Colloids and Surfaces A: Physicochem. Eng. Aspects 487 (2015) 49–57

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Counterion condensation on polyelectrolyte chains adsorbed on charged surfaces

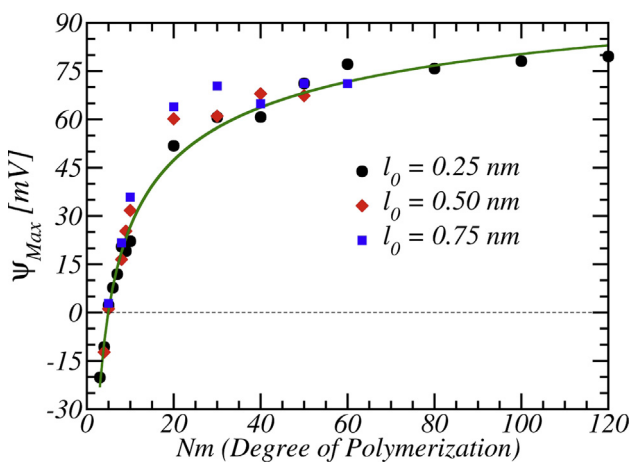
C.F. Narambuena[a,b,*], E.P.M. Leiva[a], E. Pérez[c]

[a] INFIQC – Departamento de Matemática y Física, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Haya de la Torre esq. Medina Allende, CP 5000, Córdoba, Argentina
[b] Department of Biomedical Engineering, Northwestern University, 2145 Sheridan Road, 60208 Evanston, United States
[c] Instituto de Física, Universidad Autónoma de San Luis Potosí, Álvaro Obregón 64, 78000 San Luis Potosí, México

HIGHLIGHTS

- The adsorption proceeds with a non-trivial counterion condensation on the PE chain.
- When the PE coverage on the surface is low, the chain looses most of its counterions.
- Counterions are recondensed as PE coverage degree increases.
- In order to get surface charge reversal, a minimum chain size is required.
- The end effects are important for chains with a size lower than 60 monomers.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 10 June 2015
Received in revised form 6 September 2015
Accepted 16 September 2015
Available online 21 September 2015

Keywords:
Polyelectrolyte adsorption
Counterion condensation
Electrostatic interaction

ABSTRACT

We developed a Monte Carlo systematic study into the effect of counterion condensation on the polyelectrolyte adsorption process on charged surfaces. Polyelectrolyte is modeled as a full-flexible chain whose size is characterized by the equilibrium bond length and the number of monomers per chain. The small anions and cations are explicitly modeled.

The adsorption proceeds with a non-trivial counterion condensation degree on the polyelectrolyte chain. When the polyelectrolyte coverage degree on the surface is low, the chain looses most of its counterions (anions), due to their electrostatic repulsion with the negatively charged surface. This effect is more evident when the equilibrium bond length is shorter. Counterions are recondensed as coverage degree increases, and this is attributed to two main energetic reasons: first, the chains adsorbed cause shielding of anion-surface repulsive electrostatic interaction; second, the repulsive interaction between chains adsorbed on the surface is shielded by the condensed counterions on these chains.

The amount of polyelectrolyte adsorbed and degree of condensation counterions reaches a plateau as a function of the number of chains added to the simulation box. At this point surface charge is overcompensated in a similar magnitude for the different chain types. However, the adsorbed chains keep most of their condensed counterions when the equilibrium bond length is shorter.

* Corresponding author.
E-mail address: claudio.narambuena@northwestern.edu (C.F. Narambuena).

http://dx.doi.org/10.1016/j.colsurfa.2015.09.038
0927-7757/© 2015 Elsevier B.V. All rights reserved.

Additionally, we study the size effect (number of monomer per chain) on the condensation degree on adsorbed polyelectrolyte. Condensation is highly dependent on a low chain size (low than 60 monomers approximately) since end effects are important. With a higher chain size, counterion condensation and charge reversal show a negligible correlation with chain size.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Polyelectrolytes (PEs) are polymers that in solution have an electrical charge on their monomers. Aqueous PE solutions show a number of remarkable physicochemical properties particularly different from those of neutral polymers. Furthermore, macromolecules that play a key role in biology like DNA can be considered PEs [1,2]. For this reason, gaining further insight into the molecular mechanisms that lead to these properties is of fundamental importance for understanding polyelectrolyte behavior and for potentially applying PEs to technological purposes.

The charge on their monomers may be originated by the presence of acidic or basic functional groups that can dissociate in a suitable polar solvent (generally water). When all functional groups are dissociated independently of pH, the polyelectrolyte is referred to as a strong PE; if the dissociation depends on pH, it is referred to as a weak PE. Experimental measurements indicate that the net charge on a strong PE chain is lower than the nominal value expected from the chemical structure of the polyelectrolyte and ionic dissociation. This trend can be explained by the Manning theory for counterion condensation, first proposed for an infinitely long, rod-like chain [3]. In the flexible polyelectrolyte case, the distribution of counterions is strongly influenced by the spatial localization of charges on the chain. This charge localization is determined by chain conformation, which in turn depends on the repulsion between the charges on the chain and counterion distribution. Namely, the presence of Coulombic (long-ranged) interactions in the system involves new length scales that are superimposed and can therefore affect each other in a complex fashion. This hinders the application of theoretical formalisms like renormalization group techniques and scaling ideas, which have been successfully applied to the theoretical understanding of properties of neutral polymers.

Computer simulations have played a relevant role in the understanding of counterion condensation on polyelectrolyte chains in solution. Winkler et al. [4]. have analyzed intrachain dipole formation associated with counterion condensation by molecular dynamics. Using this simulation method, Limbach and Holm [5] have studied chain end effects in the ion distribution around strongly charged, flexible polyelectrolytes. These authors found that counterions are more likely to be concentrated at the middle of the chain than at its ends. Liu and Muthukumar [6] have systematically studied the nature of this counterion condensation by Langevin dynamics simulation. They concluded that the main aspects of counterion condensation for a flexible polyelectrolyte are qualitatively inconsistent with Manning theory for an infinitely long, rigid polyelectrolyte. Wang et al. [7]. studied counterion condensation using Monte Carlo simulations. Their results indicate that ionization degree rises as polymer concentration decreases. This behaviour is opposite to that calculated from an infinitely long charged rod model. They also found that ionization degree decreases with the increase in chain length and flexibility.

Theoretical studies have been performed to consider counterion condensation on the polyelectrolyte chain when it is near a charged surface. Fleck and Von Grunberg [8] were interested in the question of whether a reverse process of condensation was possible, i.e., whether something like ¨counterion evaporationñ could be induced by the electric field generated by a charged surface. These authors considered the case of a DNA chain moving towards a lipid bilayer, showing that, due to this evaporation, the whole system could gain a considerable amount of enthalpy. This is so because the ions remaining in the system can make a significant contribution to the effective interaction between the polyelectrolyte and the surface. Sens and Joanny [9] predicted, theoretically, that most of the condensed counterions remain bound to a highly charged polyelectrolyte when it adsorbs onto a weakly charged substrate. This has been confirmed experimentally by Radeva et al. [10,11]. via electro-optics methods. They investigated how a semi-flexible long chain of NaCMC adsorbs onto the surface of an ellipsoidal colloidal particle.

Understanding the adsorption of polyelectrolytes on oppositely charged surfaces has vital relevance for numerous fields including biophysics and materials science. This has been studied in recent decades by means of different experimental techniques, which have led to a voluminous bibliography [12–17]. Furthermore, under certain circumstances, the amount of PE adsorbed is found to be larger than that required to compensate surface charge, so that a surface charge density with a charge opposite to that of the original surface is generated. This phenomenon is referred to as charge reversal or charge overcompensation.

Several theoretical studies [18–24] and computer simulations [25–38] have been undertaken to understand the phenomenon of PE adsorption and the related question of charge reversal. The usual theoretical approach was developed on the basis of numerical studies of mean field equations [20]. From this model, the concentration profile of PEs was explicitly calculated. Non-linear effects, like ion condensation on PE, are usually omitted. In addition, several studies restricted to relatively small electrostatic potentials, where the Debye–Huckel approximation can be safely applied to deal with electrostatic interactions. Polyelectrolyte adsorption was studied using various boundary conditions [18,19,21–24].

Computer simulations were carried out using Monte Carlo simulations [25–33], molecular dynamics [34–36] and Brownian dynamics [38]. Messina [26–28] performed Monte Carlo simulation of PE adsorption in the canonical ensemble, in the absence of additional salt. This author found that an (non-electrostatic) additional field is required to enhance the stability of the adsorbed PE and produce significant charge overcompensation. Narambuena et al. [30,31]. also performed Monte Carlo simulations, where charge reversal upon PE adsorption was obtained by using a coarse-grained model that only considers electrostatic interactions. Free energy changes for the adsorption process were calculated and the different contributions to this quantity were analysed. It was suggested that the entropic contribution is the driving force for this phenomenon, stemming from the release of counterions from the double layer of the PE and the charged surface. The positive enthalpy value obtained was rationalized in terms of the decrease in the number of ionic pairs upon adsorption. Nunes et al. [32]. have recently studied multiple chain adsorption, in particular, the conformation and relative arrangement of the deposited chains. Reddy and Yethiraj [37] performed explicit and implicit solvent simulations for PE adsorption at charged surfaces. All solvent models

produced similar results for the adsorption of the chain in good solvent conditions. With poor solvents, thick adsorbed layers were formed at both charged and neutral surfaces only in the case of the explicit solvent. These authors suggested that three aspects of solvent-induced interactions play a major role: a direct solvent-induced pair interaction, namely, a many-body interaction that depends on the surface area of aggregates, and a depletion interaction between aggregates and surface.

The present work is focused on the study of the adsorption of flexible polyelectrolytes on charged surfaces taking into account interaction with small ions. Our main interest centers on the study of counterion distribution around polyelectrolyte chains when chains are adsorbed on a charged surface. Counterion condensation on PE chain will be evidently influenced by the charge density of the surface and the presence of other small ions.

This study has been carried out applying Monte Carlo simulations with a coarse-grained model. Counterion condensation on adsorbed chains is studied as coverage degree increases. Counterions are released at low PE coverage degrees due to the electrostatic repulsion of PE counterions and the surface. However, counterions are recondensed as the surface becomes covered by polyelectrolyte chains.

Both polyelectrolyte adsorption and counterion condensation increase as a function of the number of chains added to the simulation box. Yet, these quantities reach a plateau where PE adsorbed overcompensates surface charge. These processes are studied systematically as a function of chain size characterized by the number of monomers per chain.

Section II, following this introduction, explains the computational model in detail. Section III describes and discusses the results of the simulation. Section IV draws the conclusion of this work.

2. Computational model

We have used a coarse-grained model called the primitive model for monomers and small ions. The solvent is modeled in terms of a dielectric continuum, i.e., an implicit solvent with a relative dielectric constant $\epsilon_r = 80$. The polyelectrolyte is modeled as a flexible chain of spheres with a diameter of $d_m = 0.2$nm positively charged $Z_{PE} = +1$. Two consecutive monomers in each chain are connected by a harmonic stretching spring whose potential is assumed to be:

$$u_{bond} = k_{eq}(l - l_0)^2 \tag{1}$$

where l is the bond length and l_0 is the equilibrium bond length. The spring constant is$k_{eq} = 10^5 k_b T/\text{nm}^2$, where k_b is Boltzmann's constant ($k_b = 1.3806488 \times 10^{-23} J \times K^{-1}$) and T is the absolute temperature (T=300K). This spring constant value is chosen to be high enough to prevent significant fluctuations of the bond length. The polyelectrolyte is made of N_p PE chains, each with N_m monomers. All the small ions of the system are considered to be rigid spheres with a diameter of $d_{si} = 0.4$nm with an embedded unit (positive or negative) charge. Since charge density at the z=0 wall is assumed to be negative, its counterions are positive.

The simulation box is rectangular with $L_x \times L_y \times L_z$ dimensions. Periodic boundary conditions are applied in the x and y directions, with hard walls at z=0 and z=Lz. The wall at z=0 has a negative surface charge density, σ_s, uniformly distributed. In the absence of PE, this wall has N_{cs} counterions, with $N_{cs} = |\sigma_s| \times L_x \times L_y$. A free (non-adsorbed) PE chain has $N_m \times f$ 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 PE chains are free and non-interacting.

Grand Canonical Monte Carlo (GCMC) [39] is the natural simulation method to study PE adsorption on a charged surface. In a simulation where all the constituents of the system are present, 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 total number of ion pairs introduced in (removed from) the system because of GCMC procedure [39]. This method automatically adjusts the number of small ions of the system to maintain the same ionic strength as that of the bulk salt concentration of $C_S = 0.001$M. 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 scheme represents properly the experimental situation, where a large amount of electrolyte in the system maintains the activity of ions practically unaltered upon polyelectrolyte adsorption or desorption. This GCMC simulation procedure is very similar to that prescribed by Torrie and Valleau [39].

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:

$$\begin{aligned} u\left(\underset{r_{ij}}{\rightarrow}\right) &= k_B T \frac{l_B Z_i Z_j}{r_{ij}}, \quad r_{ij} > d = \frac{d_i + d_j}{2} \\ u(\underset{r_{ij}}{\rightarrow}) &= \infty, \qquad\qquad r_{ij} \le d \end{aligned} \tag{2}$$

where Z_i is the charge of the particle (for ion or monomer in elementary charge units), $\underset{r_{ij}}{\rightarrow}$ is the relative position vector, $r_{ij} = \left|\vec{r_{ij}}\right|$ is the distance between particles i and j; $l_B$is the Bjerrum length:

$$l_B = \frac{e^2}{4\pi\epsilon_0\epsilon_r k_B T} \tag{3}$$

where e is the elementary charge ($e = 1.60217657 \times 10^{-19} C$) and $\epsilon_0\epsilon_r$ is the permittivity of the dielectric continuum, ϵ_0 is the vacuum dielectric constant ($\epsilon_0 \approx 8.854 \times 10^{-12} C^2 N^{-1} m^{-2}$) and ϵ_r relative dielectric constant ($\epsilon_r = 80$ for water). The Bjerrum length is interpreted as the length scale at which the Coulomb interaction between two elementary charges is comparable in magnitude to the thermal energy, $k_B T$.

The interaction between particle i and the wall is given by:

$$\begin{aligned} u(z_i) &= \frac{\sigma_s Z_i e z_i}{2\epsilon_0\epsilon_r}, \quad d_i/2 < z_i < L - d_i/2 \\ u(z_i) &= \infty, \qquad\qquad d_i/2 \ge z_i \ \text{ or } \ z_i \ge L - d_i/2 \end{aligned} \tag{4}$$

where z_i is the z coordinate of the position r_i of the particle i, and σ_s is the surface charge density of the charged wall. In order to calculate the electrostatic potential energy of this finite sample we used the external potential method (EPM). This method is proposed by Torrie and Valleau [39] and modified by Boda et al. [40]. and described in detail in Section 1 (S1) of Supporting material (SM).

The problem image forces has been considered by Messina in a previous work [26,41], where it has been demonstrated that image forces may reduce the adsorption of polyelectrolyte, but with the finding that overcharging is robust against image force. In addition, this effect appears to become smaller as the chain size increase. In the present scheme, we disregard the problem of image forces. This may lead to an overestimation (in absolute value) of the electrostatic potential; however we expect that the present chain lengths our results should be qualitatively correct.

3. Results and discussion

As discussed in the introduction, polyelectrolyte adsorption onto charged surfaces is basically an ion exchange process, where a number of small ions forming the diffuse double layer are replaced by a polyelectrolyte chain. The polyelectrolyte is also surrounded by

a counterion atmosphere, which may be partially or fully released when chains are adsorbed on the charged surface.

The ion distribution near the charged surface and the electrostatic potential corresponding to the double layer is obtained by Monte Carlo simulations. This description of a double layer was carried out for the first time by Torrie and Valleau [39]. Although these calculations are well known, they are partially revisited in Section 2 of SM (S2) since the polyelectrolyte adsorption process is modulated by the ion distribution of the double layer. Counterion condensation on a polyelectrolyte chain in solution is also well known. The key physical parameters able to account for the experimental results were monomer–monomer, monomer–counterion and counterion–counterion electrostatic interactions, determining the distribution of counterions along the polyelectrolyte chain and its effective charge.

Note that since the surface has a negative charge density, its counterions are cations. On the other hand, the polyelectrolyte chain carries a positive charge and its counterions are anions. Hence, in this report, we will use the term cations or anions to address the counterions of the surface and of the polyelectrolyte, respectively.

In addition to the attractive electrostatic interaction between a single chain and the surface, two additional electrostatic interactions are present: the interaction between anions and the charged surface, and that between the cations and the polyelectrolyte. Both are repulsive. When several polyelectrolyte chains are adsorbed on the surface the situation becomes more complex, since the interaction between chains is obviously also repulsive. As expected, polyelectrolyte adsorption and counterion condensation are modulated by all these interactions.

In order to describe the amount of charges in the system due to the polyelectrolyte chains added to the simulation box and the charges on the surface, we have defined the stoichiometric ratio in the system ξ_S as:

$$\xi_S = \frac{N_p \times N_m \times e}{|\sigma_s| \times A} \tag{5}$$

where $N_p \times N_m \times e$ is the amount of polyelectrolyte charge added to the system and$|\sigma_s| \times A$ is the amount of charge in the surface.

Fig. 1 shows six typical frames (after equilibration of MC simulation) for systems with 30-monomer chains added to the simulation box with $\sigma_s = -0.2\text{e/nm}^2$ and $c_{Salt} = 0.001\text{M}$. The charged surface (Skyblue) has a dimension of $A = L_x \times L_y = 30\text{nm} \times 30\text{nm}$, therefore, it has a total number of negative charges equal to $\sigma_S \times A = 180\text{e}$.

Each frame represents systems with different seething characterized by l_0 and ξ_S. There are two types of polyelectrolyte chains with $l_0 = 0.25\text{nm}$ (a, b and c) and $l_0 = 0.75\text{nm}$ (d–f). These frames also show three different stoichiometric ratios: $\xi_S = \frac{1}{6}$ (a and d), $\xi_S = 1$ (b and e) and $\xi_S = 1.5$ (c and f).

The addition of a single chain (30 monomers each) to the simulation box results in a value of stoichiometric ratio equal to$\xi_S = \frac{1}{6}$ see Fig. 1 (frames a and d). We can observe the adsorbed chain with a flat configuration on the surface. This chain is accompanied by a number of condensed anions lower than that corresponding to the condensation degree in solution, Section 3 of SM. This is a consequence of the electrostatic repulsion between the anions and the negatively charged surface. It should be noted that there is an important amount of cations on the surface, but these do not approach the polyelectrolyte chain due to electrostatic repulsion. Otherwise, the chain with $l_0 = 0.75\text{nm}$ presents a configuration where monomers are slightly away from the surface with respect to the previous case, and the number of condensed anions is negligible, as shown in frame1d.

According to Manning theory, counterion condensation in solution takes places when $\lambda_{PE} \gg 1$, where λ_{PE} is the Manning parameter defined as [3]:

$$\lambda_{PE} = l_B/l_0 \tag{6}$$

Thus, counterion condensation takes place when the bond equilibrium length is shorter that the Bjerrum length. This parameter plays a central role in the condensation of counterions and will be used in the present analysis. In the conditions of the present work the

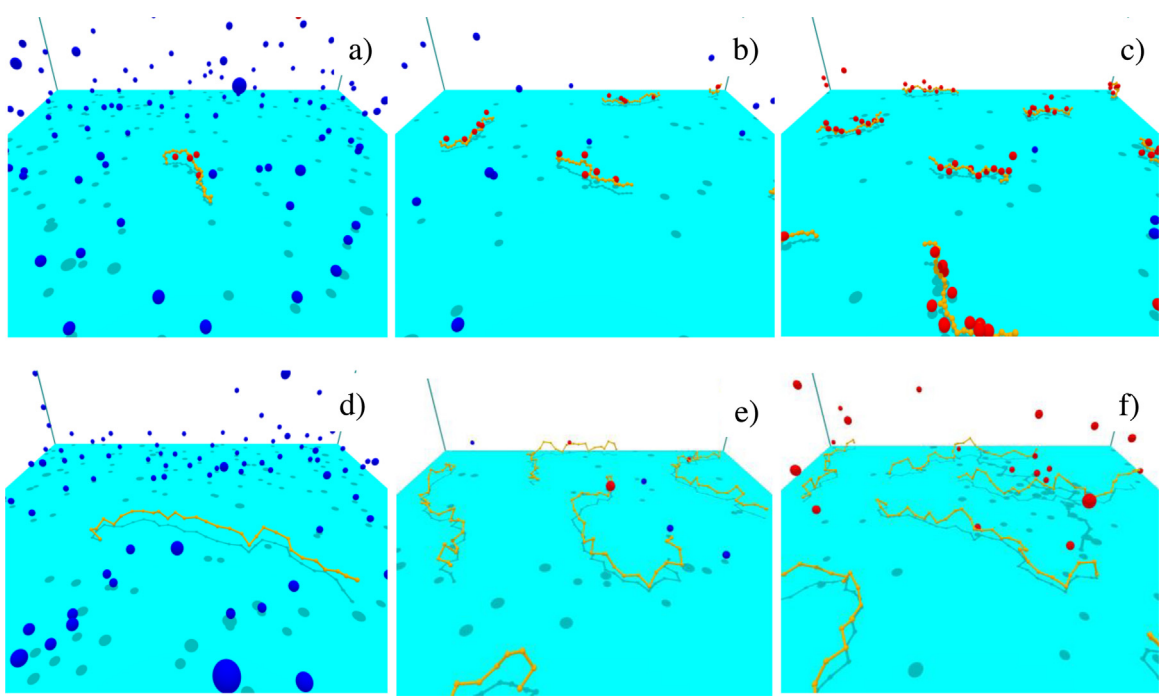


Fig. 1. Typical frames of the conformation of polyelectrolyte chain (30-monomers) and small ion positions on charged surface obtained after equilibration by Monte Carlo simulation. For different values of stoichiometric ratio ξ_S and l_0.$l_0 = 0.25\text{nm}$ for (a), (b) and (c) and $l_0 = 0.75\text{nm}$ for (d), (e) and (f). The surface is charged with a charge density ($\sigma_S = -0.2e/\text{nm}^2$). $\xi_S = \frac{1}{6}$ (a and d), $\xi_S = 1$ (b and e) and $\xi_S = 1.5$ (c and f). Monomers (green), cations (blue), anions (red). $c_{Salt} = 0.001\text{M}$.

Bjerrum length has a value of $l_B = 0.71$nm. Then with $l_0 = 0.25$nm and $l_0 = 0.75$nm, the Manning parameter has a value of $\lambda_{PE} \approx 3$ and $\lambda_{PE} \approx 1$ respectively.

Frames b and e depict the system where six polyelectrolyte chains are added to the simulation box. This addition results in a charge stoichiometric relation of 1:1; the charges of polyelectrolytes and surface ($\xi_S = 1$). The six chains are fully adsorbed both in the $l_0 = 0.25$nm as in $l_0 = 0.75$nm case. However, we can observe that counterion condensation is higher in the first case ($\lambda_{PE} \approx 3$) as seen in frame 1b.

Note that we are comparing frames a and b, where one and six chains are adsorbed respectively. We can observe that counterion condensation increases considerably when coverage degree increases. This shows that small anions prefer to be localized close to the polyelectrolyte chain with the consequent loss of translational entropy. Yet, it is possible since the adsorption of several chains has two energetic effects: the fact that the distribution of several chains on the surface shields the repulsive electrostatic interaction between the anions and the negative charged surface, favoring counterion condensation; the counterions condensed reduce the net charge of the chain and yield the shielding of the electrostatic repulsion between chains adsorbed on the surface.

With nine chains ($\xi_S = 1.5$), polyelectrolyte charges exceed the amount of charges on the surface (frame c and e). In the $l_0 = 0.25$nm case, all chains absorb and carry many condensed counterions. However, chains with $l_0 = 0.75$nm only adsorb eight chains without considerable amount of counterions.

In order to estimate quantitatively the previous observations, we have measured the local concentration of species and counterion condensation on the PE adsorbed.

The local concentration profiles of cation, anion and PE as a function of distance from the charged surface are denoted as $\rho_{Ca}(z)$, $\rho_{An}(z)$, and $\rho_{PE}(z)$ respectively. They have been calculated using the standard histogram technique. Each z_i (that is the z coordinate corresponding to the position r_i of particle i) is arranged into a histogram, where each bin extends from z to $z + dz$ and has width $dz = 0.1$nm.

Fig. 2 shows the local concentration of cation, anion and polyelectrolyte as a function of the distance from the charged surface.

Fig. 2a shows the local concentration of all species corresponding to the simulation conditions represented by frames 1a and 1d, where a 30-monomer single chain is added to the simulation box (stoichiometric ratio $\xi_S = 1/6$). The behavior of the two types of chains is compared: $l_0 = 0.25$nm and $l_0 = 0.75$nm. When a single chain with $l_0 = 0.25$nm is adsorbed, we can note that the polyelectrolyte is distributed in the range $0 < z < 1$nm, with a maximum concentration occurring near 0.3nm from the surface. This indicates that the adsorbed chain shows flat conformations due to a very thin thickness, as compared with the chain contour length $(N_m - 1)\, l_0 = 7.25$nm, the end-to-end distance of a fully extended chain configuration. The PE chain is associated with a peak of anions, which has a much lower intensity than the peak corresponding to PE, indicating that the chain has few anions condensed. We can also observe that the amount of cations is appreciable, indicating that a single chain is not enough to replace the original ion double layer of the surface. In the case of the polyelectrolyte chain with $l_0 = 0.75$nm, the PE concentration profile is restricted to the region $0 < z < 1.5$nm, i.e., the PE distribution is moved slightly away from the surface, decreasing its maximum intensity with respect to the $l_0 = 0.25$nm case. Here, the presence of anions is negligible, indicating that the chain is free of condensed anions.

An interesting situation is found when six chains are added to the simulation box (see profiles in Fig. 2b) corresponding to frames 1b and 1e ($\xi_S = 1$). After equilibration, the six chains are adsorbed in both cases $l_0 = 0.25$nm and $l_0 = 0.75$nm. However, in the first case we can note that chain adsorption occurs with an increase in anion concentration that reaches approximately ten percent of the adsorbed monomer concentration. A low amount of cations is also present. In the second case, the chains are adsorbed without the presence of small ions.

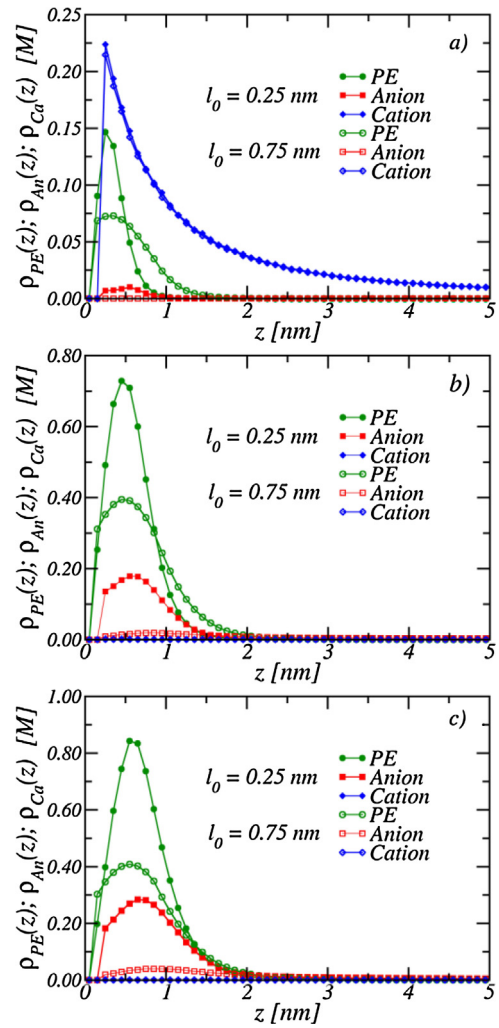


Fig. 2. Local concentration profiles of polyelectrolyte, cation and anion as a function of the distance from the surface corresponding to the frames illustrated in Fig. 1. The stoichiometric ratios were: (a)$\xi_S = 1/6$; (b)$\xi_S = 1$ and (c) $\xi_S = 1.5$. With $\sigma_S = -0.2\mathrm{e/nm}^2$ and $c_{Salt} = 0.001$M.

Fig. 2c depicts the systems corresponding to frames 1c and 1f ($\xi_S = 1.5$). We observe that the PE concentration profile has a maximum close to $z = 0.5$nm, suggesting that the adsorption of several chains results in a structure that is more extended than in the case of a single chain. The anion profile also shows a maximum close to $z = 0.6$nm, suggesting that these ions are located along the chain, while the original ionic atmosphere (cations) of the surface is completely lost. By contrast, the adsorbed amount of PE when $l_0 = 0.75$nm is lower, resulting in eight adsorbed chains from a total of nine. In this case, the PE concentration profile also presents a maximum around $z = 0.6$nm, but the anions show a wide distribution with a maximum at $z = 0.9$nm, displaced from the surface with respect to the distribution of the PE. This feature indicates that anions are preferentially in a non-condensed state.

In order to evaluate the adsorption of the different species, polyelectrolyte (PE), cations (Ca) and anions (An), we have defined the amount of adsorption Γ_{Sp} as:

$$\Gamma_{Sp} = \int_{z=0}^{z=5\mathrm{nm}} \rho_{Sp}\left(z'\right) \mathrm{A}dz' \tag{7}$$

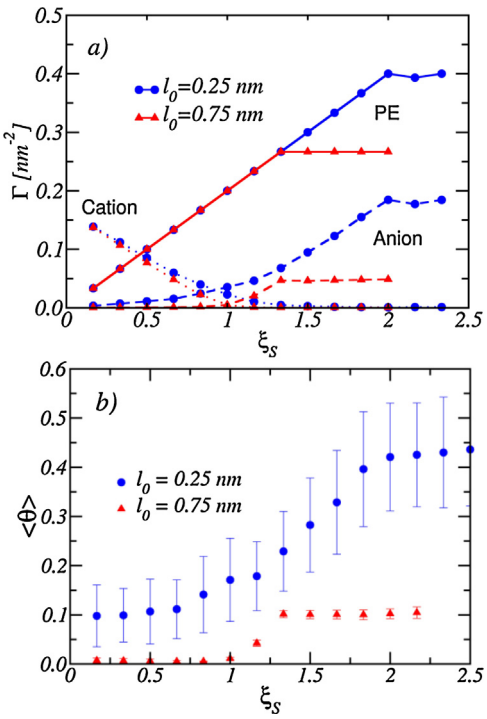


Fig. 3. (a) Adsorption amount of polyelectrolyte, cation and anion as a function of the stoichiometric ratio. Each chain has $N_m = 30$ and different values of l_0. (b) condensation degree as a function of stoichiometric ratio.

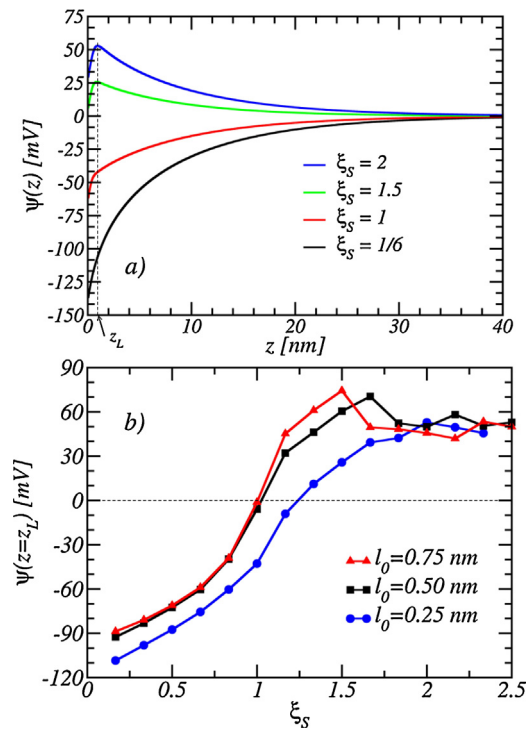


Fig. 4. (a) Electrostatic potential profile as a function of distance z for different values of stoichiometric ratio in the simulation box; chains having $N_m = 30$ and $l_0 = 0.25$nm. (b) electrostatic potential at the adsorbed layer for different l_0 values.

where $\rho_{Sp}(z')$ is the density profile of species Sp (Sp = PE, Ca, An). The integration is carried out between $z = 0$ and $z = 5$nm, since the species are mainly located in this range (Fig. 2).

The amounts of adsorption (Γ) for polyelectrolyte monomers, cations and anions on charged surface ($\sigma_S = -0.2e/\text{nm}^2$) are plotted as a function of stoichiometric ratio ξ_S in Fig. 3a. The chain has $N_m = 30$ and two different values of l_0 as mentioned above. It can be observed that the adsorption of polyelectrolyte profile starts with a linear growth as a function of the amount of added chains, and then reaches a plateau.

The first part of the profile of Fig. 3a has a linear increase in each chain added; the increment value of polyelectrolyte adsorption is equal to the number of monomers per chain adsorbed in the surface N_m/A, as long as a new chain is totally adsorbed. When $\xi_S = 1$ the amount of polyelectrolyte adsorbed ($\Gamma_{PE} \approx 0.2\text{monomer/nm}^2$) is required for counterbalancing surface charge ($\sigma_S = -0.2/\text{nm}^2$). However, in the $l_0 = 0.25$nm case polyelectrolyte is associated with significant amounts of anion and cations adsorbed, which are negligible in the $l_0 = 0.75$nm case. The adsorption plateau of the two types of chains considered here exceeds the amount of monomers needed for counterbalancing surface charge. The ξ_S value whose plateau is reached depends on the type of chain, $\xi_S \approx 2$ and $\xi_S \approx 1.33$ for $l_0 = 0.25$nm and $l_0 = 0.75$nm respectively. Clearly, in the two types of chain bonds considered here, the amount of polyelectrolyte adsorption is higher than that necessary for surface counterbalance. In particular, when $l_0 = 0.25$, the limiting amount corresponds to twice the original charge.

It can be noticed that the quantity of cation near the surface decreases upon addition of polyelectrolyte chains, since cations are displaced by the positively charged PE chains. The PE with $l_0 = 0.75$ is found to be more efficient in this displacement. The cations are completely replaced for $\xi_S \geq 1$. On the other hand, anion concentration gradually increases up to the limit for the given chain type. However, the proportion of anion in relation of PE adsorbed is higher for chains with $l_0 = 0.25$nm(around 45%), as compared to $l_0 = 0.75$nm chains (around 20%).

At this point a question naturally arises: what is the fraction of adsorbed anion condensed on polyelectrolyte chains. To answers this, we should define that an anion is condensed to the chain using a geometrical criterion. We will assume that when an anion is at a distance lower than 1 nm from a monomer, this anion is condensed on the corresponding chain. This geometrical criterion is fully explained in Section 3 (S3) of the SM. Fig. 3b shows condensation degree as a function of stoichiometric ratio. We can see that for stoichiometric ratios lower than $\xi_S \leq 0.66$, condensation has a constant value for chains with $l_0 = 0.25$, regardless of the amount of adsorbed chains. This suggests that chain coverage on the surface is so low that chains behave as if no interaction is found between them. At higher values of the stoichiometric ratio, counterion condensation has an even increase, until reaching a plateau with a condensation value close to $\langle\theta\rangle \approx 0.45$. This value is very close to those of the fraction of anions adsorbed, suggesting that most anions are condensed on polyelectrolyte chains.

The next question addressed now is how this condensation affects chain capacity for neutralizing and reverting the charge of the surface. To analyze this point, we consider the local electrostatic potential $\psi(z)$ as a function of the distance from the surface.

In order to obtain the electrostatic potential $\psi(z)$ we used the equation:

$$\psi(z) = -\frac{e}{\epsilon_0\epsilon_r}\int_z^{\infty}\left[\rho_q\left(z'\right)\left(z'-z\right)\right]dz' \tag{8}$$

where $\rho_q(z)$ is the total charge density calculated as:

$$\rho_q(z) = Z_+\rho_+(z) + Z_-\rho_-(z) + Z_{PE}\rho_{PE}(z) \tag{9}$$

The electrostatic potential profiles are plotted in Fig. 4a for different stoichiometric ratios; each chain is made of 30 monomers with $l_0 = 0.25$nm.

Upon adsorption of a single chain ($\xi_S = 1/6$), the electrostatic potential starts from very low values at $z = 0$, $\psi_S \simeq -135$mV, and then increases monotonically to zero, far from the surface. These

results may be compared with those of a surface with the same charge density ($\sigma_S = -0.2e/nm^2$) but without PE, as given in Fig. S1b, in the presence of added salt at a concentration of $C_S = 0.001$M. These two profiles look similar.

The electrostatic potential profile is slightly affected by the addition of 2 and 3 PE chains (data not shown). These profiles remain similar to that of a single chain, but overall the potential increases slightly. The increase in the number of PE chains leads to a further increase in electrostatic potential, since the negative surface charge is screened by adsorption of the positively charged polymer.

When the number of chains is 6, the amount of monomer equals the number of charges on the surface and we get ($\xi_S = 1$), that is, the ratio between the number of charges on the PE and the charge on the surface is equal to one. However, it can be observed that under these conditions, PE adsorption results in a negative electrostatic potential $\psi_S \simeq -60$mV.

When nine PE chains ($\xi_S = 1.5$) are adsorbed, the electrostatic potential profile starts from a negative value at the surface, $\psi_S \simeq 0$mV, and increases to a maximum value at $z \approx 0.95$nm, where $\psi \simeq 25$mV, indicating surface charge reversal. Then, the potential tends smoothly to zero as the distance from the surface increases.

The local maximum of the electrostatic potential becomes more pronounced when 12 chains are added to the system ($\xi_S = 2$), with a resulting value of $\psi(z \approx 0.95\text{nm}) \simeq 52$mV. All ψ maxima are located at about the same distance from the surface, namely 0.95nm, referred to by us as z_L, depicted with a vertical broken line in Fig. 4a. At large z values the potential decreases monotonically to zero in all cases.

We can summarize the behavior described in the previous paragraph by plotting $\psi_{z_L}(\xi_S) = \psi(z = z_L, \xi_S)$, i.e., the electrostatic potential at $z = z_L$, as a function of the stoichiometric ratio ξ_S, as shown in Fig. 4b. In the case of chains with $l_0 = 0.25$nm, the $\psi_{z_L}(\xi_S)$ profile starts at values close to -110mV. Then it increases, going through zero at $\xi_S \approx 7/6$ (actually $\psi_{z_L}(\xi_S = 7/6) \approx -9$mV). Since ξ_S is calculated using the number of polymer chains introduced in the simulation Np, an integer number, we must set some general criterion to estimate ξ_N, the value for which the electrostatic potential becomes null $\psi_{z_L}(\xi_N) = 0$. With this purpose, we have defined the quantities ψ_0 and $\psi_{<0}$, which are the neighboring points to the root $\psi_{z_L}(\xi_N) = 0$. ψ_0 and $\psi_{<0}$ correspond to the points preceding and following the root respectively. From these values, we can estimate the number of chains ξ_N for which ψ_{z_L} vanishes from a linear interpolation between ψ_0 and $\psi_{<0}$ according to:

$$\xi_N = \xi_{\psi 0} + \frac{\psi_0}{(\psi_{<0} - \psi_0)} \tag{10}$$

where $\xi_{\psi 0}$ is the stoichiometric ratio corresponding to ψ_0. For $l_0 = 0.25$nm, the value is $\xi_N = 1.24$. For chains with $l_0 = 0.5$nm and $l_0 = 0.75$nm, the value is close to 1.

Kleimann et al. [14]. observed experimentally this phenomenon, and referred to such a condition, $\xi_N > 1$, as a *super-stoichiometric charge neutralization,* in contrast with a *stoichiometric charge neutralization,* where $\xi_N = 1$. Kleimann et al. have proposed that super-stoichiometric behavior would be possible because a certain number of counterions could follow the adsorbed polyelectrolyte chains [14]. This proposal is in agreement with the results of our simulation.

After charge inversion is achieved, $\xi_S > 1.24$, the electrostatic potential increases by adsorbing more polyelectrolyte chains until reaching $\psi_{z_L} \approx 60$mV, where the number of adsorbed chains corresponds to thirteen ($\xi_S = 13/6$). Fig. 4b shows that, when ψ_{z_L} is plotted as a function of ξ_S, a maximum value of electrostatic potential is obtained. We represented this value with ψ_{max}. The corresponding stoichiometric ratio of maximum electrostatic potential is $\xi_{\psi_{max}}$, which stands for the maximum polyelectrolyte

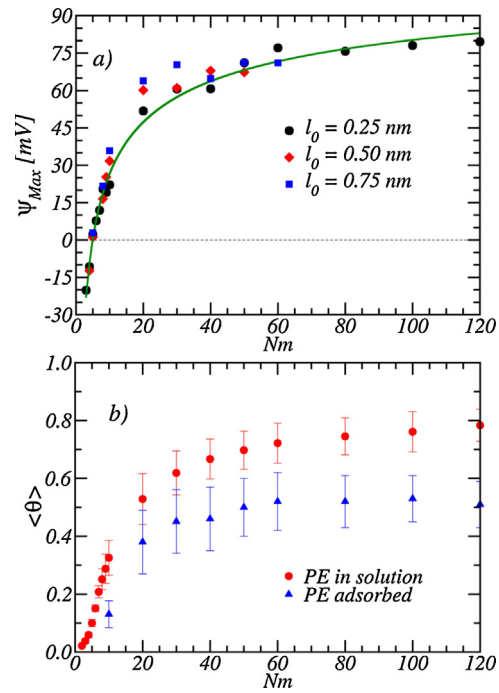


Fig. 5. (a) Maximum electrostatic potential ψ_{max} as a function of chain size for different bond distances. (b) counterion condensation degree on polyelectrolyte in solution and adsorbed on the surface for chain with $l_0 = 0.25$nm.

charge amount per unit surface charge that may be adsorbed for the given σ_S. For the chain with $l_0 = 0.25$nm, we get $\xi_{\psi_{max}} \approx 2.25$.

For the chains with $l_0 = 0.50$nm and $l_0 = 0.75$nm, the electrostatic potential increases in a similar fashion for $\xi_S \leq 1$ and ψ_{z_L} curves run about 20mV over the curve with $l_0 = 0.25$nm (Fig. 4b). These results show that the chains with the lower value of linear charge density (higher l_0) are more efficient to counterbalance surface charge. The chains having $l_0 = 0.50$nm and $l_0 = 0.75$nm neutralize the surface ($\psi_{z_L} \simeq 0$) with a stoichiometric ratio $\xi_S = 1$ since the number of condensed anions on the chains is negligible. These chains show a higher maximum electrostatic potential ψ_{max} than that with $l_0 = 0.25$nm. Furthermore, this maximum value is obtained with fewer chains, i.e., with a lower charge ratio $\xi_{\psi_{max}}$. Therefore, chains with a lower value of linear charge density appear to be more efficient at generating the charge reversal phenomenon.

The results of Monte Carlo simulation presented up to here were obtained with 30-monomer polyelectrolyte chains. We observed that counterion condensation is an important phenomenon connected with the neutralization and charge reversion of the charged surface. Counterion condensation in solution is a well known phenomenon. The condensation value is highly dependent on a low chain size since end effects are important. Then with a higher chain size, the counterion condensation shows a negligible correlation with chain size (Fig. S5 of SM).

However it is possible that the monomer number per chain affects the condensation and maximum electrostatic potential maximum ψ_{max} of the polyelectrolyte adsorbed. This point will be analyzed now.

Fig. 5a shows the effect of chain size (N_m) on the maximum electrostatic potential ψ_{max} for different equilibrium bond lengths.

We know that a monomer solution ($N_m = 1$) is, in our model, equivalent to a monovalent salt, so it will not lead to charge reversion of the charged surface (see SM). On the other hand, PE chains can also be seen as giant multivalent counterions with additional entropic degrees of freedom, eventually leading to charge reversion. However, what is the minimum size of PE chains to observe reversal? It is found that the three types of chain show similar

trends as long as chain size fulfills $N_m < 10$. It can be observed that the potential ψ_{max} has negative values for chain sizes smaller than the pentamer, i.e., the minimum chain size to cause charge reversal in the present conditions is $N_m = 5$.

Then, ψ_{max}increases until reaching a plateau of 80mV at approximately $N_m \approx 60$. Then, ψ_{max}increases has an important size-dependent behaviour for short chains, in contrast with the observation for chain sizes larger than $N_m \approx 60$, where polyelectrolyte size does not seem to matter any more. This is closely connected with the counterion condensation phenomenon, which has been experimentally observed by Scheler et al. [42,43] who showed a similar profile of counterion condensation as a function of chain size (Fig. S5 in SM).

Fig. 5b depicts counterion condensation degree as a function of chain size in solution and in adsorbed cases. The chains considered have $l_0 = 0.25$nm, and the adsorbed case corresponds to conditions of maximum electrostatic potential (Fig. 5a). The counterion condensation behaviour, as a function of size, is similar for both chains in solution or adsorbed. Both have the same limiting size $N_m \approx 60$ $N_m \approx 60$, delimiting the behavior of PE chains, and the relative importance of chain end effects. Counterion condensation decreases when the polyelectrolyte is adsorbed; yet, most of counterions remain condensed on the polyelectrolyte chains.

4. Conclusions

In the present work, we have performed Monte Carlo simulations to analyze the phenomenon of counterion condensation upon adsorption of a polyelectrolyte on a charged surface. The model has focused on the electrostatic aspects of the interaction between the polyelectrolyte chains themselves, and their interaction with the counterions and the charged surface. As described, the condensation degree shows dependence on the coverage degree in the following cases: with a low number of chains adsorbed on the surface, condensation is low due to the electrostatic repulsion of anion (PE counterions) with the negative charged surface. As coverage degree increases, counterion condensation also increases, since the adsorbed chains shield the repulsion between the anions and the surface, and at the same time, the condensed anions shield the repulsion between adsorbed PE chains.

Additionally, chains with a higher value of l_0 need a low amount of chains to neutralize and/or revert the negative surface charge. They are more effective since they have low capacity for condensing counterions. However, the maximum electrostatic potential reached by all types of chains is of the same order of magnitude. By contrast, chains with a lower value of l_0 require a higher amount of chains for surface neutralization, and for

reaching the maximum electrostatic potential of charge reversion, $\xi_S > 2$. This is due to the considerable number of counterion that remains condensed on the adsorbed chains.

The fact that the maximum value of electrostatic potential observed upon polyelectrolyte adsorption has a strong variation at a low chain size, reaching a plateau at a relatively long chain size, means that we can classify the system behavior into two groups. One labeled as oligoelectrolyte behavior, with a low polymerization degree (lower than 60 monomers) where end effects are important, and another labeled as ordinary polyelectrolyte behavior, where the degree of counterion condensation and other quantities are independent of chain size.

Another remarkable conclusion of the present work is that in order to get surface charge reversal, a minimum polymer chain size is required. Under the present simulation conditions, the minimum required is the pentameric chain. The fact that a minimum chain size is necessary to get charge reversal has been experimentally observed recently by Szilagyi et al [44]. They studied the charging and aggregation rates of carboxyl latex particles in the presence of multivalent oligoamines. The colloidal suspension is destabilized by low valence oligoamines like that of simple ions. Oligoamines of a size larger than the tetramer lead to destabilization by charge neutralization; yet, this is followed by subsequent restabilization for overcharging. This minimum size may change depending on other parameters of the system, such as concentration and type of salt added, pH, these being the subject of our next study.

Acknowledgment

C.F. Narambuena wants to thank the financial support of CLAF, for postdoctoral grant. The authors thank Prof. Scheler for the experimental values of the effective charge of PSS (Fig. S5). The computational and technical support by C. Diaz Torrejon and M. Cedillo Torres of CNS-IPICYT and R. Ramirez Carmona, J.C. Sanchez Leanos, J. Renteria Arriaga, H. Chavez and J.L. Castillo of IF-UASLP, as well as language assistance by Carolina Mosconi are gratefully acknowledged. E. Pérez thanks Conacyt (project 132056) for financial support. E.P.M. Leiva thanks financial support from CONICET PIP11220110100992, SECyT Universidad Nacional de Córdoba, and Program BID (PICT 2012-2324).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.colsurfa.2015.09.038.

References

[1] T. Radeva, Physical Chemistry of Polyelectrolytes, Marcel Dekker, New York, 2001.
[2] P.M. Visakh, O. Bayraktar, G.A. Pico, Polyelectrolytes Thermodynamics and Rheology, Springer, Cham, 2014.
[3] G.S. Manning, J. Chem. Phys. 51 (1969) 924.
[4] R.G. Winkler, M. Gold, P. Reineker, Phys. Rev. Lett. 80 (1998) 3731.
[5] H.J. Limbach, C. Holm, J. Chem. Phys. 114 (2001) 9674.
[6] S. Liu, M. Muthukumar, J. Chem. Phys. 116 (2002) 9975.
[7] T.Y. Wang, T.R. Lee, Y.J. Sheng, H.K. Tsao, J. Phys. Chem. B 109 (2005) 22560.
[8] C. Fleck, H.H. von Grunberg, E. Phys Rev, Stat. Nonlinear Soft Matter Phys. 63 (2001) 061804.
[9] P. Sens, J. Joanny, Phys. Rev. Lett. 84 (2000) 4862.
[10] V. Milkova, T. Radeva, J. Colloid Interface Sci. 298 (2006) 550.
[11] T. Radeva, K. Kamburova, J. Colloid Interface Sci. 293 (2006) 290.
[12] X.G. Briones, M.V. Encinas, D.F.S. Petri, J.E. Pavez, R.A. Tapia, M. Yazdani-Pedram, M.D. Urzua, Langmuir 27 (2011) 13524.
[13] X. Chatellier, J.Y. Bottero, J. Le Petit, Langmuir 17 (2001) 2782.
[14] J. Kleimann, C. Gehin-Delval, H. Auweter, M. Borkovec, Langmuir 21 (2005) 3688.
[15] C. Olsen, P.R. Van Tassel, J. Colloid Interface Sci. 329 (2009) 222.
[16] P.R. Van Tassel, Curr. Opin. Colloid Interface Sci. 17 (2012) 106.
[17] Z.M. Yaremko, N.G. Tkachenko, L.B. Fedushinskaya, Russ. J. Phys. Chem. A 2011 (1791) 85.
[18] D. Andelman, J.F. Joanny, L. Comptes Rendus De, Acad. Sci. Ser. Phys. Astrophysique 1 (2000) 1153.
[19] O.V. Borisov, E.B. Zhulina, T.M. Birshtein, J. Phys. II 4 (1994) 913.
[20] I. Borukhov, D. Andelman, H. Orland, Macromolecules 31 (1998) 1665.
[21] J.F. Joanny, Eur. Phys. J. B. 9 (1999) 117.
[22] M. Muthukumar, J. Chem. Phys. 86 (1987) 7230.
[23] A. Shafir, D. Andelman, R.R. Netz, J. Chem. Phys. 119 (2003) 2355.
[24] R. Varoqui, J. Phys. II 3 (1993) 1097.
[25] C.Y. Kong, M. Muthukumar, J. Chem. Phys. 109 (1998) 1522.
[26] R. Messina, Phys. Rev. E 70 (2004) 51802.
[27] R. Messina, Macromolecules 37 (2004) 621.
[28] R. Messina, C. Holm, K. Kremer, J. Poly. Sci. Part B-Poly. Phys. 42 (2004) 3557.
[29] R.S. Dias, A.A.C.C. Pais, P. Linse, M.G. Miguel, B. Lindman, J. Phys. Chem. B 109 (2005) 11781.
[30] C.F. Narambuena, D.M. Beltramo, E.P.M. Leiva, Macromolecules 40 (2007) 7336.
[31] C.F. Narambuena, D.M. Beltramo, E.P.M. Leiva, Macromolecules 41 (2008) 8267.
[32] S.C.C. Nunes, T.F.G.G. Cova, A.A.C.C. Pais, J. Chem. Phys. 139 (2013).
[33] S.C.C. Nunes, P. Pinto, A.A.C.C. Pais, J. Comput. Chem. 34 (2013) 1198.
[34] J.M.Y. Carrillo, A.V. Dobrynin, Langmuir 23 (2007) 2472.
[35] B.F. Qiao, J.J. Cerda, C. Holm, Macromolecules 2011 (1707) 44.

[36] G. Reddy, R.W. Chang, A. Yethiraj, J. Chem. Theory Comput. 2 (2006) 630.
[37] G. Reddy, A. Yethiraj, J. Chem. Phys. 132 (2010) 074903.
[38] A.S. Panwar, S. Kumar, J. Chem. Phys. (2005) 123.
[39] G.M. Torrie, J.P. Valleau, J. Chem. Phys. 73 (1980) 5807.
[40] D. Boda, K.Y. Chan, D. Henderson, J. Chem. Phys. 109 (1998) 7362.
[41] R. Messina, Phys. Rev. E 74 (2006) 49906.
[42] U. Böhme, U. Scheler, Macromol. Chem. Phys. 208 (2007) 2254.
[43] K. Huber, U. Scheler, Curr. Opin. Colloid Interface Sci. 17 (2012) 64.
[44] I. Szilagyi, A. Polomska, D. Citherlet, A. Sadeghpour, M. Borkovec, J. Colloid Interface Sci. 392 (2013) 34.