

Adsorption of a weakly charged polymer on an oppositely charged colloidal particle: Monte Carlo simulations investigation

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Abstract

Monte Carlo simulations were used to investigate the conformational and electrical properties of isolated weak polyelectrolytes in the presence of an oppositely charged particle. Titrations curves were calculated to get an insight into the role of pH on the degree of ionization and conformation of isolated chains. The effect of ionic concentration and polyelectrolyte length on the titration curves was also investigated. The complex formation between the isolated polyelectrolyte and the oppositely charged particle was considered at different pH and ionic concentration values. The adsorption/desorption limit was calculated and the effect of the polyelectrolyte adsorption on the titration curves investigated. In particular, it was demonstrated that the presence of an oppositely charged particle clearly increases the degree of ionization of the weak polyelectrolyte and that ionic concentration plays a subtle role by increasing/reducing both the attractive energy between the polyelectrolyte and the particle and the polyelectrolyte degree of ionization.

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1. Introduction

Polyelectrolytes in solutions with oppositely charged colloids are of great importance for many industrial processes [1–6] such as water treatment as flocculating/water insoluble mixtures, powder processing as dispersion agents and food technology as rheology modifiers. In addition, many biomolecules, such as DNA are also polyelectrolytes [7] and their complexations with proteins, for example, are expected to play important roles in biological processes. In environmental chemistry, interactions between inorganic colloids and polymers are also of great interest since they are expected to control colloid coagulation and the fate and transport of trace pollutants associated to inorganic colloids [8,9]. Hence, regarding the practical aspects, but also the potential theoretical interests

of these systems, a better understanding of the key factors controlling polyelectrolyte adsorption on oppositely charged colloids is, therefore, important.

For polyelectrolyte adsorption we have to make a distinction between strong and weak polyelectrolytes. The adsorption of strong polyelectrolytes onto flat or curved surfaces with an opposite constant charge density was first considered [10–13]. The effect of ionic concentration, adsorption limits and chain conformations were reported. In particular, it was shown that the charge due to the adsorbed polyelectrolyte often compensates, or overcompensates, the surface charge. It was demonstrated that the effect of the ionic strength is a subtle force balance between electrostatic attractive forces and electrorepulsive forces, causing the polyelectrolyte to adopt extended conformations at low ionic concentration and thus collapse onto the surface. Higher adsorbed amounts are generally observed for surfaces with higher surface charge densities because of the electrostatic contribution to the adsorption energy of the monomers. A decrease in the adsorbed amounts and desorption is generally observed with increasing the ionic strength.

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Adsorption of weak polyelectrolytes onto surfaces with fixed charges is more complicated owing to the fact that the linear charge density of the polyelectrolyte is strongly influenced by the pH, ionic concentration and the presence of an oppositely charged surface, with the degree of dissociation also being a function of the distance from the surface. A few years ago, a theory for the adsorption of linear polyelectrolytes was presented by Van der Schee and Lyklema [14] who extended the polymer adsorption model of Roe [15] by incorporating electrostatic interactions. This theory was then extended to weak polyelectrolytes by Evers et al. [16] and Böhmer et al. [17] by allowing the dissociation degree to vary with the distance from the surface. Then Vermeer et al. [18] demonstrated that the extended self-consistent-field (SCF) model predicts an adjustment of both the charge density of the surface and that of the polymer according to the local electrostatic potential. It should be noted that all these theories are extensions of the SCF theory of Scheutjens and Fleer [19] and that they deal with the many-chain problem. Analytical theories for adsorption of single polyelectrolyte chains have been also developed. Muthukumar [20,21] derived explicit formulae for the dependence of adsorption characteristics of polyelectrolytes onto curved surfaces (spheres and cylinders) on temperature, Debye screening length, polyelectrolyte charge density, molecular weight, and curvature. Adsorption was found to be promoted upon a decrease in temperature, chain length, and salt concentration, or upon an increase in the radius and the surface charge density of a sphere. By considering the polyelectrolyte charge fraction and salt concentration, Haronska et al. [22] proposed a theoretical model (based on a self-consistent approach) for the complex formalism of flexible polyelectrolytes and oppositely charged spheres. A particular emphasis on the influence of the finite size of both polyelectrolyte and sphere was considered. The theoretical results were compared with the adsorption of polymethacrylic acid (PMA) on a cationic micro-network, and it was demonstrated that the criterion for critical adsorption shows a different behaviour for small and large curvature. The recent scaling theory of Schiessel [23] yields an approximate treatment of the chain-sphere complex over the whole range of parameters. It permits identification of a few independent scaling parameters and leads to the construction of two-dimensional phase diagrams (one for short and one for large screening lengths) that cover the whole range of all the other parameters.

Computer simulations allow treatment of polyelectrolyte adsorption on flat or curved surfaces over a large range of parameters and in some situations can fill the gap between existing theories and experiments. For example, the complexation between a linear flexible polyelectrolyte and oppositely charged macroions has been extensively examined by Jonsson and Linse [24,25] focussing on the effect of linear charge density, chain length, macroion charge, and chain flexibility. Chodanowski, Laguerir and Stoll [26–29] investigated the adsorption of flexible and semi-flexible

chains on an oppositely charged sphere by considering curvature effects and overcharging issue. They calculated adsorption limits and comparisons were made with experimental measurements [30]. However, most of the computer simulations of polyelectrolyte adsorption have considered strong polyelectrolytes. Although titrating polyelectrolytes has been intensively studied by computer simulations [31,32], as far as we are aware, no study has yet dealt with weak polyelectrolytes. Hence a further extension of simulations to weak polyelectrolyte adsorption is desirable.

In this work, Monte Carlo simulations are used to investigate the conformations of isolated weak polyelectrolytes and the formation of complexes between a large particle and a weak polyelectrolyte of opposite charge. A coarse-grained model using a pearlnecklace chain consisting of point charges connected to each other is used to describe the polyelectrolyte, while a uniformly charged hard sphere is used to mimic a particle. The model dimensions are parameterized from the atomistic description of a weak polyelectrolyte having no hydrophobic side chains: the poly(acrylic acid) (PAA). For isolated chains, titration curves are calculated to get an insight into the role of pH on the degree of ionization and possible conformational changes. Ionic concentration and polyelectrolyte length effects on the titration curves are also considered. The complex formation between an isolated polyelectrolyte and oppositely charged particle is also considered at different pH and ionic concentration values and the effect of polyelectrolyte adsorption on the titration curves investigated. The polyelectrolyte conformations are analysed prior to and after adsorption as well as the polymer structure at the interface by considering the number of monomers in trains and radial distribution function of charged and neutral monomers. Finally the adsorption/desorption limit, which is an important practical parameter is investigated by estimating the critical pH values where adsorption occurs.

2. Monte Carlo simulations

2.1. Model and method

A coarse-grained approach is used to represent the polyelectrolyte chain as an off-lattice 3 dimensional succession of N freely jointed hard spheres. Each sphere is considered as a coarse grained monomer unit of radius σ_m with a neutral or negative charge equal to -1 situated at its centre. The bond length and consecutive interchange distances are constant (see Section 2.2). The ionization degree α represents the fraction of ionized monomers of the chain. The particle is represented as an impenetrable, uniformly charged sphere with a radius σ_p . In this study we focused on a situation where $\sigma_p \gg \sigma_m$ so as to mimic polyelectrolyte adsorption on slightly curved surface. The central point charge Q of the particle is adjusted so as to

obtain a constant surface charge density representative of experimental values. The solvent is treated as a dielectric medium with a relative dielectric permittivity constant ϵ_r taken as that of water at 298 K i.e. 78.5. The total energy E_{tot} ($k_B T$ units) for a given conformation is the sum of the repulsive electrostatic interactions between monomers and attractive electrostatic interactions between the monomers and the particle E_{el} . Excluded volume E_{ev} is also included in the model to consider hard core interactions. All pairs of charged monomers within the polyelectrolyte interact with each other via a screened Debye–Hückel long range potential,

$$u_{\text{el}}(r_{ij}) = \frac{z_i z_j e^2}{4\pi\epsilon_r \epsilon_0 (r_{ij} + \zeta)} \exp(-\kappa(r_{ij} + \zeta)) \quad (1)$$

where z_i represents the amount of charge on unit i , and r_{ij} is the distance between two monomers i and j . ζ represents an additional term to the distance between monomers to take into account the delocalization of the charges from the chain backbone (see Fig. 1).

Monomers interact with the particle according to a Verwey–Overbeek potential,

$$u'_{\text{el}}(r_{ij}) = \frac{z_i z_j e^2}{4\pi\epsilon_r \epsilon_0 r_{ij}} \frac{\exp[-\kappa(r_{ij} - \sigma_p)]}{1 + \kappa\sigma_p} \quad (2)$$

so as to exclude the presence of ionic species within the particle. Free ions are not included explicitly in the simulations but their overall effects on monomer–monomer and monomer–particle interactions are described via the dependence of the inverse Debye screening length κ^2 [m^{-2}] on the electrolyte concentration. All pairwise interactions have been calculated without taking into account cut-off distances.

Monte Carlo simulations are performed according to the Metropolis algorithm in the canonical ensemble. To

generate new conformations, the monomer positions are randomly modified by specific movements; the end-bond, kink-jump, crankshaft, pivot and reptation. After each elementary movement, the Metropolis selection criterion is employed to either select or reject the move. The polyelectrolyte and charged particle are both allowed to move. It should be noted that the chain has the possibility to diffuse further away and leave the particle surface during a simulation run (hence desorption is possible in the model). After relaxing the initial conformation through approximately 10^6 cycles (equilibration period), chain properties are calculated and recorded after a given number of steps. To generate reversible protonation/deprotonation processes, at regular simulation steps, monomers are chosen randomly in the limit of $N/4$ monomers and their charges are switched from neutral to charged state or inversely. In order to achieve an efficient conformational relaxation of the chain after switching on or off charged monomers, the protonation/deprotonation procedure is less frequent than that of the monomer movements. It should be noted that the ratio between them depends on the chain length owing to the fact that longer chains need more time to relax. The acceptance of each protonation/deprotonation process is related to the Monte Carlo Metropolis selection criterion. The energy change is defined by [33]:

$$\Delta E = \Delta E_{\text{tot}} \pm kT \ln_{10}(\text{pH} - \text{p}K_0) \quad (3)$$

where $\text{pH} - \text{p}K_0$ is a parameter which is adjusted during the simulations. $\text{pH} - \text{p}K_0$ is imposed and then α is calculated as an output data. When the monomer is protonated, the plus sign is used in Eq. (3) (conversely, when the monomer is deprotonated, the minus sign is required). To calculate titrations curves, $\text{pH} - \text{p}K_0$ values have been adjusted from -2 to 10 by increments equal to one unit. After each increment and equilibration period, the mean degree of ionization of the polyelectrolyte α is calculated on a large number of equilibrated conformations. In this study, simulations always go from neutral polyelectrolytes ($\alpha = 0$) to fully charged chains. It should be noted that similar results are obtained when titrations from fully charged to neutral chains are considered.

2.2. Model parameterization

Molecular dynamics calculations were carried out using the Cerius2 interface (MSI) along with the UFF Universal Force Field 1.02 module [34]. The geometry of a polymer containing 200 monomers was optimized to evaluate some key distances based on an atomistic description of the PolyAcrylic Acid structure. The consecutive monomer–monomer distance was found to be equal to 2.54 \AA and charge delocalization from the chain backbone i.e. the barycentre of the COO^- charge to the chain backbone equal to 1.33 \AA . To take into account charge delocalization from the chain backbone, a delocalization parameter ζ was

1- Atomistic description

Molecular dynamics calculations

- Monomer size ($2\sigma_m$)
- Mean distance between charges

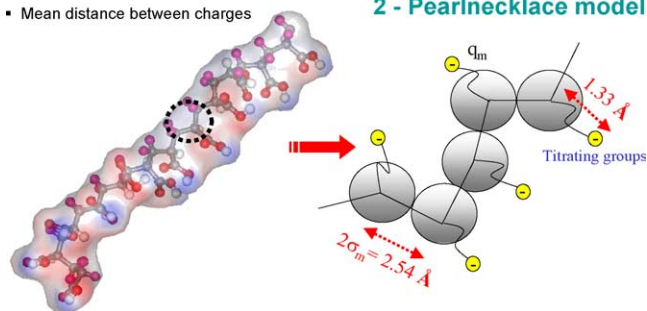


Fig. 1. Coarse grained description of the poly(acrylic acid) (PAA) system – $[\text{CH}_2\text{-CHCOOH}]_n^-$. q_m is the monomer charge equal to 0 or -1 e according to the degree of ionization α (charge delocalization was evaluated to 1.33 \AA from the monomer centre). σ_m represents the monomer radius equal to 1.27 \AA .

introduced and set to 2.66 Å (i.e. 2×1.33 Å), which is in good agreement with the calculated mean distance between the carboxylate charge barycentres ($\text{COO}^- - \text{COO}^-$) that was found to be about 5.20 Å.

To mimic the adsorption of a polyelectrolyte on a colloidal particle with small curvature, the particle radius σ_p was adjusted to 500 Å. Its central point charge Q was calculated so as to set the particle surface charge density σ to 5, 10, 50 and 100 mC/m², respectively.

3. Results and discussion

3.1. Conformations of isolated weak-polyelectrolytes

We first discuss the conformations of equilibrated isolated polyelectrolyte chains, which will be used as initial conformations for the particle–polyelectrolyte complex formation. Simulations with $N=200$ monomers at different ionic concentrations C_i (0.001, 0.01, 0.1 and 0.5 M) and as a function of $\text{pH} - \text{p}K_0$ have been carried out. Equilibrated conformations are presented in Table 1. In the inset of each case the average value of the ionization degree α is also given.

As expected, for a given C_i value, α increases with the increase of $\text{pH} - \text{p}K_0$. When $\text{pH} - \text{p}K_0 = -2$, the degree of ionization is weak and close to 0 (non-charged monomers are presented by dark grey spheres) and one observes SAW conformations. On the other hand when $\text{pH} - \text{p}K_0 = 10$ in almost all cases, fully charged polyelectrolyte chains are achieved. For a given value of $\text{pH} - \text{p}K_0$, it is demonstrated that α is strongly dependent on the ionic concentration, and in particular for higher $\text{pH} - \text{p}K_0$ values. Charge screening, by reducing the electro-repulsive interactions between the charged monomers, promotes an increase of α with an increase of $\text{pH} - \text{p}K_0$. For example, when $\text{pH} - \text{p}K_0 = 6$, fully charged polyelectrolytes ($\alpha = 1$) are achieved in the high ionic concentration regime, whereas α decreases to 0.41 at a low ionic concentration ($C_i = 0.001$ M). In the low ionic concentration regime, the intensity of the electrostatic repulsions along the chain backbone limits the degree of dissociation of the chain. It should be noted that fully charged and extended conformations are only achieved in the intermediate ionic concentration regime ($C_i = 0.01$ and 0.1 M). In that regime, charge screening promotes the charge emergence along the chain backbone and, in addition, long-range interactions are strong enough to form extended conformations. By increasing further the ionic concentration, electrostatic long-range effects are less important and as a result less extended conformations are achieved.

To characterize from a quantitative point of view the conformational change of the polyelectrolyte during the increase of $\text{pH} - \text{p}K_0$, the mean-square radius of gyration $\langle R_g \rangle^{\text{iso}}$ has been calculated (Fig. 2). It is demonstrated that chains begin to expand at intermediate $\text{pH} - \text{p}K_0$ values

depending on the ionic concentration and that the more extended conformations are achieved when C_i is equal to 0.01 M in good agreement with the qualitative analysis made from Table 1.

3.2. Titration curves of isolated polyelectrolytes

To capture the main features of pH-induced transitions, but also to bridge the gap between simulations and experiments, titration curves representing $\text{pH} - \text{p}K_0$ and the corresponding chain degree of ionization were calculated, and the effect of the ionic concentration and polyelectrolyte length investigated in a systematic way.

3.2.1. Effect of the ionic concentration on titration curves

As shown in Fig. 3, titration curves change appreciably from the dilute monoacid. Obviously the electrostatic interactions play a major role in the solution behavior of polyelectrolytes, with the presence of charges making further ionization of the chain more difficult. As the electrostatic interactions are controlled by the ionic concentration, the decrease of charge screening makes the difference between the apparent and intrinsic dissociation constant more important.

3.2.2. Effect of the polyelectrolyte length on titrations curves

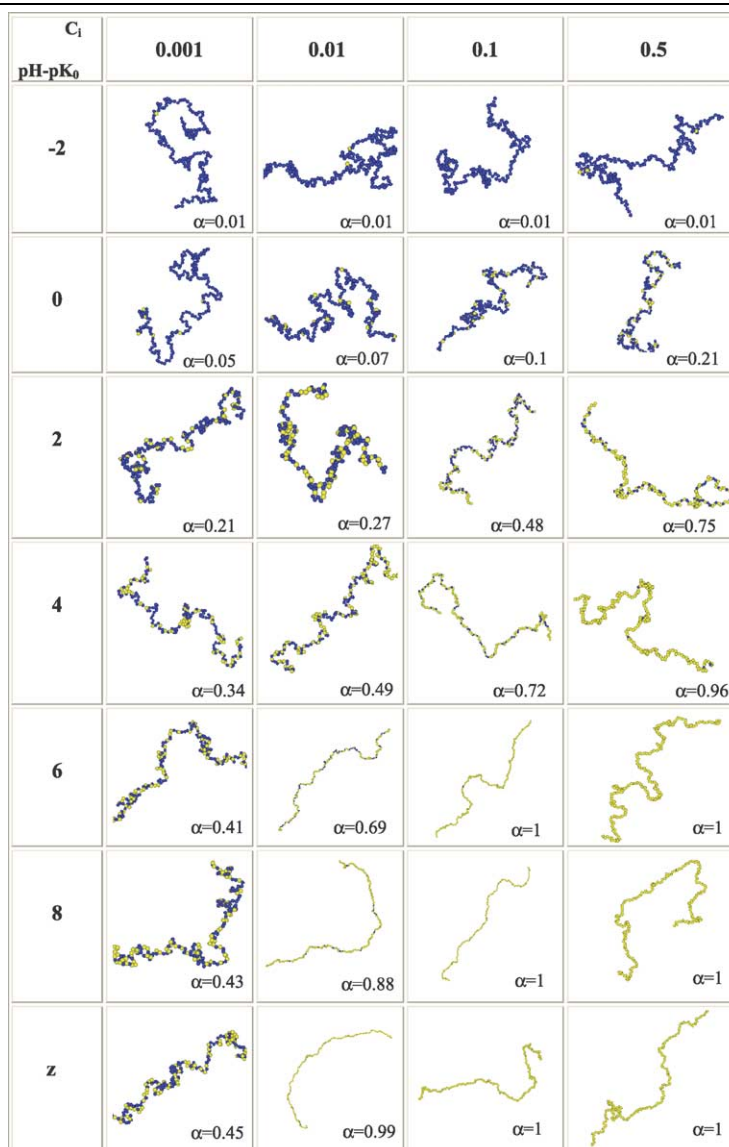
To investigate chain length effects on the conformational transitions and titration curves, MC simulations were performed by adjusting the monomer number to $N=40, 60, 80, 120$ and 200, respectively. Calculations were done at low ionic concentration $C_i = 10^{-3}$ M where size effects are expected to be most important. Fig. 4(a) demonstrates that long chains are more difficult to deprotonate (ionize) because of the increase of the total electrostatic potential on each monomer with increasing the size of the chain. However, an asymptotic behavior is observed at $N=200$. This chain length was considered in the rest of the study. It should be noted that by increasing the ionic concentration to 0.5 M (Fig. 4(b)) size effects are strongly attenuated because of the decrease with charge screening of electrostatic effects.

3.3. Particle–polyelectrolyte complex formation and titration curves

An equilibrated polyelectrolyte chain and a spherical oppositely charged particles are now confined in a spherical box not in contact with each other and the system is allowed to relax for equilibration. The $\text{pH} - \text{p}K_0$ values are then adjusted in the range from -2 to 10, the ionic concentration from 0.001 to 0.1 M (Table 2) and the surface charge density of the particle to 5, 10, 50 and 100 mC/m², respectively (Table 3). Snapshots of the equilibrated structures as well as the ionization degree of the polyelectrolyte are presented. Despite different scales being used to

Table 1

Monte Carlo equilibrated conformations of isolated weak polyelectrolyte chains ($N=200$) as a function of $\text{pH}-\text{p}K_0$ and ionic concentration C_i (0.001, 0.01, 0.1 and 0.5 M)



In the inset of each case, the average value of the degree of ionization α is given. As expected, the degree of ionization α increases with $\text{pH}-\text{p}K_0$. For a given value of $\text{pH}-\text{p}K_0$, the degree of ionization is strongly dependent of C_i .

represent the complexes, it is important to note here that the particle diameter is the same for all situations.

The polyelectrolyte chain is arbitrary considered as adsorbed when at least one monomer is in contact with the particle during more than 50% of the simulation time. Since the adsorption/desorption transition is sharp, this limit is not found sensitive to the criteria we use.

As shown in Tables 2 and 3, the weak polyelectrolyte can be desorbed or adsorbed on the particle, chain adsorption being clearly controlled by the values of the ionic concentration, particle surface charge density and $\text{pH}-\text{p}K_0$ values.

Adsorption is promoted by (i) increasing the $\text{pH}-\text{p}K_0$ value and subsequently the linear charge density of the polyelectrolyte; (ii) decreasing the ionic concentration, increasing thus the electrostatic attractive interactions between the monomer and the particle surface that we consider as the driving force for the adsorption and (iii) increasing the surface charge density of the particle. Hence, charge screening and low linear charge densities are expected to deserve chain adsorption. When the polyelectrolyte-particle interactions are not large enough to overcome the polyelectrolyte confinement near the particle (at low

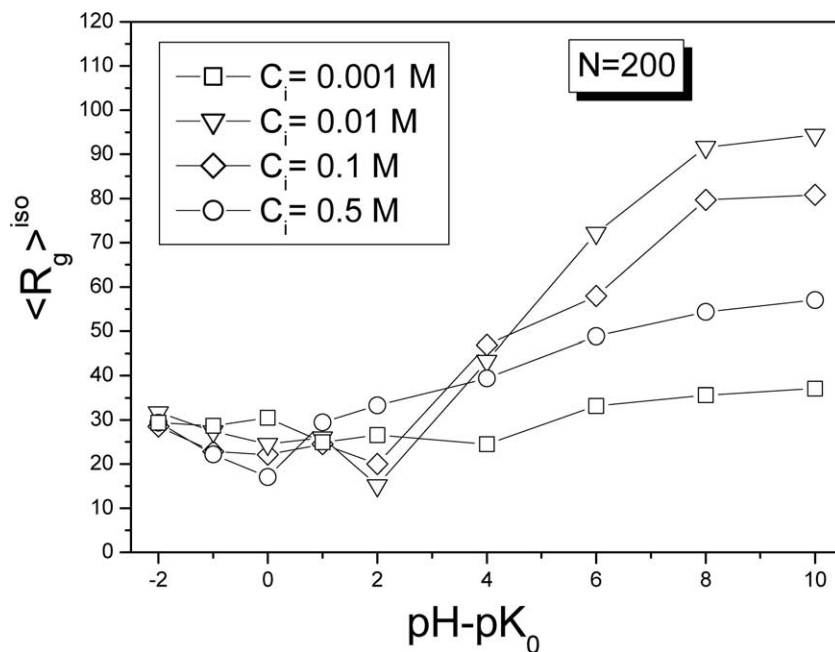


Fig. 2. Mean radius of gyration $\langle R_g \rangle^{iso}$ of an isolated polyelectrolyte chain ($N=200$) versus $pH - pK_0$ for different ionic concentrations $C_i = 0.001, 0.01, 0.1$ and 0.5 M.

linear charge density), no adsorption (or desorption) is observed. That case corresponds to low $pH - pK_0$ values.

The polyelectrolyte conformation at the particle surface results from the complex interplay of attractive particle-

monomer and repulsive monomer–monomer interactions, which can be tuned with $pH - pK_0$, and ionic concentration values. Generally, when the ionization degree is less than 0.85, the polyelectrolyte conformation exhibits loops and trains at the particle surface. By increasing further the

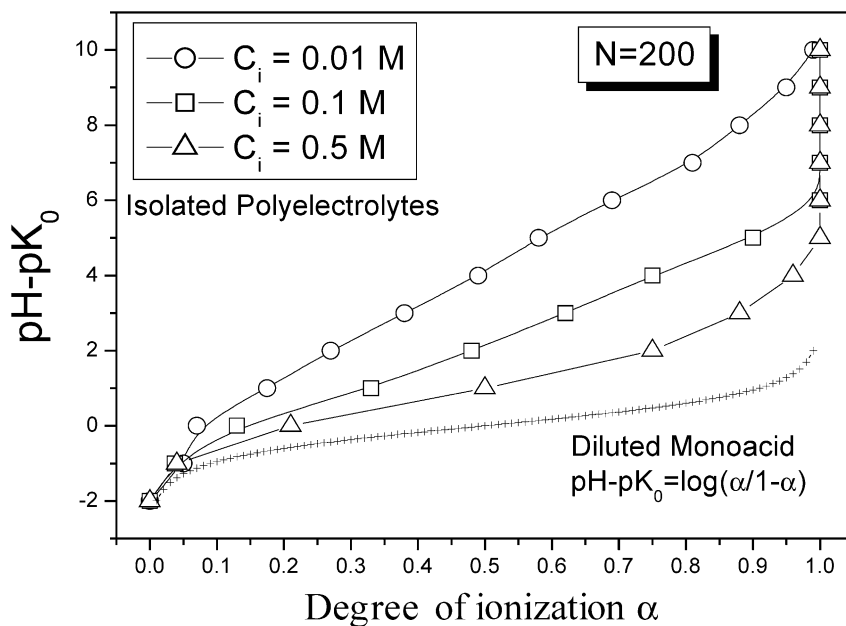


Fig. 3. Titration curves representing the chain degree of ionization α versus $pH - pK_0$ at different ionic concentrations C_i (0.01, 0.1 and 0.5 M). An isolated polyelectrolyte chain of 200 monomer units is considered. The titration curves change appreciably from the dilute monoacid. Obviously the electrostatic interactions play a major role for titrating polyelectrolytes, the presence of charges making further ionization of the chain more difficult. As electrostatic interactions are controlled by the ionic concentration, the decrease of charge screening makes the difference between the apparent and intrinsic dissociation constant more important.

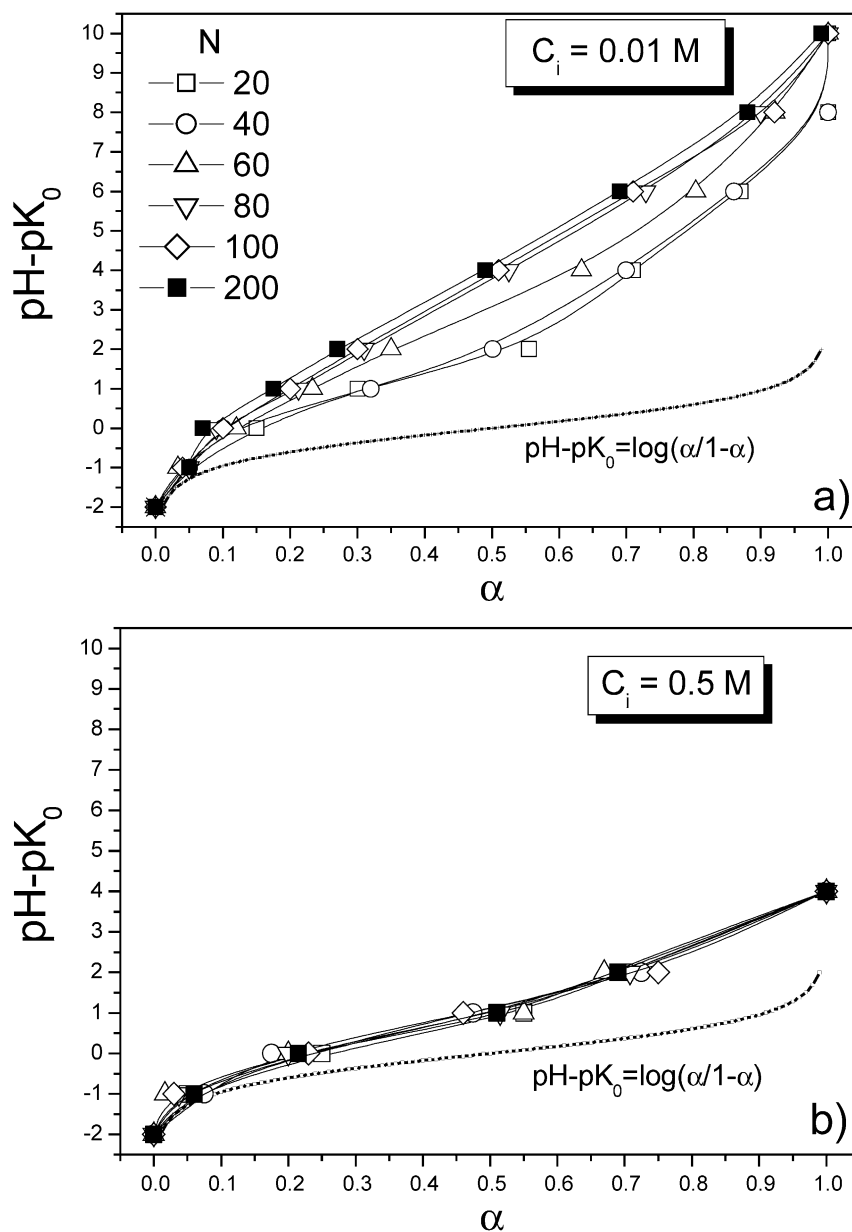


Fig. 4. (a) Titration curves for different polyelectrolyte chain lengths ($N=20, 40, 60, 80, 100$ and 200) at $C_i=0.01 \text{ M}$. Long chains are more difficult to charge. However, an asymptotic limit is reached at $N=200$. (b) Titration curves in the high salt concentration regime ($C_i=0.5 \text{ M}$) for different polyelectrolyte chain lengths ($N=20, 40, 60, 80, 100$ and 200). Size effects do not play a predominant role in that regime.

degree of ionization, the polyelectrolytes flatten (most of the monomer is present in trains) and extended or pinned conformations are achieved at the particle surface.

3.3.1. Effect of the polyelectrolyte–particle complex formation on titration curves

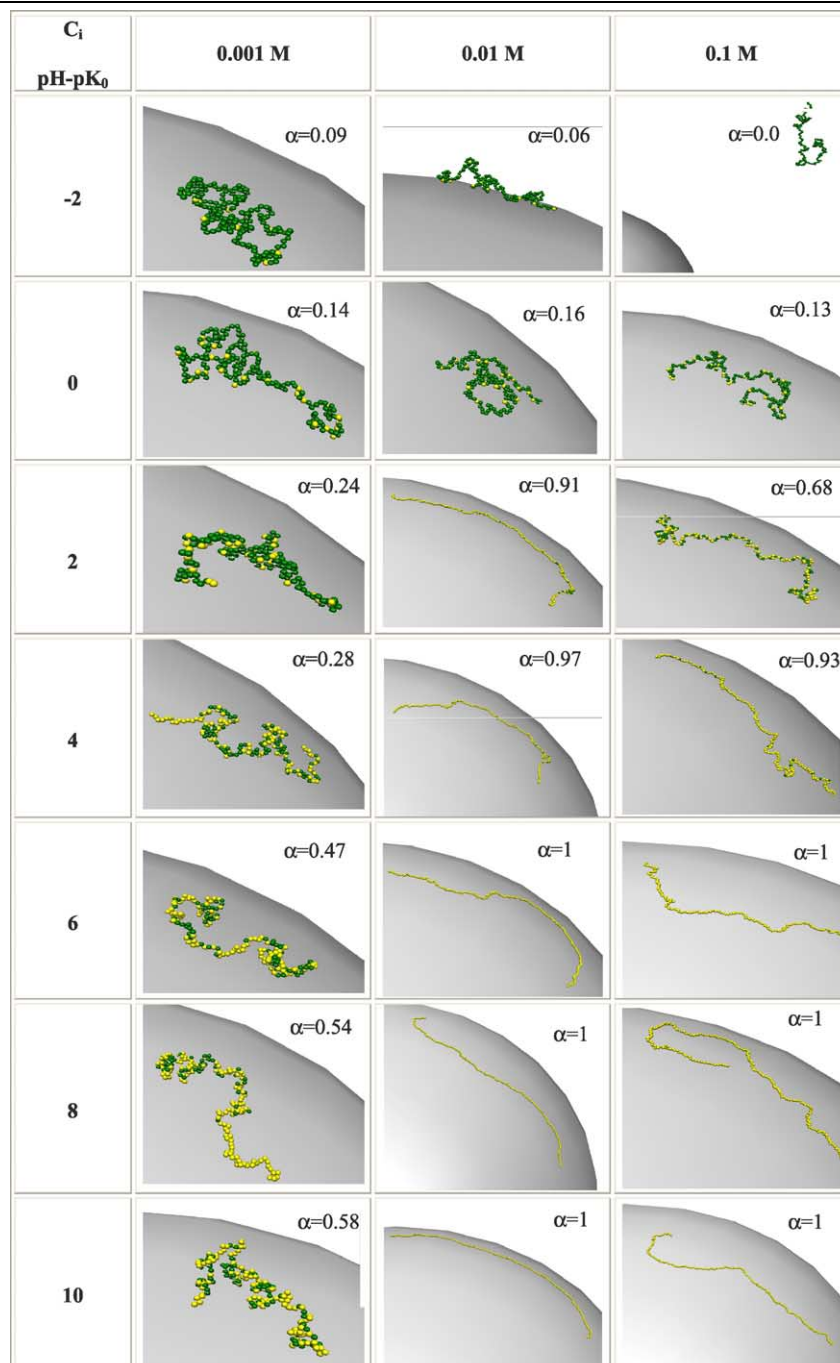
3.3.1.1. Influence of the particle charge. An important insight into the properties of weak polyelectrolytes have been gained by examining the titration curves at $C_i=0.1 \text{ M}$: the presence of an oppositely charged particle (Fig. 5(a)) clearly influences the polyelectrolyte ionization degree

which increases with the increase of the particle surface charge (for a given value of $\text{pH} - \text{p}K_0$). Hence, the presence of an oppositely charged particle makes chain deprotonation (ionization) easier by a local neutralization of the adsorbed monomer charges.

3.3.1.2. Influence of the ionic concentration. The influence of the ionic concentration exhibits a more subtle effect (Fig. 5(b)). To illustrate this effect σ was set to 100 mC/m^2 . In the low ionic concentration regime ($C_i=0.001 \text{ M}$) there are difficulties to charge the polyelectrolyte, in particular when $\text{pH} - \text{p}K_0 > 0$, the degree of ionization of the polyelectrolyte is

Table 2

Monte Carlo equilibrated structures illustrating the adsorption of the weak polyelectrolyte ($N=200$) on an oppositely charged particle surface as a function of $\text{pH} - \text{p}K_0$ for different ionic concentration C_i (0.001, 0.01 and 0.1 M)



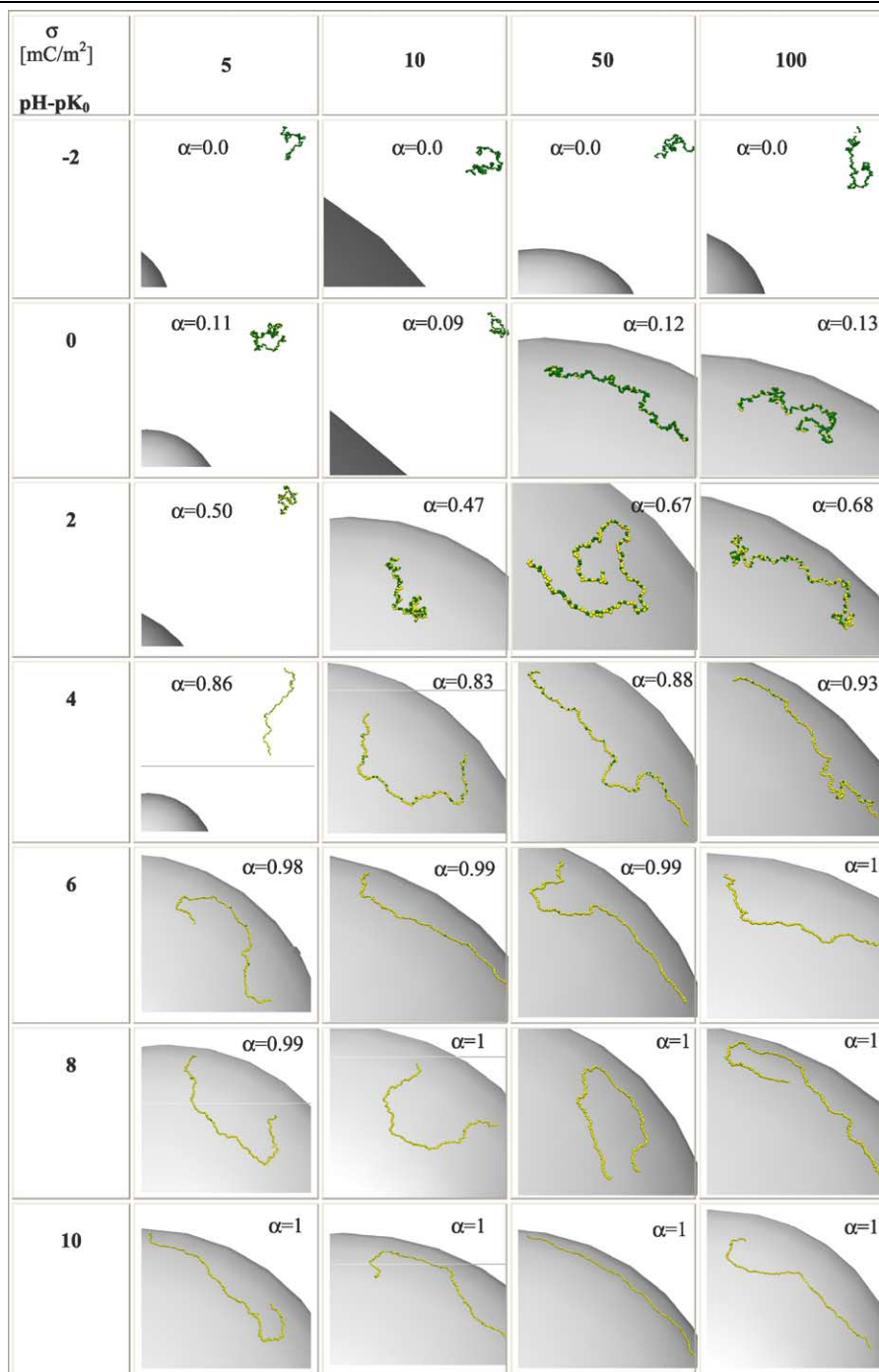
The particle surface charge density σ is equal to 100 mC/m^2 . The average value of the degree of ionization α is given in each case.

low and this situation is detrimental to the formation of flat conformations at the particle surface. On the other hand, at low $\text{pH} - \text{p}K_0$, the presence of an oppositely charged particle promotes polyelectrolyte ionization and hence adsorption. At intermediate ionic concentration ($C_i = 0.01 \text{ M}$), the chain

ionization process is still promoted when $\text{pH} - \text{p}K_0 < 0$. In addition, when $\text{pH} - \text{p}K_0 > 0$, the concomitant effect of the ionic concentration and presence of an oppositely particle (which both promote the chain ionization) results in high degrees of dissociation. By increasing further the ionic

Table 3

Monte Carlo equilibrated conformations related to the adsorption of the weak polyelectrolyte ($N=200$) on an oppositely charged particle surface as a function of $\text{pH} - \text{p}K_0$ for different particle surface charge density σ (5, 10, 50, 100 mC/m^2)



Ionic concentration C_i is set to 0.1 M. The average value of the degree of ionization α is given in each case.

concentration ($C_i = 0.1$ M), despite the fact that chain ionization is promoted, the effect of the presence of an oppositely charged particle is strongly reduced because of the decrease of the electro-attractive interaction between the particle and the polyelectrolyte. From these observations, we

can conclude that the best conditions for strong polyelectrolyte adsorption are achieved at intermediate ionic concentration.

3.3.2. Conformation of the adsorbed polyelectrolyte

We investigated the conformational changes due to

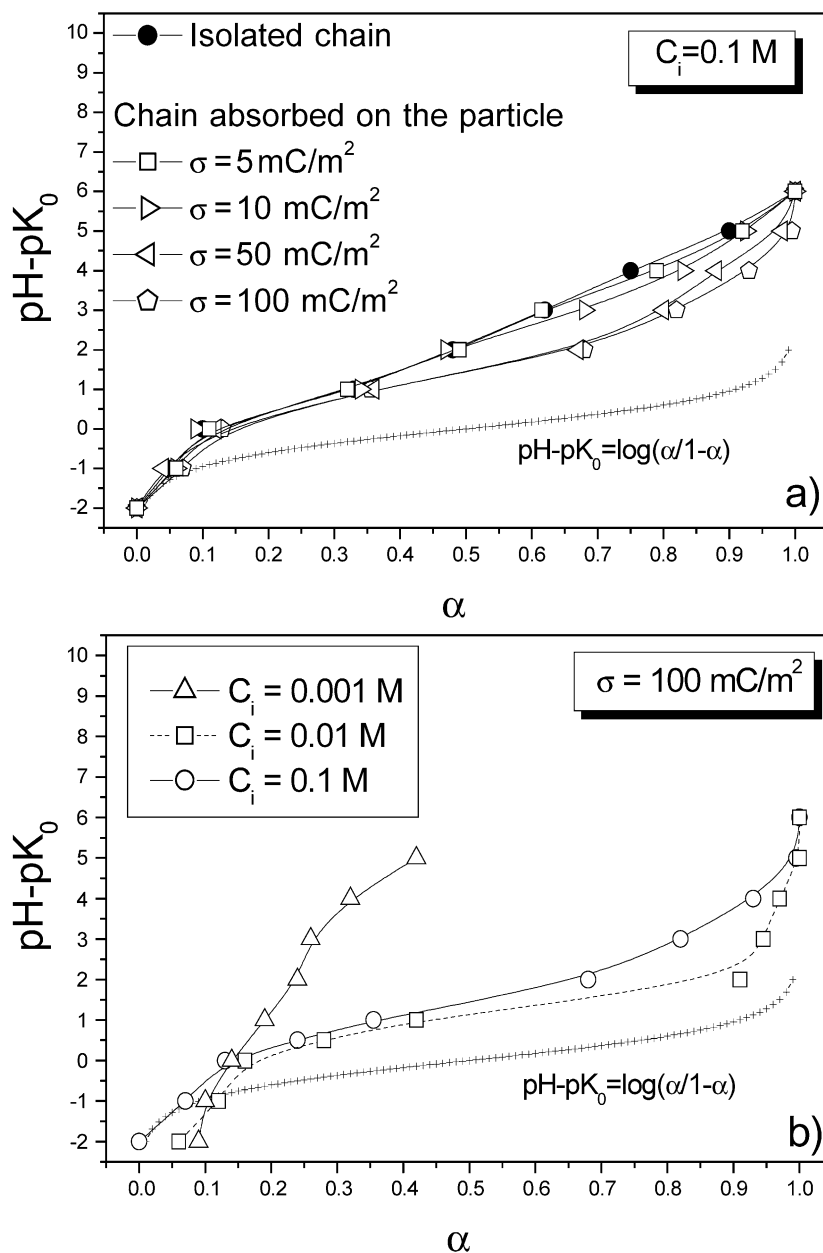


Fig. 5. (a) Titration curves of a polyelectrolyte chain ($N=200$) with the presence of an oppositely charged particle. The particle surface charge density σ is adjusted to 5, 10, 50, 100 mC/m^2 . Ionic concentration is set to 0.1 M. For comparison, the isolated chain is also represented. High surface charge particle densities clearly promote the polyelectrolyte chain ionization. (b) Titration curves of a polyelectrolyte chain ($N=200$) with the presence of an oppositely charged particle having charge density σ equal to 100 mC/m^2 . Different ionic concentrations $C_i=0.001$, 0.01 and 0.1 M are considered. The intermediate concentration regime $C_i=0.01$ M promotes in the full $\text{pH}-\text{p}K_0$ domain high degrees of ionization and hence the formation of flat conformations at the particle surface.

the polyelectrolyte adsorption by calculating the number of monomers in trains. The average number of monomers in trains as a function of $\text{pH}-\text{p}K_0$ at different particle charge density σ (1, 5, 10, 50 and 100 mC/m^2) and three ionic concentrations (0.1, 0.01 and 0.001 M) are presented in Fig. 6(a)–(c).

According to our definition of polymer adsorption, the absence of trains means that the polyelectrolyte is

not adsorbed. At low ionic concentration (Fig. 6(c)), one can observe that the number of monomers in trains is small at any particle charge density and $\text{pH}-\text{p}K_0$. According to the difficulties to ionize the chain and the strong attractive forces with the surface, the polyelectrolyte is trapped at the surface and forms trains and loops. The ionization degree is slightly increased upon adsorption. When the ionic concentration is increased to

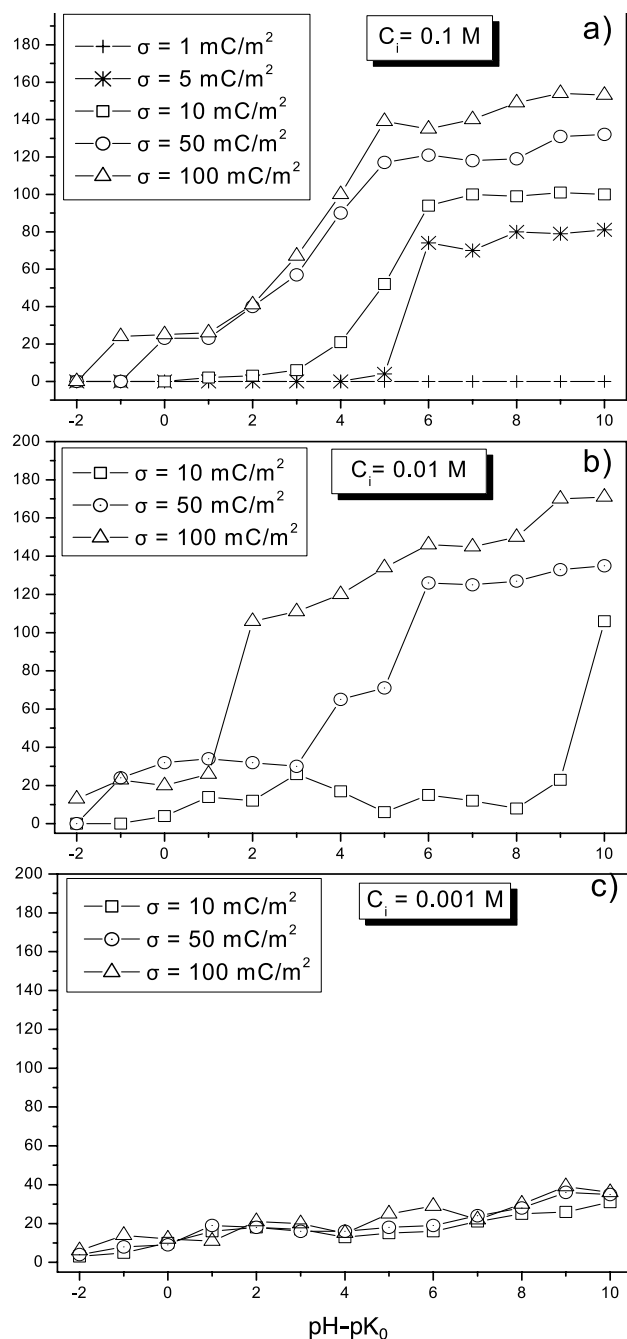


Fig. 6. Number of monomers in trains for adsorbed chains as a function of $\text{pH}-\text{p}K_0$ for different particle surface charge density σ (5, 10, 50, 100 mC/m^2) and ionic concentrations (a) $C_i=0.1$ M, (b) $C_i=0.01$ M, and (c) $C_i=0.001$ M. When the particle surface charge density increases, the number of monomer in trains increases, hence promoting the formation of flat conformations.

0.01 and 0.1 M (Fig. 6(a) and (b)), the number of monomers in trains increases concomitantly with increasing σ . At high $\text{pH}-\text{p}K_0$ values, as the ionization degrees are close to 1, flat conformations are observed. It should be noted that the number of trains reaches a

maximum value at the intermediate ionic strength (0.01 M).

The radial distribution of the charged monomers at the particle surface is now investigated. Snapshots of equilibrated conformations of adsorbed polyelectrolytes ($N=200$, $\sigma=100$ mC/m^2 , $C_i=0.1$ M) are presented in Fig. 7. Two values of $\text{pH}-\text{p}K_0$ are presented; 0 and 4 corresponding to ionization degrees equal to 0.13 and 0.93, respectively, and to a ‘trains and loops’ and flat conformation, respectively. The radial distribution function of both, all the monomers, and ionized monomers is presented as a function of the reduced distance r/σ_p . The position of the adsorption layer is found at $r/\sigma_p=1.005$. All the informations presented in Fig. 7 clearly demonstrate that the ionized monomers are preferentially situated in the vicinity of the particle surface and act as adsorption trains.

3.3.3. Adsorption–desorption limit

For a practical and rational use of polyelectrolytes, it is important to predict an adsorption–desorption limit. Calculations were made at various $\text{pH}-\text{p}K_0$ values to determine the critical $(\text{pH}-\text{p}K_0)_{\text{crit}}$ at which the polyelectrolyte is expected to be adsorbed (Fig. 8). The critical $\text{pH}-\text{p}K_0$ value where the adsorption occurs is represented as a function of the particle surface charge density σ and ionic concentration C_i . Particle surface charge density σ is adjusted from 1 to 100 mC/m^2 and ionic concentration C_i is set to 0.1 M. It can be clearly seen in Fig. 8 that the adsorption/desorption limit is dependent both on particle charge density and ionic strength. Important conclusions can be derived here to promote adsorption by (i) increasing $\text{pH}-\text{p}K_0$ and hence the polyelectrolyte degree of ionization; (ii) increasing the particle surface charge density σ and (iii) decreasing the ionic concentration.

4. Conclusion

Monte Carlo simulations have been used to explore the conformational changes and electrical behavior of a weak anionic polyelectrolyte in the presence of an oppositely charged colloidal particle. The roles of the ionic concentration, pH of the solution and particle charge density were systematically investigated. From a general point of view, adsorption is promoted by decreasing the ionic concentration, increasing the particle surface charge density and increasing the pH. However, two competing effects are playing important roles on the polyelectrolyte conformation and degree of ionization: (i) the attractive interaction between the monomers and the particle which increase the chain degree of ionization and (ii) the electrostatic repulsions along the chain which limits the degree of ionization. Our simulations point out the importance of these

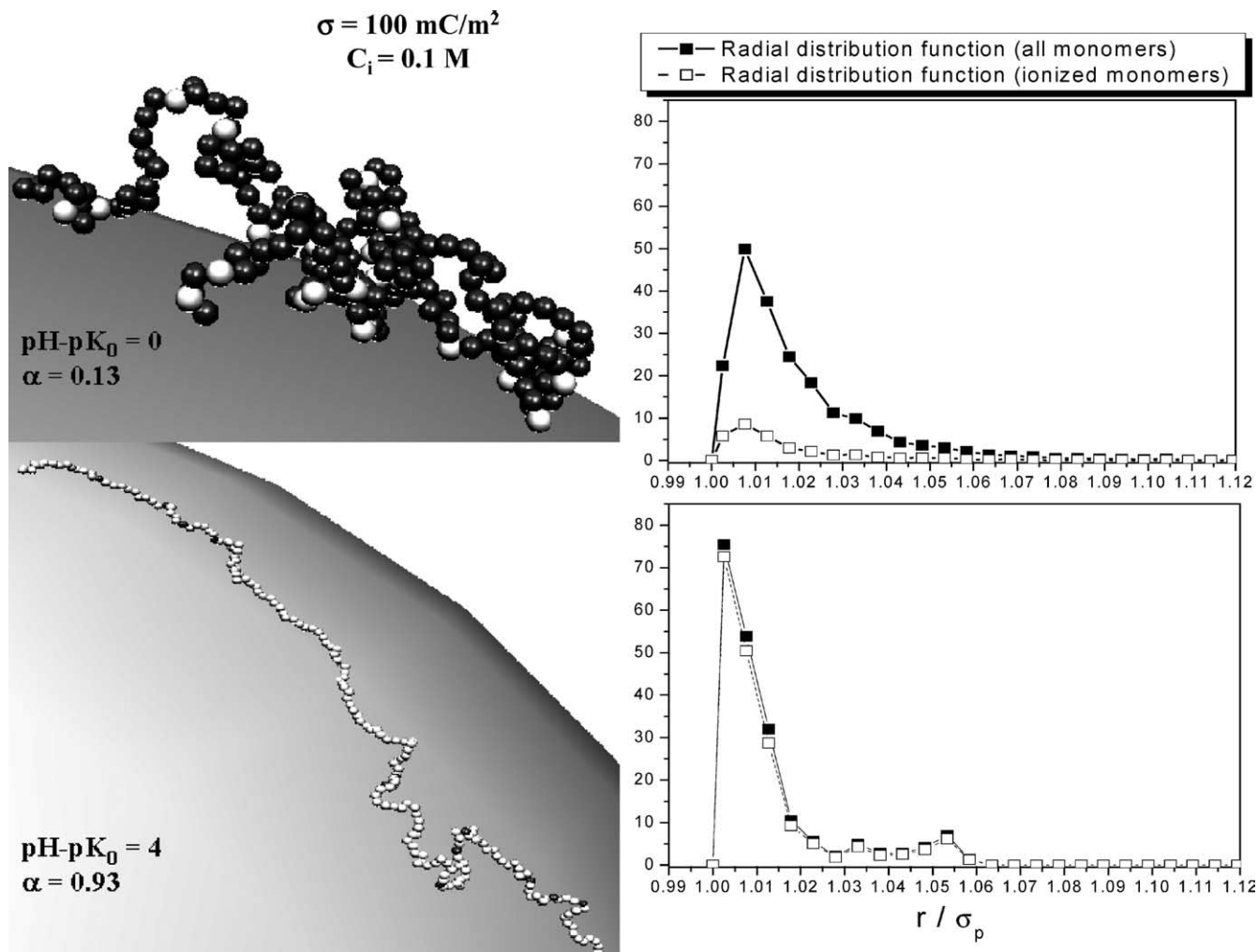


Fig. 7. Snapshot of equilibrated conformations of adsorbed polyelectrolytes ($N=200$). The surface charge density σ is equal to 100 mC/m^2 and the ionic concentration $C_i=0.1 \text{ M}$. Two values of $\text{pH-p}K_0$ are presented; 0 and 4 corresponding to ionization degrees equal to 0.13 and 0.93 and to a partially and flat conformation, respectively. Radial distribution functions are presented for each case. The charged monomers are always close to the particle and act as adsorption trains. For $\alpha=0.13$, 54% of the total number of charged monomers are situated in the adsorption layer whereas only 35% of the total number of monomers are present there.

competing effects when the ionic concentration decreases. Best conditions for strong polyelectrolyte adsorption are then observed at intermediate ionic concentrations, where polyelectrolytes adopt extended and flat conformation at the surface of the particle. When trains and loops are formed at the particle surface, most of the charged monomers are present as adsorption trains. The analysis of the titration curves clearly demonstrate that the polyelectrolyte degree of ionization is not a simple monotonic function of pH and ionic concentration, and that the presence of an oppositely charged particle greatly affect the conformation and degree of dissociation of the polyelectrolyte chain. A simple model involving one polyelectrolyte chain interacting with one particle having a constant

surface charge density has been described here. However, the model could be extended to the adsorption of several chains, so as get an insight into the role of polyelectrolyte–polyelectrolyte interactions.

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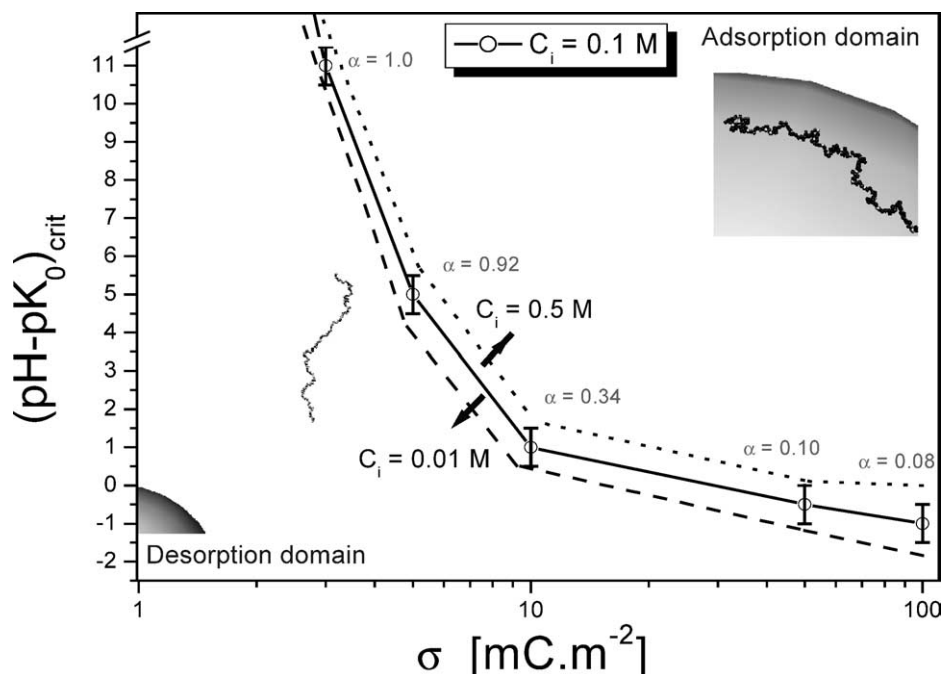


Fig. 8. Adsorption-desorption limit of the polyelectrolyte/particle system showing the critical $\text{pH}-\text{pK}_0$ values where the adsorption occurs as a function of the particle surface charge density σ and ionic concentration C_i . Particle surface charge density σ is adjusted from 1 to 100 mC/m^2 and ionic concentration C_i is set to 0.01, 0.1 and 0.5 M. Adsorption is promoted by increasing $\text{pH}-\text{pK}_0$ and so the chain degree of ionization α , by increasing the particle surface charge density σ and by decreasing the ionic concentration.

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Glossary

- $\langle R_g \rangle^{\text{iso}}$: mean radius of gyration of the isolated chain
 N : number of monomers of the polyelectrolyte chain
 σ_m : monomer radius
 q_m : charge of a monomer

α : ionization constant

ζ : scaling factor for charge delocalization

σ_p : radius of the particle

Q : charge of the particle

σ : charge surface density of the particle

C_i : ionic concentration

pK_0 : intrinsic dissociation constant of an isolated monomer
(constant)