary to study the driving force for the adsorption of PEs on charged surfaces. Because both the charged surface and the PEs are immersed in an ionic environment, the adsorption process is expected to have an important entropic component stemming from changes of the ionic atmospheres involved. In the case of the surface, its ionic atmosphere is the well-known electrical double layer.[5] On the other hand, the ionic atmosphere of the PE are the ions that may be condensed[6] or forming the corresponding double layer. It has been proposed that the phenomenon that promotes that adsorption of PE on charged surfaces is mainly entropic: On the one hand, ions retained by electrostatic interaction at the surface double layer are released upon PE adsorption. On the other hand, counterions condensed at the PE are also set free in this process.[7] Counterbalancing this effect, an entropic phenomenon discouraging adsorption is the loss of configurational entropy of the adsorbed chain upon adsorption with respect to its configurational entropy in solution.

Concerning energetic aspects of PE adsorption, it could be speculated that a favorable enthalpic change could be expected on the basis of the electrostatic interactions between the segments of the PEs and the oppositely charged surface. In addition to the electrostatic contribution, the experimental enthalpy change of the adsorption process has a complicated and unknown contribution from the changes in hydrogen bonds,

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hydrophobic and hydration forces, etc., making the assessment of the role played by the electrostatic contributions a difficult task.[8]

Numerous theoretical studies[9−15] and computer simulations[16,17] have been undertaken to understand the phenomenon of PE adsorption, and more recently, the problem of charge reversal and overcompensation. In ref 9, the theoretical approach is based on numerical studies of mean field equations by which the concentration profile of the PEs can be explicitly calculated. Nonlinear effects like the ion condensation on the PE and the substrate surface are usually ignored. Furthermore, these studies are restricted to relatively low electrostatic potentials, where the Debye−Hückel approximation can be safely employed to deal with electrostatic interactions. In refs 10−15, the adsorption of PEs was investigated by using different boundary conditions. Computer simulations have been carried out by using Monte Carlo[16] and molecular dynamics.[17] Messina[16] has performed a Monte Carlo simulation of PE adsorption in the canonical ensemble in the absence of a foreign salt. It was found that an extra (nonelectrostatic) additional field is required to stabilize PE adsorption and manage to obtain a charge reversal of the order of overcompensation (complete charge reversal).

It is also interesting to mention some experimental results that focus on thermodynamic properties for the adsorption of PE on charged surfaces. These refer to the adsorption of poly(*o*-methoxyaniline) onto glass substrate,[18] adsorption of cationic polyacrylamide onto kaolinite,[19] polyvinylimidazole onto kaolinite,[20] and adsorption of cationic polyacrylamide onto sepiolite.[21] In these studies, equilibrium adsorption isotherms were obtained at different temperatures. The results were interpreted in terms of Langmuir isotherms, and the equilibrium constants were calculated. Enthalpies, entropies, and free energies of adsorption were obtained, from which it was found that the process of PE adsorption appears to be an entropy-controlled process associated with a positive value of enthalpy.

Under the usual experimental conditions, the number of the particles in the system is so large that the change in the bulk concentration of all species involved upon the PE adsorption process is practically negligible. In other words, it is conceptually very useful to think of an adsorbing surface in equilibrium with a reservoir of species (small ions and polyelectrolyte) at a given chemical potential. These correspond, speaking in the language of statistical thermodynamics, to the conditions of a grand canonical ensemble. Thus, a simulation of this type of processes should be performed under these conditions, allowing for the exchange of small ions and polyelectrolyte molecules between the simulation box and a hypothetical reservoir where all species would be held at a constant chemical potential. The lack of this exchange of matter could lead in principle to undesired effects. In the case of lack of small ion exchange, osmotic pressure effects would arise if ions were depleted or generated upon PE adsorption. On the other hand, the lack of exchange of PE particles involves the so-called Donnan effect, where an electrostatic potential difference would develop between the simulation box and the reservoir.

To avoid the first type of osmotic effects, grand canonical conditions can be relatively easily applied to the small ions, and this is the alternative we have chosen. Concerning the second type of effects, they are more difficult to prevent because the introduction and removal PE particles from the system would require a number of total particles that is out of the reach of our current computational capabilities. All that can be done is to estimate the effect of the approximation employed. Insertion of the small ion and PE concentration into the equations that predict the Donnan potential difference between our simulation box and the reservoir yields potential difference of the order of a few mV, a rather small value.

According to the preceding discussion, in the present work we develop a grand canonical Monte Carlo (GCMC) study of PE adsorption on a charged surface by means of a primitive model for the PE and the ions. The adsorption process of the PE on the charged surface depends on parameters like surface charge density of the substrate, type and concentration of salt added, and characteristics of the PE (size of the chain, fraction of charged monomers, stiffness, etc).

On the basis of our model and MC simulations, we managed to obtain charge reversal at a surface via PE adsorption without introducing specific interaction, i.e., only considering electrostatic interactions. Moreover, we have estimated the free energy changes of the adsorption process and analyzed each of its contributions, like the entropic gain due to ion release, the conformational changes of the PE, and the enthalpic changes due to electrostatic interactions. This was performed using the mean field equations[9] along with the simulated concentration profiles, finding a reasonable agreement with the experiment. From these studies, we conclude that the driving force for the adsorption process is the increase of translational entropy of the small ions. Similarly, we show that the unexpected enthalpic positive changes can be understood in terms of the electrostatic interactions of the adsorption process. The present model and its results fully support the physical picture given by Mutukumar[8] to study the interaction between PE of different charges.

The next section describes the computational model, then the calculated properties are shown, and the corresponding analysis is performed. Finally, some experimental results from the literature are mentioned and analyzed in terms of our framework. It is concluded that the present model provides an alternative explanation for these experimental results in terms of the behavior of the small ions.

2. Computational Model

We have used a primitive model for monomers and ions. The solvent is modeled in terms of a dielectric continuum, i.e., an implicit solvent with relative dielectric constant $\epsilon_r = 78$. The polyelectrolyte is modeled as a flexible chain of positively charged spheres with diameter $d = 0.4$ nm. Two consecutive monomers in each chain are connected by a harmonic stretching spring whose potential is taken to be $u_{\rm bond} = k_{\rm eq}(l - l_0)^2$ where l is the bond length and $l_0 = 0.5$ nm is the equilibrium bond length. The spring constant $k_{\rm eq} = 1000\ k_BT/{\rm nm}^2$ is chosen to be high enough to prevent fluctuations of the bond length.

The simulation box is a rectangular box of dimensions $W \times W \times L$. Periodic boundary conditions are applied in the x and y directions, with hard walls at $z = 0$ and $z = L$. The wall at $z = 0$ bears a uniformly distributed negatively surface charge density σ_s. The polyelectrolyte is made of N_p PE chains, each with N_m monomers. The number of free ions of the system is adjusted automatically by the GCMC procedure.

All the small ions of the system are considered to be rigid spheres of diameter $d = 0.4$ nm with an embedded unit (positive or negative) charge. Because the charge density at the $z = 0$ wall is assumed to be negative, its counterions will be positive. In the absence of PE, this wall will have N_{cs} counterions, with $N_{cs} = |\sigma_s| \times W^2$. A free (nonadsorbed) PE chain will have $N_m \times f$ counterions, where f is the fraction of charged monomers in the PE ($f = 1$ in this work), yielding a total number of $N_{cp} = N_p \times N_m \times f$ counterions when all the PE chains are free and noninteracting.

In a simulation where all the constituents of the system are interacting, the number of positive N_i^+ and negative N_i^- ions will be given by $N_i^+ = N_{cs} + N_s^+$ and $N_i^- = N_{cp} + N_s^-$, where $N_s^+ = N_s^-$ is the number of ion pairs introduced in (removed from) the system.

As indicated above, the grand canonical ensemble is the natural choice to study PE adsorption on a charged surface. For a given bulk electrolyte concentration, the chemical potential of the electrolyte species is unambiguously determined and this is the chemical potential applied to our model system.

This situation is very close to the experimental one, where a large amount of electrolyte in the system keeps the activity of ions practically unaltered upon polyelectrolyte adsorption or desorption. The procedure adopted to carry out the GCMC simulation was very similar to that prescribed by Torrie and Valleau.[22]

The potential energy of the system is a sum over pair interactions between the particles of the system and single particle interactions with the wall. The pair interactions are assumed to be electrostatic and of the hard-sphere type according to:

$$u(\vec{r}_{ij}) = \frac{Z_i Z_j e^2}{4\pi\epsilon_0\epsilon_r r_{ij}}, \qquad r_{ij} > d \qquad (1)$$

$$u(\vec{r}_{ij}) = \infty, \qquad r_{ij} \le d$$

where Z_i is the charge of the particle (ion of monomer), e is the elemental charge, $\epsilon_0\epsilon_r$ is the permittivity of the dielectric continuum, $\vec{r}_{ij}$ is the relative position vector, $r_{ij} = |\vec{r}_{ij}|$ is the distance between particles i and j. The interaction between particle i and the wall is given by:

$$u(z_i) = \frac{\sigma_s Z_i e z_i}{2\epsilon_0\epsilon_r}, \qquad d/2 < z_i < L - d/2 \qquad (2)$$

$$u(z_i) = \infty, \qquad d/2 \ge z_i \text{ or } z_i \ge L - d/2$$

where z_i is the z coordinate of particle i and σ_s is the surface charge density of the charged wall.

The method used to deal with the long-range electrostatic interactions was the so-called external potential method (EPM) as first proposed by Torrie and Valleau[22] and modified by Henderson.[23]

Performing simulation where the ions in solution are explicitly taken into account avoids making further approximations in the model. For instance, the introduction of the Debye−Hückel theory would prevent the consideration of nonlinear effects in the electrostatic interactions. This could lead in the present case to a strong underestimation of these effects because, under our working conditions, electrostatic potential values are relatively high, i.e., we are working in strongly correlated electrostatic systems for which the linearization of the Poisson−Boltzmann (PB) equation is not a suitable approximation. In those cases where ionic concentration varies smoothly in space, the decay of the electrostatic interactions can be approximated by a function of an average screening length that depends only on electrolyte concentration. However, in the present case, we have electrolyte ions close to a planar surface with its own ionic atmosphere (electrical double layer), apart from the fact that the PE can also screen the electrostatic interaction between electrolyte ions. All of these lead us to consider the ions explicitly.

In addition to ion pair removal and insertion, system equilibration is achieved by taking into account motion of single particles, translation of the PE chain with its condensed ionic atmosphere, pivot motion of the PE, and flip motion of the chains.[24]

Table 1. Set of Parameters used in this Simulation

parameters	notation, value
temperature, K	$T = 300$
surface charge density, e/nm^2	$\sigma_s = 0.01-0.5$
valence of the ions	$Z_{ion} = 1$
diameter of ions and monomers, nm	$d = 0.4$
z length of the simulation cell, nm	$L = 20-40$
x,y length of the simulation cell, nm	$W = 10-20$
no. of polyelectrolyte chains in the cell	$N_p = 1-7$
no. of monomers in the PE	$N_m = 10-50$
bulk free electrolyte concentration, M	$c = 0.01$

The parameters employed in the present simulations are shown in Table 1.

Relevant quantities measured in the simulation are the concentration profiles of single cations, single anions, and PE as a function of the distance from the charged surface, here denoted as $\rho_+(z)$, $\rho_-(z)$, and $\rho_{Poly}(z)$, respectively. These quantities are calculated by using the standard histogram procedure. The electrostatic potential $\psi(z)$ may be calculated in turn from the total charge density $\rho(z) = \rho_+(z) - \rho_-(z) + \rho_{Poly}(z)$ via the equation:

$$\psi(z) = -\frac{e}{\epsilon_0\epsilon_r}\int_z^\infty [\rho(z')(z' - z)]\, dz' \qquad (3)$$

We have taken as a reference for the electrostatic potential $\psi(L) = 0$.

Simulations with charged surfaces in the absence of PE were run in order to check the performance of the procedure developed in comparison with the solution of the Poisson−Boltzmann equation, obtaining a good agreement.

3. Results and Discussion

3.1. Concentration Profiles and Electrostatic Potential. Figure 1 shows some sample configurations during the adsorption process of a 20 monomer PE chain, starting from a point far away from the surface (Figure 1a) and finishing with the adsorption of the PE on it (Figure 1d). Figure 1a shows the PE chain surrounded by its ionic atmosphere yielding an electrical double layer. A similar situation arises for the charged, polymer-free surface. In Figure 1d, it can be observed that, upon adsorption, most of the ions conforming the ionic atmosphere of the PE and that of the surface are released. In other words, the PE replaces most of its counterions by the charge of the surface, and a similar phenomenon occurs with the counterions of the surface, suggesting an efficient ionic exchange for our simulation conditions.

Quantitative results for concentration of the different species and electrostatic potential are shown in Figure 2 for the adsorption of a different number of 10 monomer polyelectrolyte chains on a surface with $\sigma_s = 0.5$ e/nm^2. Because the surface area is 10 nm × 10 nm =100 nm^2, the surface bears 50 charge units. It must be noted that the surface charge density would be neutralized with the adsorption of 5 PE chains of 10 monomers each.

In Figure 2a, we can observe that practically no anions are brought to the surface by a single polyelectrolyte chain, confirming the qualitative statement we made from Figure 1d. This contrasts with the behavior of Figure 2c, where charge overcompensation implies an electrolyte anion excess at the interface. On the other hand, the electrostatic potential behaves as expected for the different situations. In fact, Figure 2a (right)

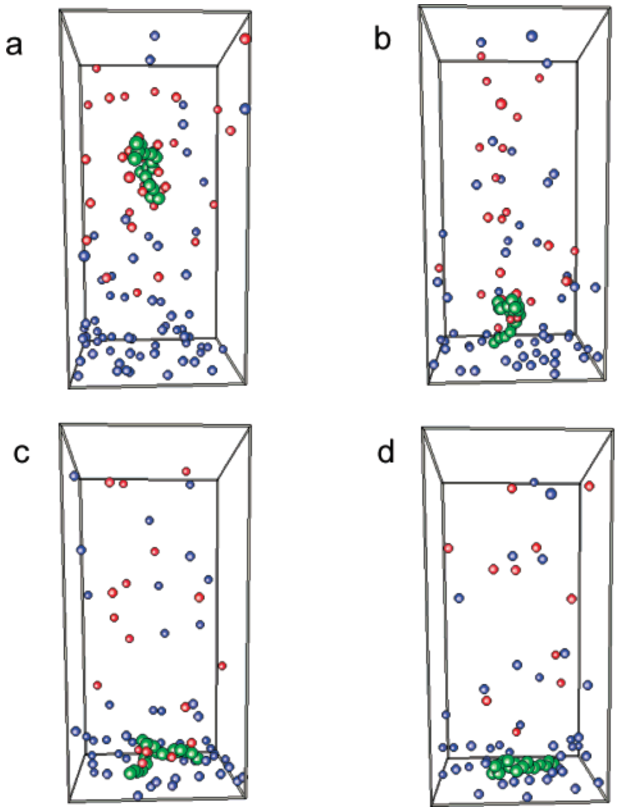

Figure 1. Sample configurations of a simulation of the adsorption of a 20 monomer PE chain on a charged surface, yielding a surface monomer density of 2 monomers/nm^2. The surface charge was $\sigma_s = 0.5$ e/nm^2. The bulk electrolyte concentration was $c = 0.010$ M. Green: polyelectrolyte monomers. Red: negative ions. Blue: positive ions.

shows the development of a surface dipole pointing toward the solution, indicating the screening of a net negative charge at the surface by the corresponding positive charge in the solution. In Figure 2b (right), the surface dipole is practically zero upon charge compensation. The addition of six chains results in the sign reversal of the electrostatic potential in Figure 2c (right), stemming from charge reversal at the surface because an excess of 20% in charge of PE is present at the surface and the direction of the dipole is reverted upon charge overcompensation.

Figure 3 compares the behavior of the electrostatic potential profiles as a function of the distance from the charged surface when polyelectrolyte chains of different length are added to the system. Figure 3a shows that the addition of five polymer chains with Nm = 10 neutralizes the electrostatic potential at about 1 nm from the surface. When large PE chains are used, charge overcompensation increases largely. Figure 3 shows that when chains of 25 monomers are used, one extra chain can be added to the system after charge neutralization (with two chains), obtaining an overcompensation of 50%. On the other hand, in the case of a chain of 50 monomers, an overcompensation of 100% results. Furthermore, under these extreme overcompensation conditions, the electrostatic potential shows an overshoot that doubles (for Nm = 25) and practically triples (for Nm = 50) that obtained with the shorter chains. Because of the relatively small size of the system with few chains, some correlations may arise when changing the number of chains. However, because the Debye length (3 Å) is considerably smaller than the box size, this effects should be small and our conclusions qualitatively valid.

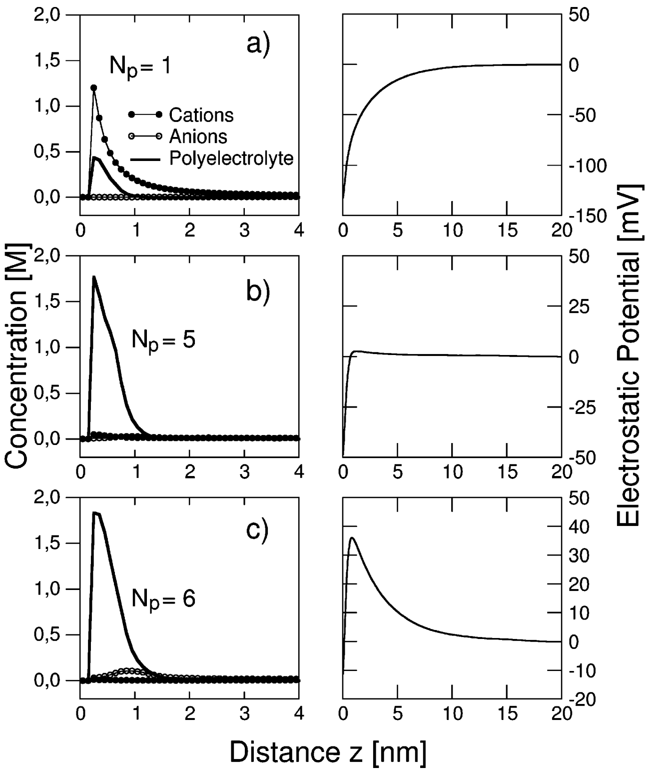

Figure 2. Left panels: Concentration of cation, anion, and polyelectrolyte as a function of the distance z from the charged surface for different number N_p of polyelectrolyte chains on a surface with $\sigma_s = 0.5$ e/nm^2. Right panels: Electrostatic potential for conditions analogous to those of the left panels.

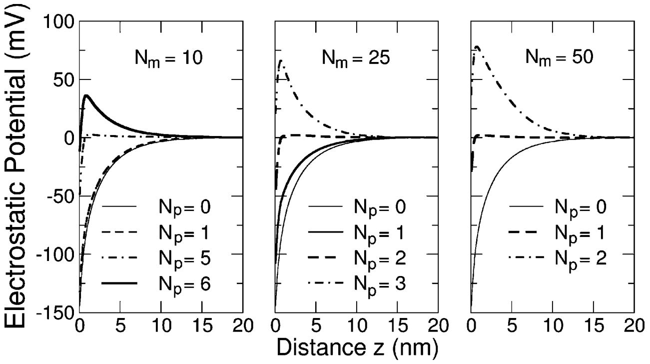

Figure 3. Electrostatic potential profiles as a function of the distance from the charged surface for the base electrolyte and upon the addition of polyelectrolyte chains of different lengths. Addition of 10 (left panel), 25 (center panel), and 50 (right panel) monomer chains, yielding surface monomer densities of 0.6, 0.75, and 1.00 monomers/nm^2 under overcompensation conditions, respectively. The surface charge density of the polymer free surface is the surface -0.5 e/nm^2.

As mentioned above, any surface, PE, or particle bearing an electric charge will generate an electrical double layer (EDL) when immersed in electrolyte solution. In the case of the surface, we observe an excess of counterions and a defect of coions, with a magnitude that depends on the surface charge density and the quantity of salt added.[5] A similar situation but with reversed charge occurs in the case of PEs.

To study the ionic exchange generated in the system upon PE adsorption, simulations were performed with a surface charge $\sigma_s = 0.1$ e/nm^2. Because $A = 20$ nm $\times$ 20 nm $= 400$ nm^2 in the present simulation box, this yielded an equivalent of 40 elemental charges on the wall. The replacement of monovalent counterions at the surface by different numbers of PE chains added is evident in Figure 4, where the excess of positive ΔN_i^+

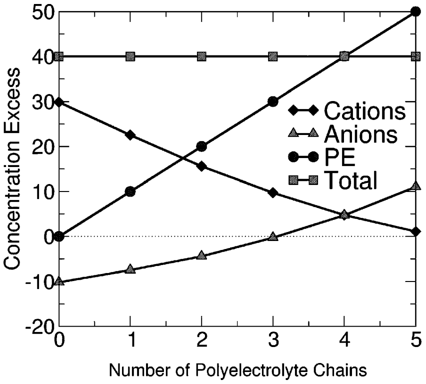

Figure 4. Concentration excess of different species as defined according to eq 4 as a function of the number of polyelectrolyte chains added to the system. The total charge of the surface is $\sigma_s A = -40$ e. The charge of each polyelectrolyte chain +10 e.

ions and the excess of negative ΔN_i^- ions as a function of the number of polyelectrolyte chains added to the system were plotted.

Both were defined according to:

$$\Delta N_i^+ = \int (\rho_+(z) - \rho_0)\, dV \tag{4}$$

$$\Delta N_i^- = \int (\rho_-(z) - \rho_0)\, dV$$

where ρ_0 is the bulk electrolyte concentration.

We find a clear correlation between the decrease of the number of free cations and the amount of polyelectrolyte added to the system. However, under the present conditions, a one-to-one correlation between added polyelectrolyte charge and removed free positive charge is not observed because the excess of negative charge is found to increase with the addition of polyelectrolyte. This is a consequence of the fact that the depletion of anions plays an important role in screening the surface charge. Note that already in the absence of polyelectrolyte, for $N = 0$, the −40 surface charge is screened by an excess of 30 positive charges and a depletion on 10 free anions. This effect is reduced for higher surface charge densities, where the surface charge is mainly screened by the excess of cations.

3.2. Calculation of the Free Energy of the PE Absorption Process. Measurement and calculation of free-energy differences is central to the understanding of the polyelectrolyte adsorption process. We have attempted the calculation of the free energy for PE adsorption from the concentration profiles of the ions and the polyelectrolyte as described in this section. As we pointed out in the Introduction, we should have rather used grand canonical rather than Canonical conditions of the PE. Because the results of both ensembles converge in the limit of the independent particle approximation, it can be stated that our results are valid in the limit of solutions dilute in the PE.

Within the mean field approximation, the free energy of the system can be written as a sum of three contributions:[9]

$$F = F_{\mathrm{pol}} + F_{\mathrm{ions}} + F_{\mathrm{elec}} \tag{5}$$

In this equation, F_{elec} denotes the contribution due to the electrostatic interactions in the system, while F_{pol} and F_{ions} denote the nonelectrostatic contributions due to the polyelectrolyte and the small ions respectively. F_{pol} can be written as,:[9,25]

$$F_{\mathrm{pol}} = k_B T \int \left[\frac{a^2}{6}|\nabla\phi|^2 + \frac{1}{2}\nu\phi^4\right] dr \tag{6}$$

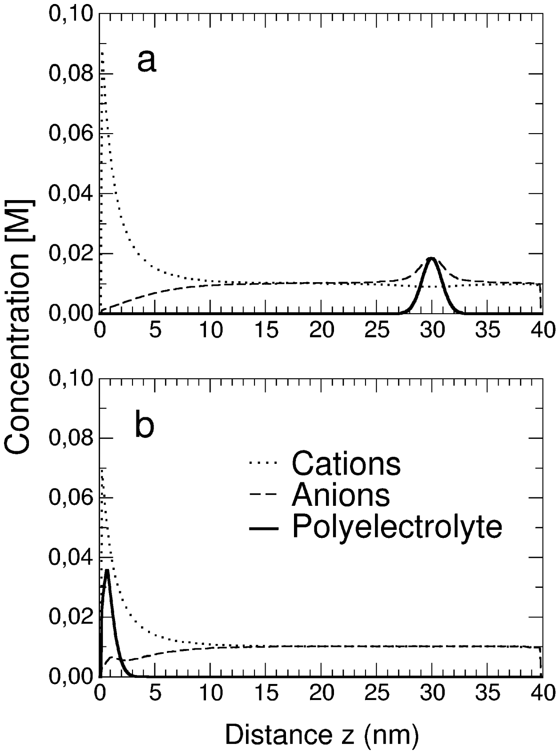

Figure 5. Simulation of the adsorption of a 10 monomer PE chain on a surface, yielding a surface monomer density of 0.05 monomers/nm^2. (a) Cation, anion, and monomer concentration as a function of the distance from the charged surface, where the PE is far from the charged surface; (b) after allowing for PE adsorption.

where the polymer order parameter $\phi(r)$ is related to the local monomer concentration $c(r)$ via the relationship $c(r) = |\phi(r)|^2$, and we refer the free energy to a zero bulk concentration. a is the effective monomer size and ν is the excluded volume contribution, and we have omitted the contribution due to the translational motion of the center of mass of the polymer. The free energy of the small ions F_{ions} is given by:[9]

$$F_{\mathrm{ions}} = \int \left\{ k_B T \sum_{i=\pm} [c^i \ln c^i - c^i - c_b^i \ln c_b^i + c_b^i] - \mu^i (c^i - c_b^i) \right\} dr \tag{7}$$

where $c^i(r)$, $c_b^i(r)$, and $\mu^i(r)$ are the local concentration, the bulk concentration, and the chemical potential of the ions $i = \pm 1$.

The different free energy contributions to the adsorption of a polyelectrolyte chain were calculated at different charge densities of the surface. As the initial state, we have considered the polyelectrolyte chain at a point far from the surface where the interaction between double layers is negligible. The center of mass of the polymer chain was maintained at 30 nm from the surface through the application of a harmonic potential. As the adsorbed (final) state, we have considered the polyelectrolyte chain at a distance from the surface corresponding to the maximum of the monomer density. Parts a and b of Figure 5 show the concentration profiles for PE, anions, and cations for these two situations in the case of a PE made of 10 monomers and a surface charge density of 0.1 e/nm^2. All the concentration profiles were calculated from the corresponding histograms, by binning the z-axis in 0.01 nm steps. The contribution F_{pol} and F_{ions} were calculated from eqs 6 and 7 by using the concentration

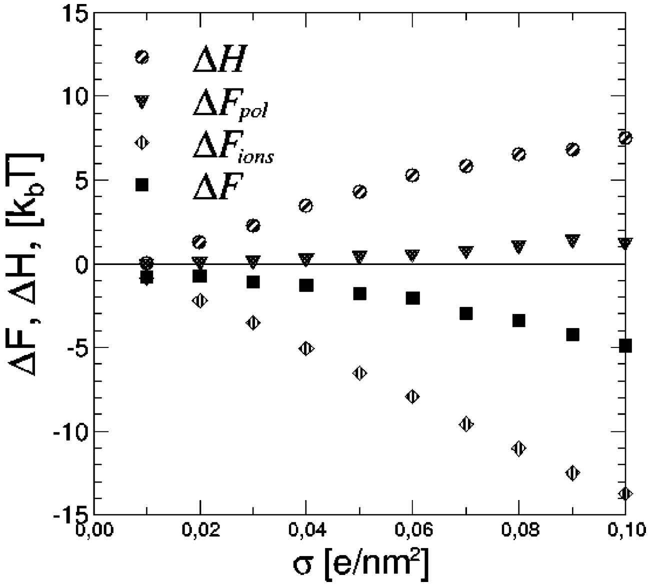

Figure 6. Enthalpic and entropic contributions to the free energy of adsorption or a polyelectrolyte 10 monomer chain at different surface charges. The surface monomer density is the same as that reported in Figure 5.

profiles obtained from the simulation. F_{elec} was obtained directly from the simulation. According to the computational model described in this work, the total internal energy of a system consists of two parts: bond stretching energy and Coulomb interaction. Because the distance between monomers barely fluctuates, only the Coulomb interaction is important for the energy change of the system. Our simulations were carried out at a constant volume of the system. However, because in the condensed phase volume changes are expected to be small, we approximate in the following considerations the enthalpy changes by the corresponding energy changes, so that $\Delta F_{\mathrm{elec}} = \Delta U_{\mathrm{elec}} \approx \Delta H$.

Figure 6 shows that the nonelectrostatic ionic contribution to the free energy of adsorption, ΔF_{ion}, presents a linear behavior in all the range of charge densities considered, remaining always negative. ΔF_{pol} is always positive, denoting the loss conformational entropy of the PE upon adsorption. This effect becomes more important for increasing surface charges. The enthalpy of adsorption is always positive, indicating that on energetic grounds the adsorption process is not favorable. ΔF_{ion} is larger in magnitude than ΔF_{elec}, resulting in a global negative value of free energy of adsorption, denoting the spontaneous nature of the adsorption process. The present results suggest that counterion release entropy is the dominant contribution to the free energy of polyelectrolyte adsorption. To understand the positive enthalpy value obtained, it is useful to consider the electrostatic contributions to the energy before and after adsorption, which are given by the concentration profiles shown in parts a and b of Figure 5, respectively. Before adsorption, the charged surface and the PE are interacting with their own counterions. After adsorption and concomitant release of counterions, interactions mainly occur between the charged surface and the PE. Thus, the adsorption process leads to the disappearance of a considerable number of ion pairs, with the consequent energy increase. Numerical evaluation of the ion profiles before and after adsorption according to Figure 5 shows that ca. 5 anions and 5 cations disappear from the system and go back to the reservoir.

Runs with chains of different lengths (not shown here) yielded an increase in the enthalpy and entropy changes roughly proportional to the length of the chain for chains with more than 10 monomers. On the other hand, the enthalpy changes for short chains deviated from this trend because the number of anions condensed on the positive chains decreases more rapidly the shorter the chain. For example, the average number of condensed anions on the chains (at distances smaller than 1 nm from center of the beads) is 1.1, 3.5, 6.1, and 8.8 for 5, 10, 15, and 20 monomer chains respectively.

Table 2. Experimental Values of Δ*H* and Δ*G* are Expressed in kJ/mol; Values between Parenthesis are Given in $k_{\mathrm{B}}T$ Units; Δ*S* is Expressed in J/molK

Δ*H*	Δ*S* (J/mol K)	Δ*G* (kJ/mol)	ref
20 (7.8)	184	−35.4 (−13.8)	18
23.2 (9.1)	95.1	−5.1 (−1.9)	19
19.9 (7.8)	69.1	−0.73 (−0.3)	20
24.3 (9.5)	100.4	−5.6 (−2.2)	21

As mentioned in the Introduction, the experimental evaluation of thermodynamic properties for PE adsorption in various systems suggests that this phenomenon appears to be an entropy-controlled process, associated with a positive value of enthalpy. Some of these values are shown in Table 2. In some of these articles (refs 18−21), it has been suggested that the reorientation or restructuring of water around nonpolar solutes or surfaces may be responsible for these observations. According to this, water rearrangement upon PE adsorption would be very unfavorable in terms of entropy because this process disturbs the existing water structure and imposes a new and less ordered structure on the surrounding water molecules. As a result of the adsorption of PE onto charged surface, the number of the water molecules surrounding PE molecules decreases, and thus the degree of the freedom of the water molecules increases. Therefore, the positive values of Δ*S* would suggest increased randomness at the solid−solution interface. As we have shown, our model provides an alternative explanation in terms of the behavior of the electrolyte. Further theoretical and experimental research is required to determine the amount that each of these effects contributes to the mentioned systems, but the present simulations shows that the ionic effects are relevant and should be taken into account.

4. Concluding Remarks and Perspectives

In this work, we have focused on the electrostatic aspects of the adsorption thermodynamics of polyelectrolytes on charged surfaces, making specific calculation of the relative enthalpic and entropic contributions. The present results suggest that the entropic contribution is the driving force of this phenomenon, stemming from the release of counterions from the double layers of the PE and the charged surface. The positive enthalpy value is rationalized in terms of the decrease of the number of ionic pairs upon adsorption. Although at this stage the model is rather simplistic to be directly applied to experimental systems, it puts forward new viewpoints concerning PE adsorption on charged surfaces. Computational models where the solvent is explicitly considered are desirable and will allow discriminating between the present ionic and solvent effects. Before this extension, which will be more demanding computationally, the effect of the change of the electrolyte concentration as well as the formation of polyelectrolyte multilayers need to be further examined. An interesting system is the formation of self-assembled polyelectrolyte nanorings like those found in the work of Perez et al.[3]

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