POLYELECTROLYTES AT LIKE-CHARGED SURFACES: HOW TO MAKE THEM STICK

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Application of AFM to biological systems requires the deposition of aqueous solutions of biomolecules onto surfaces and partial immobilization of the biomolecules. In most cases the biological molecules as well as the substrates are charged in aqueous solutions and it proved to be challenging to find the conditions for polymer adsorption. Therefore the mechanism of adsorption of charged polymers onto charged surfaces has to be understood.

We propose a mean-field theory for the interactions of like-charged polyelectrolytes and plane surfaces in the presence of 1:1 and 2:1 electrolyte, which takes into account long-range van der Waals and double-layer forces. As the first approximation we have considered a surface of a substrate to be featureless and flat with the even distribution of charge. A polymer is considered as an assembly of evenly charged cylinders. The theoretical description of the long-range forces acting between the cylinder and the surface in electrolyte solution has been developed on the basis of the mean-field DLVO (Derjaguin-Landau-Verwey-Overbeek) theory. The analytical expression for the polymer/surface interaction energy as a function of polymer/surface separation, surface charge densities of the polymer and the substrate, temperature, salt concentrations of the solution and dielectric properties of the surface, polymer and the solvent has been obtained. It takes a particularly simple form in the limit of low cylinder and substrate surface charge densities (Debye-Huckel approximation), which is applicable to proteins on the surfaces at certain pH of the solvent.

Since a mean-field approximation has been used the theory is applicable for the description of polymer/surface interactions up to the distances equal to approximately half of the Debye length of the solvent. Short-range effects may significantly contribute to both attraction and repulsion energies in this regime. Therefore depending on the balance of both short- and long-range interaction energies the equilibrium distance of the polymer above the surface may be shifted towards lower or higher separations with respect to that obtained using the mean-field approximation. However, even in these limitations the mean-field theory predicts well the behaviour of polyelectrolytes at charged surfaces.

The theoretical predictions were verified against the results of AFM imaging of DNA adsorbed onto mica surface in NaCl, MgCl₂ and NiCl₂ solutions as well as the mixtures of NaCl and 2:1 electrolytes. The theoretical data suggest that 1:1 electrolyte is not able to induce DNA adsorption onto mica surface, while the addition of relatively low concentrations of divalent cations leads to the DNA adsorption.

Mg²⁺ and Ni²⁺ are the representatives of two classes of divalent cations with respect to their interaction with DNA molecule. Ni²⁺ ions tend to bind to DNA molecule while Mg²⁺ do not bind to DNA, but form a diffuse layer in the vicinity of the macromolecule. Therefore the mechanism of divalent ions induced adsorption of the DNA onto a mica surface is different for these two classes of cations. The adsorption of DNA in MgCl₂ solutions is due to the strong enhancement of the attractive van der Waals interactions along with a weak contribution to the repulsive double-layer interaction by Mg²⁺ ions, which results in the overall attraction of the DNA to the mica surface at certain concentrations of MgCl₂. On the other hand, binding of Ni²⁺ to the DNA molecule effectively lowers its surface charge. Therefore the double-layer component of the interaction energy becomes negligibly small compared to the van der Waals component which ensures the adsorption of DNA even at concentrations of NiCl₂ as low as 1mM compared to 35mM of MgCl₂ required for the adsorption in the same conformation.
We have found that when the adsorption is governed by long-range forces DNA adopts an ideal 2D conformation, while a compressed 2D–3D projected conformation is adopted by DNA molecule in the regime of the overall long-range repulsion and short-range attraction. The theory is able to predict the transition from one regime to another at 35 mM MgCl$_2$ (Figure). The comparison of the theoretical and experimental data allows us to estimate the minimum interaction energy required for DNA adsorption in ideal 2D conformation, which was found to be equal to 0.8 kT.

Our results showed that the theory is able to predict the conditions, such as solvent composition, pH and temperature, for polyelectrolyte adsorption onto like-charged surfaces as well as to account for the conformational properties of a polymer at the surfaces. Therefore it can be used as a simple tool for choosing the optimum experimental setup for the desired adsorption properties of polyelectrolytes on the like-charged surfaces.

**Figures:**

AFM images of DNA in aqueous MgCl$_2$ solution adsorbed on fully charged mica surface. Concentrations of MgCl$_2$ in solution are 30 mM (left) and 35 mM (right) respectively. Our theory predicts MgCl$_2$ concentration of 35 mM for the transition from projected to ideal 2D conformation to take place.