Colloid Polym Sci (2002) 280: 789–797
DOI 10.1007/s00396-002-0705-0

ORIGINAL CONTRIBUTION

Marcin Brynda
Pierre Chodanowski
Serge Stoll

Polyelectrolyte–particle complex formation. Polyelectrolyte linear charge density and ionic concentration effects. Monte Carlo simulations

Received: 26 November 2001
Accepted: 7 March 2002

M. Brynda · P. Chodanowski · S. Stoll (✉)
Analytical and Biophysical Environmental Chemistry (CABE), Department of Inorganic, Analytical and Applied Chemistry, University of Geneva, Sciences II, 30 quai E. Ansermet, CH-1211 Geneva 4, Switzerland
e-mail: serge.stoll@cabe.unige.ch

Abstract The influence of the linear charge density (LCD) of a polyelectrolyte on its adsorption on an oppositely charged colloidal particle is investigated by Monte Carlo simulations. Adsorption characteristics are studied at different linear charge densities and ionic concentrations and for a given polyelectrolyte/particle size ratio so that particle curvature has full effect. The isolated polyelectrolyte goes through a smooth transition from a collapsed structure to an extended rod-like conformation with increasing the linear charge density in the low ionic concentration regime. In the high ionic concentration regime, the polyelectrolyte is less sensitive to the increase in the linear charge density and adopts a coil conformation. We found that complex formation is promoted by decreasing the ionic concentration and increasing the linear charge density and that large changes in the polymer dimensions are observed at the adsorption–desorption limit. By adjusting the linear charge density and ionic strength, we demonstrate that the adsorption–desorption limit corresponds to a sharp transition from non-adsorbed to adsorbed conformations and that the mean adsorption energy per monomer has to be less than –0.4 kT to achieve adsorption. We calculated that the linear charge density at the adsorption–desorption limit is related to the Debye-Hückel length according to $LCD^{crit} \sim \kappa^2$. At small values of the linear charge density and low ionic strength (no adsorption is observed at high ionic strength), a large amount of monomers are present in loops and tails. By increasing LCD, the amount of monomers in trains reaches a maximum value and the polyelectrolyte adopt flat conformation at the surface of the particle.

Keywords Polyelectrolyte–particle complex · Polyelectrolyte linear charge density · Monte Carlo simulation

Introduction

Destabilization/stabilization of colloidal solutions by the use of oppositely charged polymer chains has recently attracted the interest of many research groups over the world because of their importance in many systems such as waste water treatment [1], trace metals circulation in the environment [2] or complexation of DNA by specific proteins [3]. An important task in understanding colloidal mixtures is to account for the main and pertinent interactions resulting from the different chemical entities present in solution. For example, environmental systems include a variety of biopolymers and polysaccharides produced by microorganisms, phytoplankton or water flora as well as mineral particles such as clays, silicates, iron and manganese oxides [4]. Such a diversity of compounds, solution chemistry (pH, ionic strength), aggregate formation, and sedimentation results in a variety of processes and interactions such as electrostatic interactions, van der Waals forces, hydrogen bonding, which can be investigated separately at different levels.

As biological and natural systems generate an extensive range of phenomena involving the presence of charged macromolecules (polyelectrolytes), the driving forces controlling the behaviour of systems containing polymers and colloids are mainly of electrostatic origin. In addition the electrical colloid/solution interface (charge density, presence of a double layer, etc.) as well as chemical diversity of polymers makes possible a variety of different charge distributions. In particular, charges on polyelectrolytes can be of different origin. The presence of side groups such as –COOH or –OH can lead to the dissociation and emergence of the corresponding point charges. The adsorption of ionic species from the solution makes possible the appearance of electrostatic charges on neutral polymers. Physical properties of complex biological systems such as DNA are strongly dependent on electrostatic phenomena between that polyelectrolyte and the surrounding charged species [5, 6, 7, 8]. It was recently suggested [9], that proteins and DNA interact as a positively charged sheath surrounding a negatively charged core of corresponding linear charge density respectively. Charge density distribution is then a key parameter for the understanding of interactions in biological and natural systems.

Although a large number of papers deal with the influence of the surface charge density of colloids on the adsorption process [10, 11, 12, 13], only a limited number of studies were published on the effect of the linear charge density of the polymers. Recently the influence of polyelectrolyte linear charge density on complexation processes of ferrihaemoglobin by different polyelectrolytes was investigated [14]. HS (Heparan sulfates)–protein interactions are known to be mainly electrostatic. HS have been shown to actively participate in vital biological processes from early development to adult life in multicellular organisms. Adar et al. [15] calculated the charge density of Heparan sulfates motifs as the ratio of charged to non-charged residues close to 1 and concluded that the important factor is not only the charge density but rather charge distribution that allow specific interactions for the fine tuning of highly regulated receptor activities.

A significant linear dependence between charge density (sulphate-to-carboxyl ratio) and enzymatic activity of Heparins as a human leukocyte elastase activity inhibitors was investigated by Volpi [16]. Rouzina et al. [17] described a force induced melting of the DNA double helix and concluded that the measured dependence of DNA overstretching force on solution ionic strength was mainly due to the differences between linear charge densities of cross-linked and non-cross-linked DNA. The influence of the charge density of polyelectrolyte on adsorption processes on spherical and cylindrical surfaces was also investigated by Von Goeler and Muthukumar [18] suggesting that the density profile of adsorbed polyelectrolytes is linked to their linear charge density.

The importance of modelisation in chemistry has been rapidly growing in the last years; at the same time computer simulation has become well established as a powerful research tool for directly relating the physicochemical properties of a chemical entity to its atomic structure. Today the amazing evolution of the speed of computer processors allows investigations of more and more complex and large systems. Monte Carlo simulations on polyelectrolyte adsorption on planar or spherical surfaces have been performed by several groups. The critical conditions necessary for adsorption of uniformly charged polyelectrolyte on planar or spherical surface as well as kinetics of adsorption and the role of charge sequences in amphoteric polyelectrolytes were investigated by Muthukumar [19]. Chain flexibility, linear charge density and micelle radius were considered by Linse et al. [20, 21] to investigate the behaviour of a polyelectrolyte–micelle complex. Sintes [22] studied the adsorption characteristics at different temperatures for chains of various stiffness using semiflexible polymer chain adsorbed on a flat, homogenous surface.

In previous work [23] we performed off-lattice Monte Carlo simulations of strong hydrophobic polyelectrolytes in the Debye-Hückel approximation. The simulation showed a cascade of complex configurational transitions with different ionic salt concentration. We showed that such a transition could be generated by small colloidal particles [24], which are irreversibly adsorbed on the polymer chain. Recently we described in detail the complex formation between a charged colloidal particle and an oppositely charged polyelectrolyte. The formation of a polyelectrolyte–particle complex was investigated with special attention focused on the effect of the particle size [25], chain length, ionic concentration and chain intrinsic stiffness on the adsorption/desorption limit, the interfacial structure and the overcharging issue [26].

The main purpose of this article is to make clear how the linear charge density (LCD) of a polyelectrolyte chain influences the formation of a complex between a chain and an oppositely charged particle, to calculate adsorption/desorption limits and investigate the polyelectrolyte conformations at the particle surface. Since screening effects of added salt are known to play a major role in controlling the conformation and polyelectrolyte/particle interaction, we also focused on the influence of the ionic strength. We also investigated the transition state between the non or partially adsorbed and totally adsorbed polymer. The sharpness of this transition is discussed versus the linear charge density and ionic strength.

Model

The basic features of the model are similar to those of ref. [26]. The important difference in this study is the inclusion of uncharged monomers along the chain backbone. The polymer chain is represented by an off-lattice three-dimensional pearl-necklace model. The chain contains N freely jointed beads of diameter σ_m whose length is equal to the Bjerrum length $l_B = 7.14$ Å. The colloid and the polymer are confined in a spherical and reflecting box with a diameter equal to twice the totally extended polymer length. The excluded volume interaction is assured by the impenetrable character of both the particle and chain monomers. Monomer-monomer interactions within the polyelectrolyte are described by a long-range repulsive electrostatic potential. All charged monomers interact via a screened Debye-Hückel potential defined as:

$$U_{\mathrm{el}}(r_{ij}) = \frac{z_i z_j e^2}{4\pi\varepsilon_r\varepsilon_0 r_{ij}}\exp(-\kappa r_{ij}) \qquad (1)$$

where z_i, z_j represent the charge of i-th, j-th monomer and r_{ij} the distance between them. The interaction between the charged monomers and the colloidal particle is described by a Verwey-Overbeek potential [27], which takes into account the exclusion of ions inside the particle:

$$U_{\mathrm{el}}(r_{ij}) = \frac{z_i z_j e^2}{4pi\varepsilon_r\varepsilon_0 r_{ij}}\frac{\exp[-\kappa(r_{ij}-\sigma_p)]}{(1+\kappa\sigma_p)} \qquad (2)$$

where σ_p represents the particle diameter.

The influence of the ionic strength C_i is described through the Debye screening length κ:

$$\kappa^2 = 1000e^2 N_A \sum_i \frac{z_i^2 C_i}{\varepsilon_0\varepsilon_r k_B T} \qquad (3)$$

The present study was carried out on polyelectrolytes with a fixed number of monomers ($N = 100$), introducing a variable linear charge density (also referred to as LCD) from 0.01 to 1 (all monomers ionized) and considering different ionic strengths from 0 to 1 M. According to the results of previous calculations [25], the colloid/monomer radius ratio σ_c/σ_m was fixed at 10 so that the curvature of the colloid has its full effect on polymer adsorption. The colloid has a central point charge, Q, which corresponds to a surface charge density of +100 [mC/m^2], which is a typical value for colloids found in natural systems. According to the Debye-Hückel approximation the solvent was treated as a dielectric continuum with a relative dielectric constant corresponding to water at room temperature ($\varepsilon_r^{298\mathrm{K}} = 78.5$). For the purpose of this study an algorithm allowing a regular distribution of the charge along the polyelectrolyte was considered. Charges on the polyelectrolyte beads were assigned in order to maintain the longest possible distance between them along the chain backbone.

The Metropolis Monte Carlo method was used to sample the configurational space of the polyelectrolyte and polyelectrolyte/particle complex. Reptation and internal movements such as the pivot, kink-jump and crankshaft were used to produce efficient and ergodic sampling. To characterize the conformational properties of polyelectrolyte, the mean-square radius of gyration $<R_g^2>$ and the mean-square end-to-end distance $<R_{ee}^2>$ were calculated. In addition to these macroscopic parameters (R_g^2 and L_{ee}^2 give only information on the polymer dimensions without describing any particular configurational features), the number of monomers in trains, loops and tails was also calculated to achieve a quantitative picture of adsorbed chains. To determine the position of the monomers along the coordinate radial to the surface, spherical layers around the surface were defined. The thickness of each layer was set to one monomer radius except for the first one, which was set to two monomer radii to avoid volume exclusion near the surface.

Results and discussion

Isolated polyelectrolyte chains

The electrostatic interactions between charged monomers are well known as a driving force in the process of stretching/collapse of isolated polyelectrolytes. In this context it is interesting to know how the conformation of the isolated chains is related to the linear charge density. Hence we first calculated the conformational changes of the chains ($N = 100$) with variable LCD at different ionic concentrations C_i. In the second part of this work these equilibrated free chains will be used as starting conformations for the polyelectrolyte/particle complex.

The influence of the LCD on the polymer mean-square radius of gyration is presented in Fig. 1 a. As expected, an increase of $<R_g^2>$ is observed with increasing the linear charge density. This increase of the $<R_g^2>$ value with LCD is quasi linear. $<R_g^2>$ variations with LCD are less pronounced in the high salt limit because of the screening of the repulsive monomer-monomer interactions. The same trend is observed for the end-to-end distance $<L_{ee}^2>$, which is plotted against LCD in Fig. 1b at different C_i values.

We compared our results with those obtained by Hooper et al. [28] with on-lattice simulation of hydrophobic electrolytes. By renormalising our $<R_g^2>$ values and introducing the normalized radius of gyration $<R_g^2>_{\mathrm{norm}}$, we found $<R_g^2>_{\mathrm{norm}}$ values slightly higher at high LCD, in accordance with chain finite size effects [26] ($N = 40$ for Hooper and $N = 100$ in our simulations). In contrast, our normalized end-to-end distance $<L_{ee}^2>_{\mathrm{norm}}$ values were found smaller at high LCD values. In order to eliminate size effects we performed simulations at $N = 40$ with the same conditions used by Hooper and co-workers. In both cases our values of $<L_{ee}^2>_{\mathrm{norm}}$ and $<R_g^2>_{\mathrm{norm}}$ were significantly smaller at high LCD. This effect was attributed to the lattice influence in the Hooper's model which could significantly restrict some internal motion in the polyelectrolyte and thus influence the radius of gyration and end-to-end distances. Nevertheless, the general behaviour of the radius of gyration an end-to-end distance versus linear charge density of the chain was found to be in accordance with our results.

We also calculated the expansion factor ($r = <L_{ee}^2>/<R_g^2>$) which gives quantitative information on the conformational changes and expansion degree of polyelectrolytes (Fig. 2). For the very small values of the

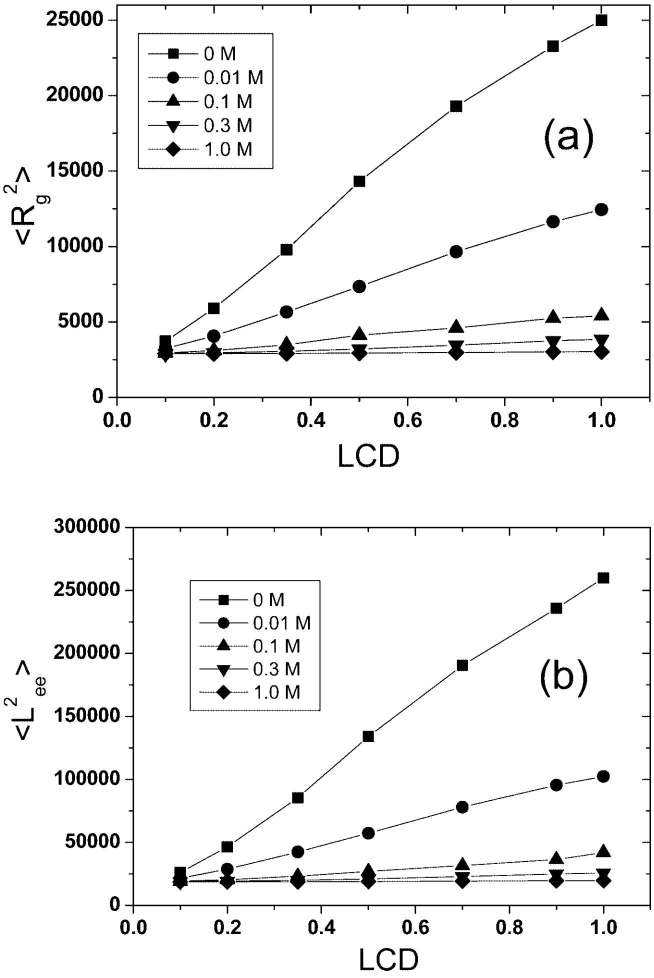


Fig. 1. **a** Mean square radius of gyration $<R_g^2>$, and **b** mean square end-to-end distance $<L_{ee}^2>$ as a function of the linear charge density (LCD) for isolated chains

LCD (quasi neutral chain domain), the value of the expansion factor r is close to 6.5 for all ionic concentrations C_i (this value was calculated to be 6.3 for flexible chains by Stevens and Kremer, 1995) while for the chains on which all monomers are charged r asymptotically reaches 10.5 in the low salt concentration regime. This latter value is a little smaller than the predicted $r=12$ for the rod like conformations due to the chain thermal fluctuations which locally affect the monomer distribution. That means that even for 100% charged polyelectrolyte the rod like structure is never achieved when $T=298$ K.

To achieve a visual picture of the polyelectrolyte conformations, snapshots of equilibrated configurations of polymers versus C_i and LCD are presented in Table 1. Accordingly to the trends observed for $<R_g^2>$ and $<L_{ee}^2>$ in the low salt regime (0–0.01 M), a monotonic transition from a coiled polymer at small LCD to the very extended structures at the high LCD is observed.

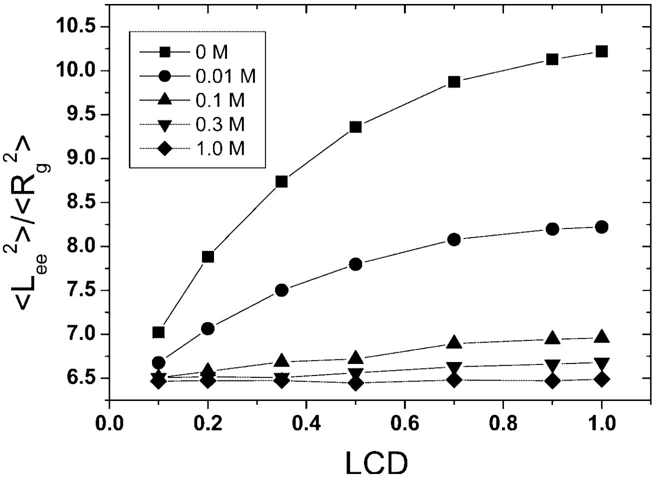


Fig. 2. Expansion factor $r=<L_{ee}^2>/<R_g^2>$ versus the linear charge density (LCD) at different ionic concentration for the isolated chain

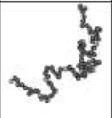
As the effect of salt screening becomes more significant at higher ionic strengths, the polymer configuration is not sensitive to the increase of LCD. As a result, the polyelectrolyte adopts in all cases Self Avoiding Walk (SAW) configurations when $C_i>0.3$ M.

Adsorbed polymers

It is well known that the presence of an attractive colloidal particle in the vicinity of a polyelectrolyte is expected to modify its conformation. The influence of the LCD on the polyelectrolyte conformation is checked with the colloidal particle. In Figs. 3a and b the mean-square radius of gyration and mean-square end-to-end distance are plotted versus the LCD.

The analysis of Fig. 3a shows two different regimes, corresponding to non-adsorbed (A) and adsorbed (B) polyelectrolytes respectively. In regime A, one observes high $<R_g^2>$ values ($>3\times10^3$ [Å^2]) which are identical to those obtained for isolated chains in similar conditions. In regime B these values are rapidly decreasing ($\sim2\times10^3$ [Å^2]) immediately after polyelectrolyte adsorption. It is worth noting that for small ionic strengths (0–0.01 M) the polymer is always adsorbed on the surface of the colloid. This explains the low values of the $<R_g^2>$ which decrease smoothly with the LCD. When C_i is in the range 0.1–0.3 M, the curves show first an increase in the $<R_g^2>$ value which are the same as for the free chains (regime A) then a sharp transition is observed to the lower values of $<R_g^2>$ (regime B) corresponding to adsorbed conformations. Finally, when $C_i=1.0$ M the curve exhibits the same increase in the $<R_g^2>$ value as for the free chains. Since there is no adsorption at this ionic strength no transition in the $<R_g^2>$ value is

Table 1. Monte Carlo (MC) equilibrated conformations of isolated charged polymers as a function of the ionic concentration C_I and polyelectrolyte Linear Charge Density (LCD). Bright monomers represent charged monomers. By decreasing C_I and increasing the LCD, long range electrostatic interactions promote the formation of elongated structures. Note that because of the lack of available space different scales have been used to represent the chains (the contour length is constant and equal to $N = 100$ monomers)

C_i [M] Linear Charge Density (LCD)	0	0.01	0.1	0.3	1
0.1					
0.2					
0.35					
0.5					
0.7					
0.9					
1.0					

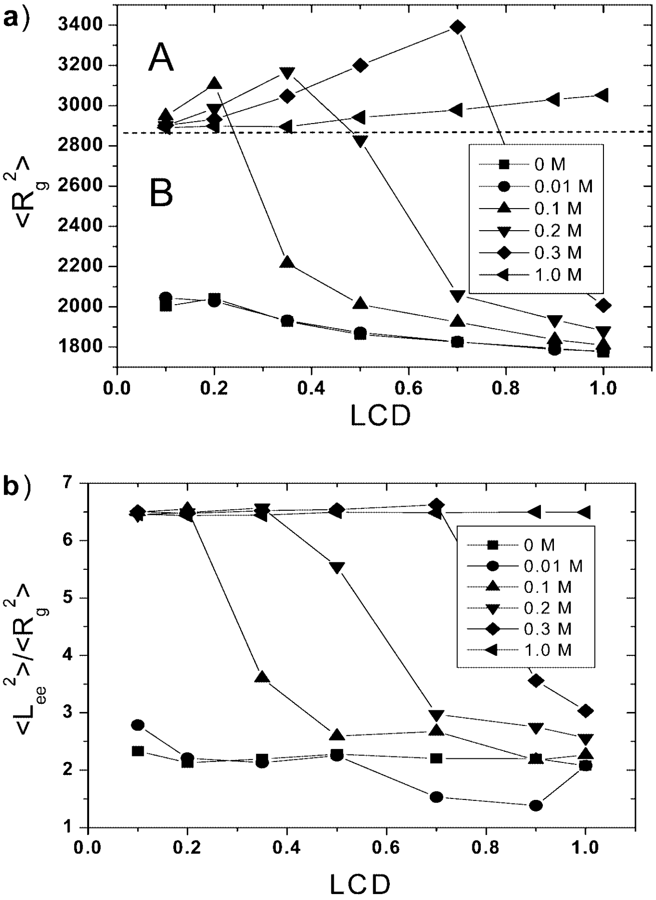


Fig. 3a, b. a Mean square radius of gyration $<R_g^2>$, and **b** expansion factor $r = <L_{ee}^2>/<R_g^2>$ versus the linear charge density (LCD) at different ionic concentration for the polyelectrolyte in presence of the oppositely charged particle. Non-adsorbed (*A*) and adsorbed (*B*) regimes are delimitated by dashed lines

observed. Similar trends are also observed for the $<L_{ee}^2>$ values. It is also interesting to explore the expansion factor *r* for the polyelectrolyte/particle system (Fig. 3b). For the non-adsorbed chains the *r* values are identical to the free chain values and close to 6.5. When adsorption occurs with higher linear charge density the value of *r* decreases immediately. For adsorbed polymers the *r* values are comprised between 1 and 3.

A qualitative picture of the polyelectrolyte/particle complexes has also been achieved by representing equilibrated structures as a function of C_i and the LCD (Table 2). It is clearly demonstrated that the absorption/desorption limit is moved from the higher to the lower ionic strengths with decreasing LCD. Hence, when the linear charge density is small, adsorption is promoted by increasing the attractive interactions between monomers and particle. For example when $C_i = 1.0$ M the polymer is never adsorbed on the colloid whereas when $C_i = 0.1$ M adsorption occurs only when LCD > 0.3.

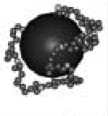
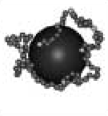
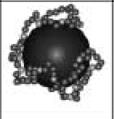
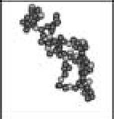
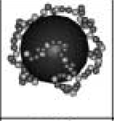
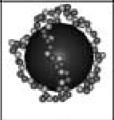
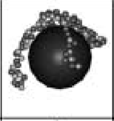
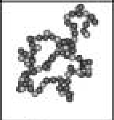
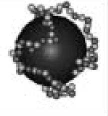
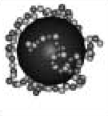
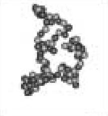
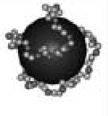
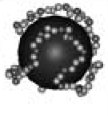
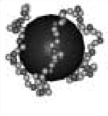
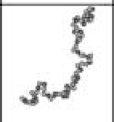
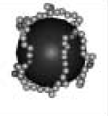
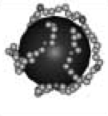
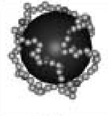
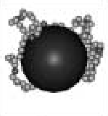
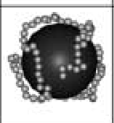
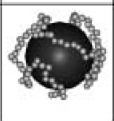
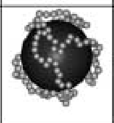
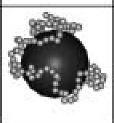
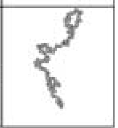
Conformation of the adsorbed polyelectrolytes

The conformation of adsorbed polymers are usually described in terms of trains, loops and tails. In Figs. 4a, b and c we present the average number of monomers in trains, loops and tails as a function of C_i and LCD for the colloid/polyelectrolyte complex.

Trains

The adsorption mechanism of the polyelectrolyte at the colloid surface can be derived by analysing curves

Table 2. MC equilibrated conformations of polyelectrolyte/particle complexes versus C_i and LCD. The LCD is clearly controlling the adsorption/desorption limit and polymer conformation at the particle surface. When screening is important, no adsorption is observed

C_i [M] Linear Charge Density (LCD)	0	0.01	0.1	0.3	1
0.1					
0.2					
0.35					
0.5					
0.7					
0.9					
1.0					

in Fig. 4a. In absence of trains, according to our definition of polymer adsorption, the polyelectrolyte is never adsorbed. This is observed when $C_i = 1.0$ M. In the others situations, after a critical value of the LCD, one can observe a monotonic growth of monomers in trains with the increasing LCD. At a given LCD, with decreasing ionic strength the number of trains is growing, which means that polyelectrolyte chains adopt flat conformations at the interface. At this point it is worthwhile remembering that the number of monomers in trains reflects the adsorbed amount of polyelectrolyte, Γ:

$$\Gamma = \frac{N^*}{N} \tag{4}$$

where N^* represents the number of adsorbed monomers lying in the first layer.

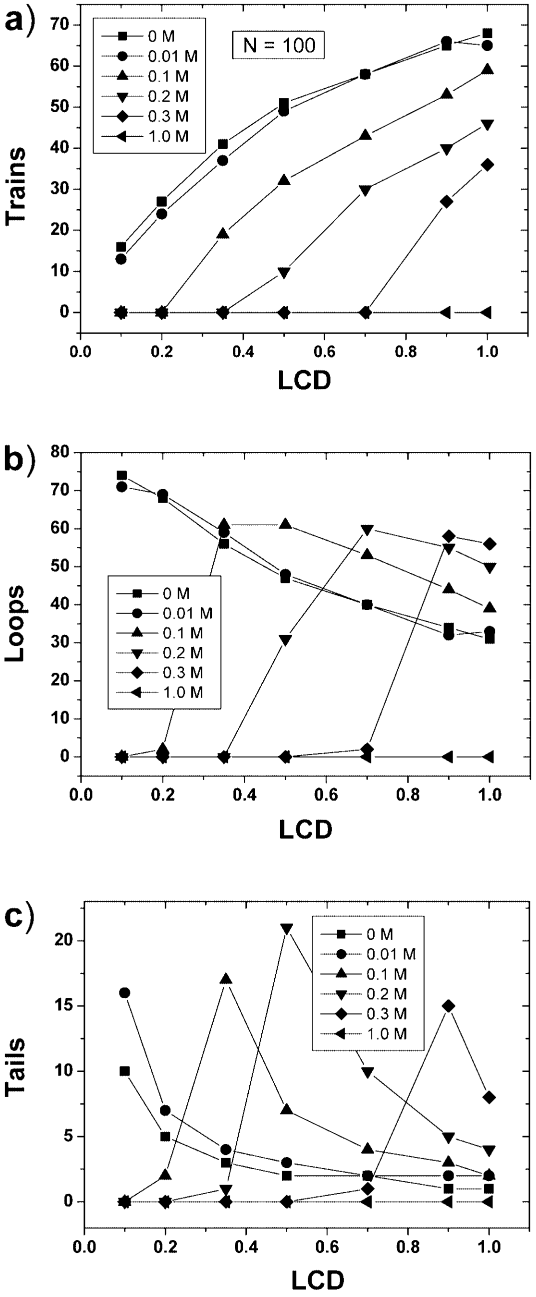


Fig. 4a–c. a Number of monomers in trains, **b** loops, and **c** tails as a function of the linear charge density (LCD) at different ionic concentration for the polyelectrolyte/particle complex

Loops

According to Fig. 4b, globally the number of monomers in loops decreases with increasing LCD and with decreasing C_i. Here one can also observe a sharp transition between the non adsorbed and adsorbed regime. A maximum value is reached just after adsorption, then a smooth decrease with increasing LCD is observed. The monomers in loops are then transferred into trains.

Tails

When $C_i = 0$ and 0.01 M, the number of monomer in tails monotonically decreases with the increase of LCD. In the other cases, a maximum value is obtained at the adsorption/desorption limit.

As the polymer is only weakly adsorbed at the small values of LCD and low ionic strength, an important balance is observed in favour of loops and tails instead of configurations where the monomers are in trains. As the three parameters are correlated, the proportional changes can be easily observed; with increasing LCD the amount of monomers in trains is increasing whereas the amount of monomers in tails and loops is decreasing. At higher values of LCD the number of monomers in trains reaches a maximum and finally decreases slowly with increasing further the values of LCD.

Energy of adsorption

In order to determine an optimal criterion to obtain a realistic adsorption/desorption limit, one must carefully check the energy variation of the polyelectrolyte/particle system during the adsorption process. In the Monte Carlo Metropolis algorithm, the adsorbed configuration is accepted from an energetical criterion when (i) the ΔE resulting from the MC step is negative, (ii) the Metropolis selection criterion p given by:

$$p = exp\left(\frac{-\Delta E}{k_B T}\right) \qquad (5)$$

is greater than a randomly generated number comprised between 0 and 1. In our simulation the configuration is considered as "adsorbed" when at least one monomer is positioned in the delimited volume near the surface (first layer). According to the Metropolis algorithm the energy fluctuations of the system can give rise to a sequence of conformations in which one "adsorbed " configuration is followed by a "non-adsorbed" one, where the chain may diffuse further away and leave the particle surface. This adsorption/desorption process is expected to be more or less pronounced depending on C_i and the LCD during the simulation time. In order to determine when the simulation succeeded in the "average adsorbed" or "average desorbed" situation, we introduced a contact probability parameter, P_c, which is equal to the total amount of adsorbed configurations over all configurations obtained during a simulation run. At this point the polyelectrolyte is arbitrarily considered as being "adsorbed" when $P_c = 0.5$.

To check the validity of this arbitrary choice from an energetical point of view we estimated the mean average adsorption energy per monomer as a function of LCD. We considered the average value E_A, which takes into account the energy of adsorbed configurations E_i^{Ads} only

$$E_A = \frac{\sum_{i=1}^{K} E_i^{Ads}}{NK} \qquad (6)$$

where K represents the number of MC steps corresponding to adsorbed configurations, E_i^{Ads} the adsorption energy (here the monomer–colloid electrostatic interaction) of the corresponding complex and N the number of monomers. This value corresponds to an overall mean adsorption energy per monomer of simulated conformations where at least one monomer is adsorbed at the colloidal surface. As shown in Fig. 5, the mean adsorption energy (given in kT units) per monomer becomes more and more important by decreasing the ionic strength. Because of the electrostatic monomer-monomer repulsions and important electrostatic persistence length of the polyelectrolyte at low C_i value, the attractive energy between the particle and the monomers has to be large enough to overcome the chain confinement energy.

When $C_i < 0.3$ M, for a given C_i value the adsorption energy slowly increases with increasing LCD. The difference between a weakly and fully ionised chain is approximately equal to 1 kT and related to the chain conformation at the interface.

By comparing Fig. 5 values with the adsorbed conformations (i.e. $P_c \geq 0.5$), we found that adsorption occurs when the mean energy per monomer is more negative than –0.4 kT (*hatched* zone in Fig. 5). This

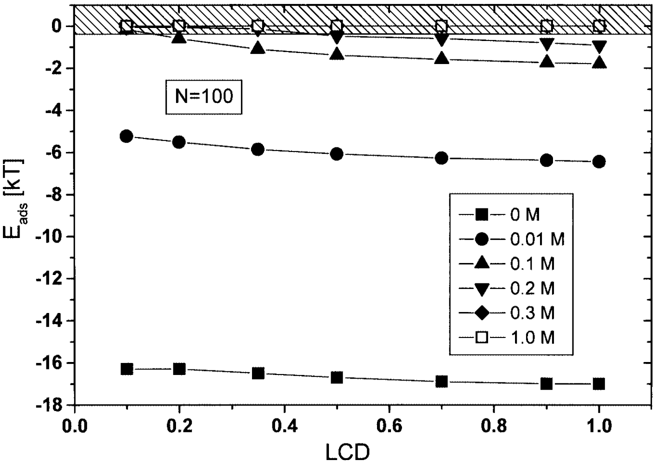


Fig. 5. Mean adsorption energy per monomer for the polyelectrolyte/particle complex as a function of C_i and LCD. The points situated within the *hatched* zone correspond to non-adsorbed conformations

value which is in agreement with theoretical and experimental data [29] is slightly smaller than those found in our previous studies where the adsorption/desorption limit energy was estimated to be close to –1 kT. The difference is mainly due to the calculation method. In our previous work the energy by monomer was estimated by placing one monomer on the particle at adequate C_i and calculating the resulting interaction. In this study the overall energy of a given conformation is calculated and then divided by the number of monomers in the chain. Hence, the resulting adsorption energy is slightly smaller since not all the monomers are exactly positioned on the colloidal surface.

Adsorption–desorption limit

As explained above, polyelectrolyte chains were considered as adsorbed when $P_c = 0.5$. We estimated the critical values of adsorption at different salt concentrations by adjusting the linear charge density. The examination of the P_c values versus LCD (Fig. 6) shows a sharp transition which seems to be more gradual by increasing the ionic strength. As small changes in the LCD values generate very important changes in the absorption ratio, we calculated the critical linear charge density LCD^{crit} at which adsorption-desorption is observed. We plotted the critical LCD adsorption value versus C_i in Fig. 7 and observed a linear dependence with a slope equal to 2.5. The curve delimitates the frontier between the desorption and the adsorption domains. The critical Linear Charge Density LCD^{crit} dependence versus κ is shown in the inset of Fig. 7a. The LCD^{crit} is related to κ according to:

$$\text{LCD}^{\text{crit}} \approx \kappa^{y} \tag{7}$$

where $y = 2$ was estimated by plotting log(LCD) vs. log(κ).

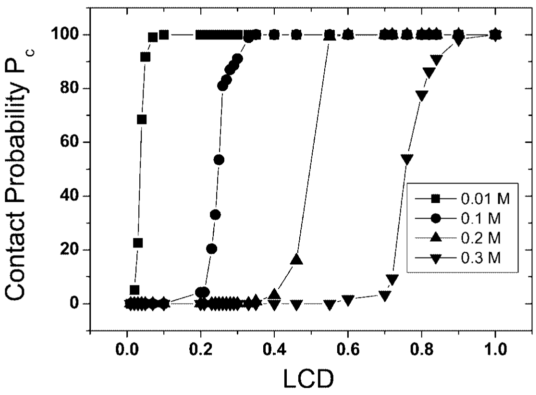


Fig. 6. Contact probability parameter P_c versus the linear charge density (LCD) between the polyelectrolyte and the particle

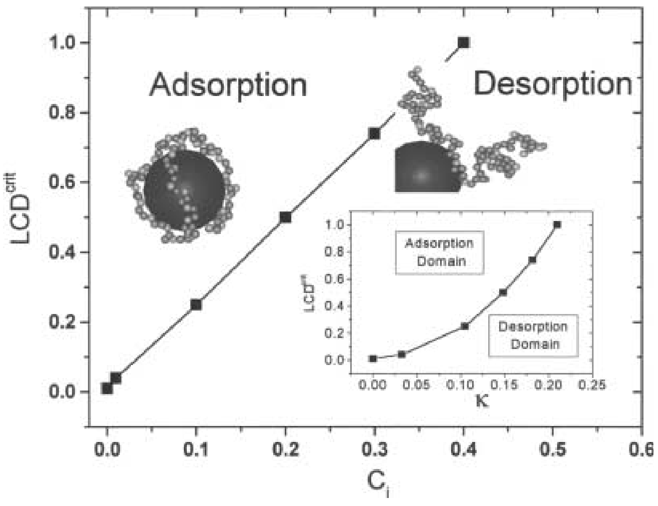


Fig. 7. Critical value of the linear charge density LCD^{crit} as a function of C_i. In the inset LCD^{crit} is plotted against κ. Adsorption and desorption domains are delimitated by the corresponding curves

Outlook and conclusion

In this paper we have presented a preliminary study of the influence of the polyelectrolyte linear charge density on the behaviour of isolated flexible polyelectrolytes and their adsorption on colloidal particles. Monte Carlo simulations were used to isolate some molecular factors that control polyelectrolyte conformations in solution, at the interface, and the adsorption-desorption limit. We believe that Monte Carlo simulations constitute a useful approach to address the optimisation of colloid–polymer mixtures.

Polyelectrolyte adsorption is promoted by increasing the attractive energy between the charged monomers and the oppositely charged particle. This is achieved by (i) increasing the linear charge density of the polyelectrolyte, or/and (ii) decreasing the ionic concentration to promote electrostatic attractive effects. Calculating the adsorption-desorption limit, we found the critical linear charge density LCD^{crit} scales as $\text{LCD}^{\text{crit}} \sim \kappa^2$. By focusing on the variations of the polyelectrolyte dimensions and probability of contact, we found a sharp transition at the adsorption–desorption limit, which appears to be more gradual by increasing the ionic strength. Adsorption occurred when the mean attractive energy par monomer is more negative than –0.4 kT. By analysing the monomer fraction in loops, tails and trains, we demonstrated that at small values of the linear charge density and low ionic strength a large amount of monomers are present in loops and tails. By increasing the linear charge density, the amount of monomers in trains reaches a maximum value and polyelectrolytes adopt flat conformations at the particle surface. A first approach involving one charged polyelectrolyte with a variable linear charge density has been investigated at a given particle/monomer size ratio, but it can be extended to more precise modelling by including explicit counterions, hydrophobic interactions and to concentrated systems involving several chains and particles. We are currently extending our investigations to examine the effect of chain length and particle charge on the formation of polyelectrolyte–particle complexes.

Acknowledgments We gratefully acknowledge the financial support received from the following source: Swiss National Research Project No. 2100-061750.00/1 and University of Geneva.

References

1. Napper DH (1983) Polymeric stabilization of colloidal dispersions. Academic Press, New York
2. Buffle J, Wilkinson K, Stoll S, Fillela M, Zhang J (1998) Environ Sci Technol 32:2887
3. Luscombe NM, Austin SE, Berman HE, Thornton JM (2000) Genome Biology 1:1
4. Buffle J, van Leeuwen HP (1992) Environmental particles. Lewis, London
5. Anderson CF, Record MT (1982) Annu Rev Phys Chem 33:191
6. Khan MO, Mel'nikov SM, Jönsson B (1999) Macromolecules 32:8836
7. Khan MO, Jönsson B (1999) Biopolymers 49:121
8. Lyubartsev AP, Nordenskioeld L (1997) J Phys Chem B 101:4335
9. Symmons MF, Welsh LC, Nave C, Marvin DA, Perham RN (1995) J Mol Biol 245:86
10. Tsao HK, Sheng YJ (2001) J Colloid Inter Sci 233:124
11. Dolgobrodov SG, Lukashkin AN, Russel IJ (2000) Hear Res 150:83
12. Dolgobrodov SG, Lukashkin AN, Russel IJ (2000) Hear Res 150:94
13. Yuan Y, Oberholzer MR, Lenhoff AM (2000) Colloid and Surfaces A 165:125
14. Xia JL, Dubin PL, Kokufuta E, Havel H, Muhoberac BB (1999) Biopolymers 50:153
15. Adar R, Yayon A, (2001) Biochem Biophys Res Commun 283:1
16. Volpi N (1996) Biochim Biophys Acta 1290:299
17. Rouzina I, Bloomfield VA (2001) Biophys J 80:894
18. von Goeler F, Muthukumar M (1994) J Chem Phys 100:7796
19. Muthukumar M (1999) Colloid-Polym Interact:175
20. Jonsson M, Linse P (2001) J Chem Phys 115:3406
21. Carlsson F, Linse P (2001) J Phys Chem B 105:9040
22. Sintes T, Sumithra K, Straube E (2001) Macromolecules 34:1352
23. Chodanowski P, Stoll S (1999) J Chem Phys 111:6069
24. Chodanowski P, Stoll S (2000) Colloid Polym Sci 278:406
25. Chodanowski P, Stoll S (2001) J Chem Phys 115:4951
26. Chodanowski P, Stoll S (2001) Macromolecules 34:2320
27. Tanford C, Kirkwood JG (1957) J Am Chem Soc 79:5333
28. Hooper HH, Beltran S, Sassi AP, Blanch HW, Prausnitz JM (1990) J Chem Phys 93:2715
29. Fleer GJ, Cohen Stuart MA, Scheutjens JMHM, Cosgrove T, Vincent B (1993) Polymers at interfaces. Chapman & Hall, London, UK