

INTRODUCTION

In 1979 *Tanaka et al.* showed experimental evidence of pH dependence for the adsorption of different polyelectrolytes (PE), on that work could be observed maximum adsorption values for different PE studied (Figure 1). Then on 1990 other research group, *Blaakmeer et al.*, showed more experimental confirmation of this dependence and proposed also a first theoretical model (Figure 2).

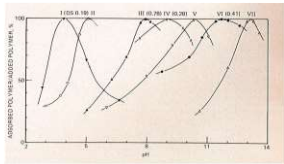


Figure 1: Here are shown the adsorbed amount of different PE exhibiting absorption maximums at different pH values in function with their functional group.

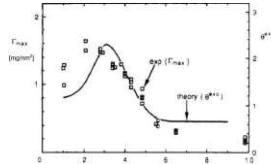


Figure 2: Adsorbed amount (Γ) as a function of the pH for the adsorption of polyacrylic acid onto a cationic latex with a charge density $\sigma_p = 160 \text{ mC/m}^2$ in 0.1 N KNO_3 .

With that background, the present work was proposed as a new theoretical approach using a coarse grain model for the system and a Monte Carlo method to simulate the adsorption process of weak-polyelectrolytes (WPE) on a cationic structured surface, for different pH values and concentrations.

THE COARSE GRAINED MODEL

The simulation box of sizes $L_x \times W_x \times W_y$, was used, with two rigid walls both situated at $z=0$ and $z=L$, respectively. The adsorption was set on $z=0$ with an area $W^2 = 845 \text{ nm}^2$. The other four sides were fixed by a periodic contour condition in order to minimize the finite size effects (Figure 3).

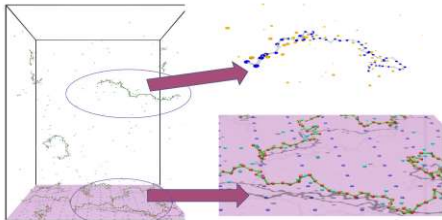


Figure 3: (A) The Simulation box. (B) Detailed scheme of a coarse grained PE model (blue) surrounded by an atmosphere of counterions (yellow). (C) Detailed image showing fixed ions (blue) on the surface forming a square lattice structure on the base of the box at $z=0$, adsorbed PE chains (red and green) and adsorbed counterions (light blue).

Weak-polyelectrolytes and “free” ions were modeled as classical rigid spheres (monomers) with electrostatic potential (eq. 1) with the difference that on WPE chains the bond between next neighbours monomers are harmonic oscillators (eq. 2) and two possible electrostatic charge states ($q=0$ or $q=-e$) were allowed to simulate ionization process by Monte Carlo simulation.

$$(1) \quad U_{Ej}(r_{ij}) = \begin{cases} l_b \frac{q_i q_j}{r_{ij}} & \text{if } r_{ij} > \frac{d_i}{2} + \frac{d_j}{2} \\ \infty & \text{if } r_{ij} \leq \frac{d_i}{2} + \frac{d_j}{2} \end{cases} \quad (2) \quad U_{\text{Bond}}^i = k_{\text{bond}} (l_{i,i+1} - l_0)^2$$

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THE MONTE CARLO METHOD

The Monte Carlo method use the statistical mechanics ensembles to calculate numerically all thermodynamic measurements of an equilibrium system. In order to solve it, is necessary fix the degrees of freedom (DF) as an important part of the model. For this work each PE has three DF: Translation (T), pivotal rotation (P) and flip rotation (F), in contrast with small ions that only the T degree is assumed. Then the probability of change P_{ch} of each spatial configuration is calculated by the usual Metropolis formula:

$$(3) \quad P_{ch}^T = \min(1, \exp(-\beta \Delta U)) \quad , \quad \text{with } \beta = 1 / k_B T \quad \text{and } \Delta U \text{ the change of energy } U \text{ for both consecutive states.}$$

Then, we also modeled the ionization process of a WEP independently using a semi-grand canonical version of the Metropolis formula. For this, each monomer can be ionized ($q=-e$) or deionized ($q=0$) in function of the charge probability of change (P_{ch}^q):

$$(4) \quad P_{ch}^q = \min(1, e^{-\beta \Delta U \pm \ln(10)(\text{pH}-\text{pKa})}) \quad ,$$

In contrast with the spacial process here some new small ions can be created or deleted when is required in function of keep the electroneutrality of the system

Observables

(5) Ionization degree.

$$\alpha_{PE} = \frac{\int_{z=0}^{z=1} \rho_m(z) dz}{\int_{z=0}^{z=1} c_m(z) dz}$$

(6) Amount of adsorbed PE.

$$\Gamma = \int_{z=0}^{z=1} C_m(z) dz$$

(7) Electrostatic potential

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

RESULTS

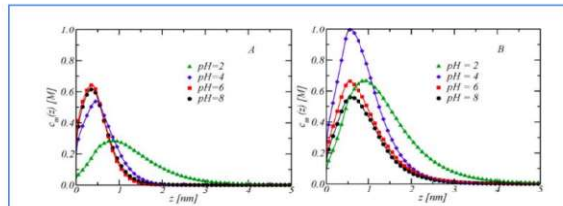


Figure 4: Monomer concentration (C_m) vs. distance (z) with the surface, for different pH values $N_p=4$ (A) and $N_p=10$ (B).

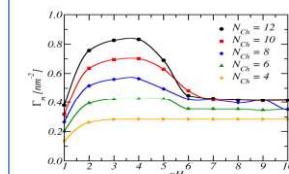


Figure 5: PE adsorption on the charged surface as a function of pH at different number of PE chains added to the system.

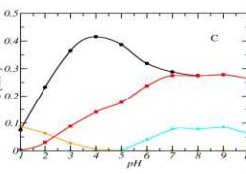


Figure 6: Adsorbed amount of total (black), charged monomers (red) and small ions (yellow) close to the charged surface as function of pH when $N_p = 10$.

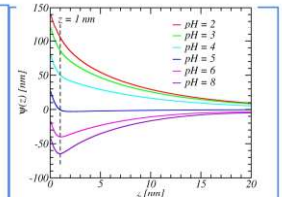


Figure 7: Electrostatic potential as a function of the z distance from the charged surface ($N_p = 10$).

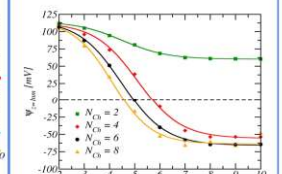


Figure 8: Effect of pH on the electrostatic potential at $z = 1 \text{ nm}$, ψ_{1nm} .

* The PE chains have $x_p = 60$ monomers and $l_p = 0.50 \text{ nm}$. The solution has a salt concentration equal to 1 mM .

CONCLUSION HIGHLIGHTS

- We observe the appearance of a maximum value in the adsorbed amount of chains vs. pH curves in certain conditions. The adsorption maximum is localized at a pH-value close to the intrinsic $\text{pK}_{\text{Oa}} = 4.25$ value of the PE titratable groups (see black curve on Figure 6).
- It is important to note that the charged monomer adsorbed amount is a monotonous function with the pH, and does not exhibit any maximum in any circumstance (see red curve on Figure 6).
- We also observed that the PE amount of negative charge increase caused in increasing the pH-value is accompanied by a decrease in the small anion (yellow curve on Figure 6) adsorbed amount and an increase in the small cation adsorbed amount (cyan curve on Figure 6). This ionic exchange at high pH-values allows us to observe the charge reversion phenomenon in surface caused by the PE chains adsorption (Figure 8).

Finally we want to highlight that we do not include non-electrostatic interaction between the system particles in our simulations. This means that the above mentioned conclusions are a natural consequence of the coulombic interaction of the system species and the acid/base