POLITECNICO DI TORINO

Master's Degree in Environmental Engineering

Master Thesis

Adsorption and desorption of a positively charged polymer on silica and implications for environmental processes

SUPERVISOR
Prof. Alberto Tiraferri

CANDIDATE
Emmanuele Castiglione

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Abstract

The adsorption and desorption behavior of a strong polycation, PDADMAC (polydiallydimethylammonium chloride), on silica was studied together with the influence of this polyelectrolyte on the surface potential and aggregation of silica colloids. This is relevant for environmental systems, such as coagulation-flocculation processes and the fate of nanoparticles in aquatic environments. The behavior of this system was investigated under different aqueous conditions by combining measurements with the QCM-D (Quartz Crystal Microbalance with Dissipation monitoring) and a DLS (Dynamic Light Scattering) instrument. QCM-D was used to understand the interactions driving adsorption of PDADMAC on flat silica, and especially the phenomena causing subsequent desorption from the solid surface. DLS was employed to study the aggregation and disaggregation behavior of silica nanoparticles following adsorption and desorption of PDADMAC under different conditions.

Results showed that the adsorption rate increases strongly with increasing ionic strength (IS) of the solution and with increasing pH, consistent with literature reports. Furthermore, under the same conditions, the adsorption was slightly larger when PDADMAC of higher molecular weight was used. Adsorption is irreversible if aqueous conditions remain the same as during the adsorption processes. However, desorption can be triggered changing IS and/or pH. By lowering the pH, the electric potential due to protonation of the silica surface charges is reduced and the lower potential can no longer counteract the dense positive charges of PDADMAC chains previously deposited, some of which desorb and return in solution. Lowering IS, the potential due to the like charges of neighbouring chains produces the same effect of driving desorption of some of these chains. The results suggest that the barrier for desorption is relatively high and significant changes of solution chemistry are needed to

trigger re-suspension of previously deposited chains. These mechanisms have important implications for environmental processes because they suggest that, once adsorbed, polymeric chains tend to remain attached to solid surfaces and govern their behavior. These mechanisms also have direct impact on the stability of colloidal systems.

Measurement of the electrophoretic mobilities of silica nanoparticles in the presence of PDADMAC show that increasing the IS the dose of PDAMAC necessary to achieve system iso-electric potential (IEP) is larger and that the adsorbed amount of polymer at saturation is also larger, thus suggesting that adsorbed amounts are governed by electrostatic repulsions between the adsorbed polyelectrolyte chains. When the solution conditions are changed, this change can trigger a complex aggregation and disaggregation behavior, also showing an energy barrier for disaggregation of previously aggregated particles.

Introduction

Polyelectrolytes, polycations and polyanions, are charged polymers consisting of ionizable groups bound to polymer backbone chains. They have a strong propensity to adsorb on solid surfaces; thus, they are used in many industrial applications, for example as antifouling agents preventing protein adsorption and bacteria fouling. In the last years, polyelectrolytes have been intensively applied in biotechnology, for instance, in encapsulation of drugs and their release in a controlled way, in biosensing, and in protein and enzyme immobilization and separation [1]. The stability of charged colloidal particles, in many industrial processes, is controlled thanks to the addition in the suspensions of polyelectrolytes of opposite charge. The stabilization of these suspensions is essential to ensure long shelf-life of consumer products, such as foods, paints, or cosmetics. The important role of the additive, in this case, is to decrease the destabilization to the point in which aggregation of the colloidal particles becomes negligible. On the other hand, rapid destabilization of these suspensions is essential in several processes, such as papermaking, water and wastewater treatment, or ceramic processing. Thereby, suitable additives cause rapid aggregation of suspended particles and a following formation of flocs, which can be subsequently separated and processed [2]. Other emerging applications of polyelectrolytes comprise, for instance, the stabilization of metallic iron nanoparticles for environmental remediation. Furthermore, polyelectrolytes are employed to produce functional or protective surface coatings. Such coatings may be utilized to control the surface properties, including wetting, adhesion, lubrication, or biological resistance. Several polyelectrolytes provide the possibility to tune such properties through outside stimuli, such as solution composition or temperature [3].

PDADMAC (polydiallydimethylammonium chloride) is a commonly employed water-soluble polycation with highly hydrophilic, positively charged quaternary ammonium groups. In the past, it was used in order to manufacture papers with high electroconductivity. Currently, PDADMAC is applied in several industrial fields, for instance in paper manufacturing, in water treatment plants, and in the mining industry. Furthermore, PDADMAC is effective in protein immobilization, in the separation of biomolecules and removal of bacteria from sludge. PDADMAC is even effective in flocculation of latex and silica particles [1]. Aside from the commercial interest of PDADMAC, this substance is frequently used in scientific research due to its interaction with negatively charged colloids or polyelectrolytes. For this reason, interesting studies were carried out to explain the arrangement of the PDADMAC chains in aqueous media [1]. Finally, PDADMAC can be exploited like a stabilizer and linker, and like an ‘‘anchor layer’’ or to produce multilayers of polyelectrolytes of desired structure and coverage. [1].

The adsorption behavior of polyelectrolytes on solid surfaces can be investigated by applying innumerable experimental techniques [4]. In particular, the QCM-D (Quartz Crystal Microbalance with Dissipation monitoring) was extensively used to investigate surface layers of wet mass, which also includes the mass of the trapped and hydration solvent, while the DLS (Dynamic Light Scattering) was utilized to investigate the thickness of adsorbed PDADMAC on oppositely charged particles, to evaluate the change of electrophoretic mobility and to quantify the dimension of particles under different IS and pH conditions [5]. Although these techniques can also be used to study the desorption process, there are very few studies in literature in which this was done.

In this thesis, the adsorption and especially the desorption behavior of PDADMAC on and from silica surfaces in aqueous solution is investigated with QCM-D (flat solid surfaces) and DLS (nanoparticles). The aqueous chemical parameters, IS and pH, are varied to investigate their effect on adsorbed amount of PDAMAC on silica and to trigger desorption of previously adsorbed chains. The hypothesis to be tested is that polymer desorption may be favoured upon specific aqueous changes and that resuspension of chains leads to complex aggregation and disaggregation behavior of colloids, which will be here preliminarily discussed.

Chapter 1

State of the art

This chapter draws generously from a number of published articles on the topics of interest and it attempts to summarize the useful information contained in these publications, which is useful to understand and interpret the results obtain in this thesis. Some of these articles are listed and referenced here and their titles are: “Stability of negatively charged latex particles in the presence of a strong cationic polyelectrolyte at elevated ionic strengths” [2], “Polyelectrolyte adsorption, interparticle forces, and colloidal aggregation” [3], “Overview of DLVO theory” [6], “Protonation of silica particles in the presence of a strong cationic polyelectrolyte” [7], “Probing effects of polymer adsorption in colloidal particle suspensions by light scattering as relevant for the aquatic environment: An overview” [8], “Polyelectrolyte adsorption: electrostatic mechanisms and nonmonotonic responses to salt addition” [9], “Effect of charge density, molecular weight, and hydrophobicity on polycations adsorption and flocculation of polystyrene lattices and silica“ [10], “Adsorption of poly(ethyleneimine) on silica surfaces: effect of pH on the reversibility of adsorption” [11], “Polyelectrolyte adsorption on oxides” [12], “Equilibrium aspects of polycation adsorption on silica surface: how the adsorbed layer responds to changes in bulk solution” [13], “Adsorption of polyelectrolytes to like-charged substrates induced by multivalent counterions as exemplified by poly (styrene sulfonate) and silica” [14], “Transition from completely reversible to irreversible adsorption of poly(amido amine) dendrimers on silica” [15], “Effect of polyelectrolyte charge density on the adsorption and desorption behavior on mica” [16], “Flocculation and stabilization of colloidal silica by the adsorption of poly-diallyl-dimethyl-ammoniumchloride (PDADMAC) and of copolymers of DADMAC with N-methyl-N-vinylacetamide (NMVA)” [17].

1.1 DLVO theory

The DLVO theory is named after Boris Derjaguin, Lev Landau, Evert Verwey and Theodoor Overbeek. These researchers developed a theory about colloidal stability, thanks to which interactions between colloidal particles and their aggregation behavior were explained. Moreover, it is also being used to interpret particle deposition to planar substrates and to rationalize forces acting between interfaces. The theory was originally formulated for two identical interfaces (symmetric system), which corresponds to the case of the aggregation of identical particles (homoaggregation). This concept was then extended to two different interfaces (asymmetric system) and to aggregation of different particles (heteroaggregation). This latter case, when there is a high size difference between the particles, can be approximated with the deposition of particles to a planar substrate. In the figure below all these processes are illustrated [6].

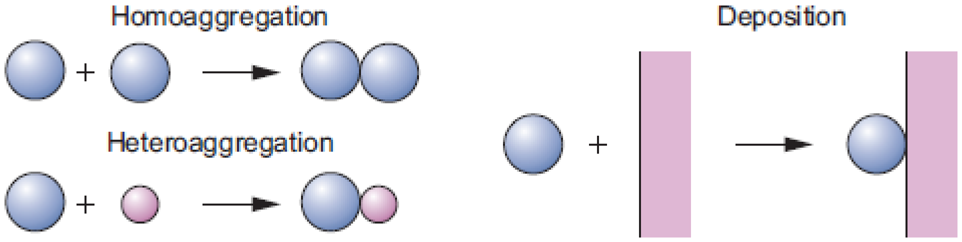

Figure 1.1.1 Different aggregation process of colloidal particles, extracted from [6].

These different types of aggregation are caused from a force F acting between two charged objects through an aqueous electrolyte solution, which is assumed to have two principal contributions:

$$\boldsymbol{F} = \boldsymbol{F}_{vdW} + \boldsymbol{F}_{dl}$$

namely, the attractive Van der Waals force F_{vdW} and the repulsive electric double layer force F_{dl}. The Van der Waals force derives from dispersive interactions between permanent and fluctuating dipoles of the constituent molecules, called also London dispersion force. It can be approximated, for a pair of particles of radius R, as:

$$\boldsymbol{F_{vdW} = -\frac{RH}{12h^2}}$$

where H is the Hamaker constant, which characterized its strength, and h is the surface separation. This expression is valid when the particles radius R is large with respect to the surface separation h, when the retardation effects are negligible and when the Derjaguin approximation is invoked. The other contribution to the resultant force F, the electric double layer force, can be viewed to originate from the osmotic pressure resulting from the overlap of the diffuse part of the double layers. It can be expressed for two identical particles, considering the Derjaguin approximation, as:

$$\boldsymbol{F_{dl} = 2\pi R\varepsilon_0\varepsilon\kappa\psi_{eff}^2 e^{-\kappa h}}$$

where φ_{eff} is the effective electric potential, that is equal to the surface potential for a weakly charged surface. On the other hand, for a highly charged surface, the Poisson–Boltzmann theory suggests that it converges to a constant value given by:

$$\boldsymbol{\psi_{eff} = 4k_b\frac{T}{q}}$$

where k_b is the Boltzmann constant, T is the absolute temperature in kelvin and q is the charge of an electron equal to 1.602×10^{-19} coulombs [3].

The force F, obtained by the sum of the two contributions, has the profile shown in the left panel of the Figure 1.1.2. It is dominated at large and small distances by the Van der Waals force, whereas the double layer force predominates at intermediate distances. In the right panel of the same Figure, instead, the potential energy profiles are displayed. The *primary minimum* is the deep attractive well resulted from the combination of these forces with the DLVO force. However, at larger distances, the energy profile moves then across a maximum, and subsequently passes through a superficial minimum, which is referred to as the *secondary minimum*. The representation of both profile allows to note that the energy profile goes through a maximum or a minimum when the force disappears. In the symmetric situations, the profiles are the same whether the sign of the charge is positive or negative. [6].

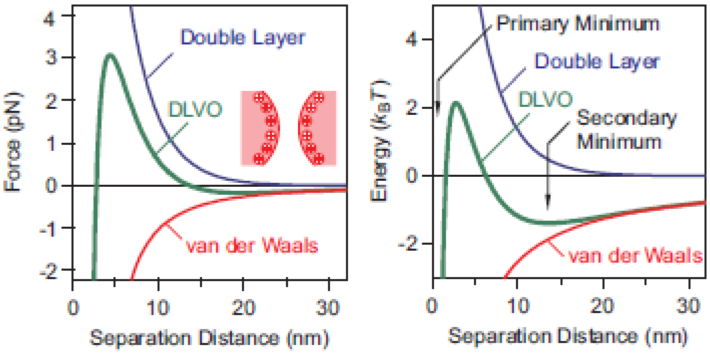

Figure 1.1.2 Force profiles in the left and potential energy profiles in the right, extracted from [6].

The main feature of the DLVO theory, summarized in this paragraph, is the capability to well describe the modification of the surface charge and the forces due to the adsorption of polyelectrolyte on an oppositely charged colloidal surface. At first, when no polyelectrolyte is added in solution, the forces are dominated by double layer repulsion. However, the addition of polyelectrolyte leads to a progressive neutralization of the surface charge and the repulsive forces weaken. Therefore, the interactions between colloidal particles and their aggregation behavior can be investigated in the entire range of the polyelectrolyte dose [3].

The isoeletric point (IEP) is the point where the electrophoretic mobility vanishes, leading to rapid aggregation and an unstable suspension. At this point, in fact, the interaction between the particles is dominated by attractive van der Waals forces because the diffuse layer is poorly developed and thus electrostatic repulsion is weak due to diffuse layer overlap. Away from the IEP, diffuse layers expand and their overlap leads to repulsive interactions, with which the aggregation becomes slow and the suspension becomes stable. This behavior creates the characteristic U-shaped plot of the stability ratio as a function of the polymer dose, with a minimum near the IEP. The stability ratio is a dimensionless parameter characterizing suspension stability and is calculated with this formula:

$$\boldsymbol{W = \frac{k_{fast}}{k}}$$

where k is the measured aggregation rate constant and k_{fast} is the fast aggregation rate constant at salt concentrations above the Critical Coagulation Concentration in the absence of polyelectrolyte [2].

1.2 The modified Stern model

The basic Stern model was especially successful to catch many features of the charging characteristics of water–oxide interfaces. The presence of adsorbed polyelectrolytes, as explained in the previous paragraph, leads to an important change in charged surfaces, so similar approach was proposed to describe the charging behavior of such systems. However, the basic Stern model fails to describe it because the charges originating from the adsorbed polyelectrolyte cannot be placed in the same plane as the charged groups at the surface (0-plane). For this reason, the modified Stern model was developed, which permit to achieve a better description of the charging data because the charged sites, originating from the polyelectrolyte, are placed at the origin of the diffuse layer (d-plane). This model can be successfully used for the study of the behavior of the charged silica surface, originated from the second step dissociation of the singly coordinated silanol groups:

$$SiOH \leftrightarrows SiO^{-} + H^{+}$$

The total concentration of the surface sites Γ_0 is given by the sum of the protonated and deprotonated sites:

$$\Gamma_0 = \Gamma_{SiO^-} + \Gamma_{SiOH}$$

The surface charge density is given by the surface concentration of dissociated silanol groups:

$$\sigma_0 = -e\Gamma_{SiO^-}$$

The charge of the diffuse layer is given by the classical Grahame equation:

$$K = -\frac{2kT\epsilon_0\epsilon\kappa}{e} sinh\left(\frac{e\psi_d}{2\kappa T}\right)$$

where ψ_d is the diffuse layer potential, ϵ_0 is the dielectric permittivity of vacuum, ϵ the dielectric constant of water, and the Debye length κ^{-1} is given by relation:

$$\sigma_d = \frac{2e^2cN_A}{kT\epsilon_0\epsilon}$$

where c is the molar concentration of a monovalent salt and N_A the Avogadro's number. The drop of the surface potential close to the interface is modelled with the so-called Stern layer of a constant capacitance:

$$C_S = \frac{\sigma_0}{\psi_0 - \psi_d}$$

In the basic Stern model, the diffuse layer charge $\boldsymbol{\sigma_d}$ just compensates the surface charge $\boldsymbol{\sigma_0}$. In the modified Stern model discussed here, it is further considered the surface charge due to the adsorbed polyelectrolyte, which is assumed to be located at the origin of the diffuse layer (d-plane). In this case, the charge balance is:

$$\boldsymbol{\sigma_0 + e\Gamma_{N,s} + \sigma_d = 0}$$

where $\Gamma_{N,s}$ is the surface concentration of the positively charged surface-bound polyelectrolyte sites. The charging behavior of the surface is obtained by solving the above equations simultaneously. In the absence of the adsorbed polyelectrolyte (i.e., $\Gamma_{N,s} = 0$) the basic Stern model is recovered [7].

1.3 Adsorption of polyelectrolytes to planar substrates

The adsorption process is a chemical-physical phenomenon that consists of the accumulation of one or more substances on a surface. It is widely exploited in industrial processes because it leads to durable and rapid modification of the surface properties, above all the adsorption of polyelectrolytes which is frequently irreversible. The adsorbed mass and the conformation of the adsorbed film are governed by:

- properties of the polymers: molecular mass, architecture, composition and type of charged groups;
- solution properties: pH, ionic strength and the type of ions present;
- surface characteristics: for example, the charge density [8].

Other than classical DLVO force, in aqueous solutions, the tendency of polyelectrolytes to adsorb at surfaces is frequently further promoted also by a non-electrostatic attraction, for example, brought about by hydrophobic forces [9].

The classical random sequential adsorption (RSA) describes a process where particles are randomly introduced in a system, in this case an aqueous system, and they can only adsorb on a surface. They cannot overlap to any previously adsorbed particle and, once adsorbed, they remain bound for the rest of the process. It is suitable for the description of the irreversible adsorption processes of proteins, colloidal particles and polyelectrolytes, where they are modelled as circular disks because this is the simplest RSA model (Figure 1.3.1).

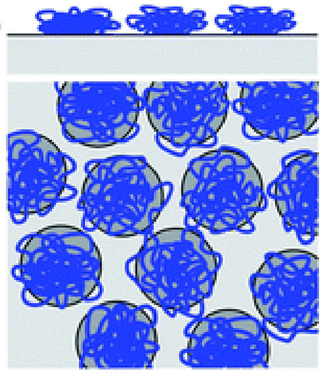

Figure 1.3.1 Graphical illustration of the RSA model for circular disks, extracted from [3].

The kinetics of the adsorption process relate the rate of change of the adsorbed number density with time t to the number concentration c of the polyelectrolyte in solution as:

$$\frac{d\Gamma}{dt} = k_a c\mathrm{B}(\Gamma)$$

where k_a is the adsorption rate coefficient of the polyelectrolyte and $\mathrm{B}(\Gamma)$ is the blocking (or available surface area) function. The Langmuir adsorption model suggests that:

$$\mathrm{B}(\Gamma) = \begin{cases} 1 - \frac{\Gamma}{\Gamma_0} & for\ \Gamma < \Gamma_0 \\ 0 & for\ \Gamma \geq \Gamma_0 \end{cases}$$

where Γ_0 is the adsorbed number density at saturation, which corresponds to the jamming limit within the RSA model. Finally, the adsorbed mass per unit area is achieved by multiplying the adsorbed number density G with the mass of the polyelectrolyte.

Although in this thesis the surface conformation was not considered for the final purpose of the study, the introduction of the RSA model permits to understand the influence of the different forces acting on the adsorption process. It asserts that polyelectrolyte chains adsorb to the substrate individually and the film remains laterally heterogeneous because the spacing between the chains is mainly dictated by the electrostatic repulsion between the adsorbing chains. Furthermore, the strong oppositely charged forces, acting between the adsorbing polyelectrolyte and the substrate, are to flatten the adsorbed chains. Accordingly, an adsorbed polyelectrolyte layer will be typically thin and laterally heterogeneous [3].

1.4 Adsorption of polyelectrolytes to colloidal particles

Highly charged polyelectrolytes tend to adsorb on the planar surface in very thin layer with most of segments in trains, whereas higher number of tails and loops can be formed if the same polyelectrolyte adsorbs on charged particles with dimension smaller or comparable to the size of the polyelectrolyte in solution. This behavior can be also found with lowly charged polyelectrolyte adsorbed on flat surface. This discrepancy in molecular conformation of adsorbed polyelectrolyte can significantly influence the flocculation mechanisms in colloidal dispersions [10].

When polyelectrolytes are dissolved in a suspension of oppositely charged colloidal particles, they will also adsorb to their surface, but it is important to distinguish the two cases illustrated in Figure 1.4.1: unsaturated layer and saturated layer. The first situation occurs when the total polyelectrolyte concentration is low, in fact, the polyelectrolyte will adsorb to the particle surface until no polyelectrolyte is left in solution. Conversely, when the total polyelectrolyte concentration is high, the polyelectrolytes will adsorb to the particle surface until a saturated layer is created [3].

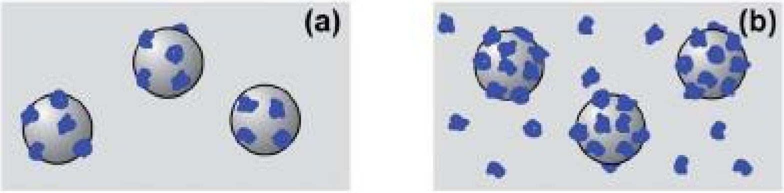

Figure 1.4.1 Schematic representation of (a) the unsaturated layer and (b) the saturated layer with excess polyelectrolyte in solution, extracted from [3].

At increasing dose of polyelectrolyte, the adsorbed chains decrease the particle charge, until this charge is neutralised at the isoelectric point (IEP). Increasing the dose further, the adsorption process goes on beyond the IEP, which leads to a charge reversal. This build-up of the opposite charge is called "overcharging". If the amount of polyelectrolyte is sufficient to reach saturation, the adsorbed amount stays constant beyond this dose. Consequently, any polyelectrolyte that is later added remains dissolved in solution, whereas below saturation the adsorption process of the polyelectrolyte is quantitative [2]. Thus, in presence of a sufficient quantity of charged polymers, the adsorption process will almost be strong enough to produce "overcharging"; that is, at certain distance away from the surface, it will seem to have a charge with a sign opposite to the "bare" surface charge. Therefore, when two these surfaces, or colloidal particles, approach, this process of overcharging will develop an interaction free energy barrier, prior to attractive bridging and correlations at short-range [9].

1.5 Some notions about desorption of polyelectrolytes from solid surfaces

The desorption of adsorbed polyelectrolytes from oppositely charged surfaces is an unfavourable process due to the large number of surface/segment contacts, which imply an important kinetic barrier that must be surpassed [11]. There are a lot of ways to induce the desorption of pre-adsorbed polyelectrolytes: changing ionic strength, changing pH, changing temperature, adding other types of surface-active substances, ex-changing polyelectrolytes or polyelectrolytes with electrolytes.

Hoogeveen et al. [12] studied the reversibility of the adsorption of polyvinylpyridine (PVP^+) and polydimethylaminoethyl methacrylate (AMA) on TiO_2 by deliberately creating nonequilibrium situations by changing the pH conditions. The decrease of pH created a surplus of positive charge on the surface and consequently a high electrostatic potential, which was the driving force for the desorption. They summarized the desorption process in two steps: reconformation of the adsorbed layer, governed by the breakup of the bonds and the formation of other bonds, and detachment from the surface, in which the bonds are only broken.

Samoshina et al. [13] conducted a similar study, but they used a high molecular weight polyacrylamides (CPAM) and they also investigated the effects on the desorption process of the reduction of the ionic strength. They obtained a fast desorption of the adsorbed mass with this change due to the reduced screening of the charge, which in turn increases the electrostatic repulsion between adsorbed molecules.

There are other routes to achieve desorption, e.g., through competition for the adsorption sites at the surface-competitive adsorption. There are experimental studies on systems in which the polyelectrolyte competes with an equally charged surfactant for the adsorption sites on an oppositely charged surface [9]. Tiraferri et al. [14] demonstrated that desorption can be induced by rinsing the adlayer with a solution containing counterions of lower valence. In one study, desorption of a layer adsorbed in the presence of trivalent lanthanum ions was increasingly rapid in solutions with increasing concentration of NaCl, indicating that bound La^{3+} in the adsorbed layer was exchanged with Na^+, and the resulting polyelectrolyte layer containing Na^+ became unstable and desorbed. Desorption was stopped by reintroducing a $LaCl_3$ solution, whereby Na^+ ions was exchanged back with La^{3+} ions.

Different studies confirmed that a protein will desorb more slowly if it has more time to relax to a flatten conformation and to find different anchor points on the surface and that adsorbed proteins do not readily desorb upon dilution, but they can yield their place to other compounds with more affinity in the adsorption process. This same behavior was shown for PAMAM dendrimers by Longtin at al. [15]: the main result of their experiments is that the desorption is more efficient when the adsorption process was previously conducted at low pH or at high IS. In the first case, the desorption process is favoured by the lower number of segments connected to the surface, whereas, at high IS, the adsorbed layer is expanded and swollen due to the reduction of the polyelectrolyte-surface interaction and so with a IS decrease the segments of the polyelectrolyte located far from the surface are more easily desorbed [13].

Rojas et al. [16] in their study entitled “Effect of polyelectrolyte charge density on the adsorption and desorption behavior on mica” concluded that polyelectrolytes are more easily desorbed by addition of an anionic surfactant than by addition of inorganic salt like NaCl. The association between polyelectrolytes and surfactants, resulting in incorporation of negative charges in the adsorbed layer, is of fundamental importance for the desorption process.

1.6 Some literature results of adsorption and desorption of polyelectrolytes on oppositely charged surfaces

Michna et al. [1] determined kinetics of adsorption and monolayer stability of PDADMAC. The authors acquired bulk characteristics of the polyelectrolyte using the DLS and microelectrophoretic measurements. Then, from these measurements, they calculated the hydrodynamic diameter, zeta potential and the amounts of electrokinetic charge per molecule. Finally, they evaluated kinetics of PDADMAC adsorption under in situ conditions using the QCM-D and streaming potential measurements. The latter allowed one to derive the calibration dependencies of the zeta potential on the polyelectrolyte coverage for various ionic strengths successfully interpreted in terms of the 3-dimensional (3D) electrokinetic model. This model enables to derive a relationship between the zeta potential of surfaces and the polyelectrolyte coverage, with which one can quantitatively study the desorption kinetics of PDADMAC under monolayer stability.

Bauer et al. [17] investigated the zeta potentials, diffusion coefficients, and rates of flocculation of silica suspensions as a function of added concentration of PDADMAC and of copolymers of DADMAC with *N*-methyl-*N*-vinyl-acetamide (NMVA), as well as of adsorbed amount, of pH and of ionic strength to achieve a quite broad point of view about the flocculation and stabilization behavior. They concluded that the magnitude of the negative zeta potentials of the silica particles decrease with increasing salt concentration as well as with increasing polyelectrolyte concentration because of screening and neutralization of the surface charges, respectively. The isoelectric point, instead, is reached at the same amount of adsorbed chains regardless of the charge density of the adsorbed polyelectrolyte and of the ionic strength. However, at high ionic strength the zeta potential plateau decreases due to the screening of the charges of the adsorbed macroion segments. In the adsorption plateau, the suspensions are stabilized electrostatically at low ionic strength, electrosterically at medium ionic strength and sterically at high ionic strength.

Maroni et al. [18] studied the role of surface chemistry on the adsorbed mass, but mostly they investigated the influence of the polymer charge using strong and weak polyelectrolytes of negative and positive charge, as well as an uncharged polymer. According to their results, the electrostatic forces were dominant for polyelectrolytes with a high density of ionized charges and the attractive double layer interactions guarantee great adsorption on oppositely charged surfaces and the formation of flat films. On the contrary, high salt concentration induced the formation of more swollen layers. Subsequently, they observed that the decrease of the chain−chain electrostatic double-layer repulsion, caused by the reduction of the polymer charge density or by its degree of dissociation, enabled a larger density of polymer material on the surface at saturation. Furthermore, lower polymer charge density or addition of salt decreased the energy barrier for adsorption on surfaces bearing the same sign of electric potential as the polyelectrolyte.

Popa et al. [19] investigated the adsorption of PDADMAC on planar silica substrates as a function of pH and ionic strength. The study was conducted with reflectometry in an impinging-jet cell and complemented by atomic force microscopy (AFM) and ellipsometry investigations. They observed that the adsorption plateau is independent of the polymer concentration at higher concentrations. Furthermore, with increasing ionic strength, the adsorption rate coefficient increases, and this effect can be explained by the corresponding decrease of the hydrodynamic radius of the polymer. The adsorbed amount also increases with increasing pH, and this increase is probably related to the increase of the surface charge of the silica substrate.

Chapter 2

Materials and methods

2.1 PDADMAC

PDADMAC (Polydiallydimethylammonium chloride), in Figure 2.1.1, with two different molecular weights, < 100 kg/mol and 400-500 kg/mol, was used in the QCM-D experiments. Only the behavior of PDADMAC with low molecular weight was studied by DLS. The substances were purchased from Sigma–Aldrich. PDADMAC with low molecular weight was provided with a concentration of 35% weight solution in H_2O and with a density of 1.09 g/mL at 25 °C; instead, PDADMAC with high molecular weight was provided with a concentration of 20% weight solution in H_2O and with a density of 1.04 g/mL at 25 °C. A stock solution of 1 g/L of both polymers was prepared by overnight dissolution in Milli-Q water under gentle stirring. For the experiments, they were diluted in the same water, while the pH of the solution was adjusted with HCl and NaOH and the ionic strength with NaCl.

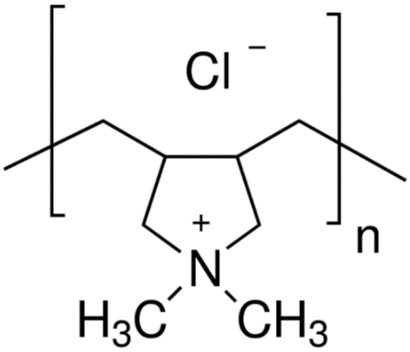

Figure 2.1.1 PDADMAC (Polydiallydimethylammonium chloride), extracted from [17].

2.2 Silica surfaces and particles

QSensor QSX 303 with SiO_2 as top coating material were used for the QCM-D experiments. LUDOX TM-50 colloidal silica with a molecular weight of 60.08 g/mol was purchased from Sigma–Aldrich for the DLS experiments and it was provided with a concentration of 50% weight suspension in H_2O and with a density of 1.4 g/mL at 25 °C. A stock solution of 10 g/L was prepared by overnight dissolution in Milli-Q water under gentle stirring.

2.3 Quartz Crystal Microbalance

A QCM sensor consists of a thin quartz disc sandwiched between a pair of electrodes and its operation principle is rather simple. Thanks to an alternated voltage, the sensor can be excited to oscillate at its resonance frequency, which depends on the total oscillating mass of the sensor, but also on the surface adhering layers. Therefore, the QCM performs as a very sensitive balance because the frequency decreases when a thin and rigid film is attached to the sensor and it is proportional to the mass of the film [20].

In our adsorption and desorption experiments, QCM-D Q-Sense pro by Biolin Scientific was utilized, which allow real-time study of changes in the mass and viscoelastic properties of the polyelectrolyte layer, enabling close monitoring of the surface exchange process. However, it cannot supply the actual adsorbed mass (dry mass) of the adsorbent, but it records the mass of the adsorbent together with the solvent that couples with the formed layer.

There are different theories for calculation of the sensed mass, which take into account the change in frequency registered by the sensor, but in this work the Sauerbrey relation is used:

$$\boldsymbol{m^* = -\frac{C\Delta f}{n}}$$

where C is a constant, which for our crystals is equal to 0.177 mg/m^2, Δf is the change in frequency during the adsorption/desorption process, and n is the overtone number [9]. Although this equation is rather simple, it requires that the adsorbed mass should be sufficiently rigid not to deform during the oscillation. Hence, the linear relationship between frequency and mass might not hold for viscoelastic or dissipative films because the layer does not completely couple to the crystal oscillation. In this thesis, the physical properties of adsorbed mass layer were not studied, but QCM-D would permit to investigate it with the monitoring of the crystal oscillation decay, from which the energy dissipation, D, is evaluated:

$$\boldsymbol{D = \frac{E'}{2\pi E}}$$

where E' is the energy dissipated during one oscillation and E is the total energy stored in the quartz oscillator. Materials that form viscous layers on a crystal provide higher D factors due to their deformation during oscillation. Accordingly, the $\Delta D/\Delta f$ ratio gives details on how much energy is dissipated for a unit change in frequency: a low value corresponds to more compact layers, while a high ratio relates to non-rigid structure [4].

2.3.1 Experiment procedure with QCM-D

Silica surfaces, before each use, were treated with the following procedures:

1. UV/ozone treatment for 10 minutes;
2. Prepare of a solution of 2 % sodium dodecyl sulfate in Milli-Q water;
3. Immerse the sensor surfaces in this SDS solution for 30 minutes at room temperature;
4. Rinse with Milli-Q water;

5. Dry with nitrogen gas;

6. Piranha solution for 10 minutes

7. Rinse with Milli-Q water.

In the beginning of each adsorption experiment, a solution of the desired electrolyte concentration and pH was pumped through the cell until a baseline signal was recorded, which indicates that the equilibrium was reached. Adsorption was then started by injecting a PDADMAC solution of the desired polyelectrolyte concentration with the same IS and pH of the background solution. When the adsorption of PDADMAC reached saturation, as displayed by a plateau in the signal, the solution was again substituted with a PDADMAC-free solution of the same composition. No significant change in mass was observed when the cell was flushed with this solution, evidencing that the adsorption process was irreversible and that the layers formed on silica were always stable in the same solution used for the adsorption. The final step was performed to evaluate any eventual desorption from the substrate. A solution with different IS and/or pH was pumped through the cell until equilibrium was reached and then, the background solution was introduced in the cell one final time, in order to compare the desorption signal with that of initial background [4].

2.4 Dynamic light scattering experiments

Dynamic light scattering is ideal for the size measurement of colloids and nanoparticles. The operation principle of DLS is that fine particles and molecules that are in constant random thermal motion, called Brownian motion, diffusing at a speed related to their size, smaller particles diffusing faster than larger particles. The speed of Brownian motion is also influenced by the temperature, hence precision temperature control is essential for accurate size measurement. In order to measure the diffusion speed, the particles are illuminated by a laser and the scattering intensity, which will fluctuate with time, is detected using a sensitive photodiode detector. Subsequently, a digital autocorrelator analyses the intensity changes and it will develop a correlation function that can be analyzed to provide the size and the size distribution. In this thesis, the Zetasizer Nano (Malvern) series was adopted [21]. As DLS explores the temporal fluctuations of scattered light, and therefore provides direct access to the diffusion coefficient or the hydrodynamic radius of the particles, this technique is applicable over a wide size range down to nanosized particles, and when conducted in a time-resolved fashion, it further provides a direct probe of suspension stability [8].

Two types of experiments were conducted with DLS: electrophoresis and size measurements. Electrophoresis is defined as the motion of dispersed particles relative to a fluid under the influence of a spatially uniform electric field. This electric field is responsible for two different types of force: one on the surface charge and another one on the ions in the diffuse layer, situated at some distance from the particles surface. The origin of this latter force is explained by the double layer theory, according to which, all surface charges in fluids are screened by a diffuse layer of ions, which has the same absolute charge but opposite sign with respect to that of the surface charge. Consequently, this force has direction opposite to that acting on the surface charge and, although it is applied to the ions in the diffuse layer, part of it is transferred all the way to the particle surface through viscous stress. This part of the force is also called electrophoretic retardation force (Figure 2.4.1).

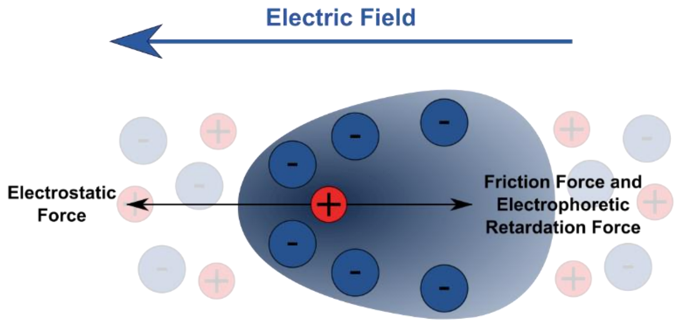

Figure 2.4.1 Illustration of the electrophoresis and of the different forces applied to the particle surrounded in an electric field, extracted from [22].

Therefore, the force acting on the ionic double layer reduces the particles movement due to the electrostatic force but, supposing a moderate strength of this electric field and a low Reynolds number, the drift velocity of a dispersed particle v is merely proportional to the applied field, so the electrophoretic mobility μ_e is defined as:

$$\mu_e = \frac{v}{E}$$

In 1903, Smoluchowski developed the most well-known and widely used theory of electrophoresis:

$$\mu_e = \frac{\varepsilon_r \varepsilon_0 \zeta}{\eta}$$

where ε_r is the dielectric constant of the dispersion medium, ε_0 is the permittivity of free space, η is dynamic viscosity of the dispersion medium, and ζ is zeta potential. However, the Smoluchowski theory is valid only for sufficiently thin double layer, when particle radius α is much greater than the Debye length:

$$\alpha\kappa \gg 1$$

Increasing thickness of the double layer carries out to removing the point of retardation force further from the particle surface. Under this condition, Hückel formulated the following relation for electrophoretic mobility:

$$\mu_e = \frac{2\varepsilon_r\varepsilon_0\zeta}{3\eta}$$

useful for some nanoparticles and non-polar fluids, where Debye length is much larger than in the usual cases [22].

2.4.1 Experiments procedure with the DLS instrument

Initial electrophoretic mobility measurements, conducted with Malvern Zetasizer Nano, can be divided in two great categories: sweep of pH and sweep of PDADMAC. In the first case, a stock suspension of particles in the absence of PDADMAC or in the presence of an excess of PDADMAC was prepared. Aliquots of this suspension were placed in a beaker in which the pH was adjusted before measurement thanks to addition of small quantities of HCl and NaOH stock solutions (50 mM). In the second type of tests, a stock suspension at desired pH was prepared in beaker of 500 mL. Aliquots of this suspension were placed in smaller beakers and a desired amount of varying amount of PDADMAC stock solution was added to these suspensions. This was repeated for each PDADMAC dose, defined as the mass of PDADMAC divided by the mass of particles in the suspension.

Conversely, size experiments were conducted to investigate the aggregation behavior of silica particles in the presence of PDADMAC and upon changes of solution chemistry. For this purpose, changes of pH or IS were forced in the suspension to trigger re-suspension of previously deposited chains, aggregation or disaggregation, and size measurements were conducted before and after changes in chemical conditions, always accompanied by measurement of the electrophoretic mobility under each condition. The size experiments were organised in five plus one steps:

1. size measurement at the initial chemical condition (A) in the absence of PDADMAC;
2. addition of the PDADMAC dose to reach IEP to promote aggregation (known from previous electrophoresis experiments);
3. size and electrophoretic measurements with this "IEP dose" at the initial condition (A);
4. change of solution chemistry to reach the new condition (B);
5. electrophoretic mobility and size measurements under the new condition (B);

5+1. Also, electrophoretic mobility and size measurements were conducted directly under condition B and upon addition of the "IEP-dose" related to condition A. In this case, condition B was not reached upon a change in chemical condition.

These steps were rigorously followed respecting a simple protocol about the solution preparation. Firstly, a suspension of 500 mL with the desired pH and IS under condition A was prepared. Subsequently, aliquots of this stock suspension were placed in smaller beakers and the chemical condition was here changed. As such, the change of pH or IS was induced already in the presence of PDADMAC at the "IEP-dose" of condition A. On the contrary, in the final 5+1 step, PDADMAC was added at the appropriate dose (the "IEP-dose related to condition A) when the suspension was already under condition B.

Chapter 3

Results and discussions

3.1 Adsorption and desorption experiments with QCM-D

3.1.1 Adsorbed mass of PDADMAC on flat silica at saturation

All experiments were conducted with 10 mg/L of PDADMAC, a strong polyelectrolyte. This cationic polyelectrolyte was of two different molecular weights: < 100 kg/mol and 400-500 kg/mol, referred to as low and high molecular weight, respectively. First of all, the adsorbed mass layer of two PDADMAC in different circumstances was summarized in Figure 3.1.1.1 and in Figure 3.1.1.2. In this section of the thesis, the adsorbed mass of the two polymers, following the adsorption step, was graphed in columns with two colours: light grey and dark grey for low and high molecular weight, respectively. During an adsorption experiment, upon introduction of the polymeric solution, the adsorbed mass increases in time. After a transient period, the adsorption process saturates and leads to an adsorption plateau. Here, we present the value of this saturation plateau.

The adsorbed mass at saturation increased strongly with increasing ionic strength due to the progressive screening of the electrostatic repulsion between the adsorbing polyelectrolyte chains. Furthermore, the adsorbed amount increased with increasing pH and this effect is probably induced by the corresponding increase of the silica surface charge [19]. The highest value, in fact, was reached with a 250 mM solution of NaCl at pH 10. On the contrary, 3 mM solution of NaCl at pH 2.5 is the condition related to the lowest amount of adsorbed PDADMAC. Finally, the data in the two figures point out that, under the same conditions, the adsorption was slightly larger with PDADMAC of higher molecular weight. It was shown by other authors that at large ionic strength, $C_{NaCl} > 0.1$ M, the adsorbed amounts increase with molecular weight due to longer loops and tails [23].

Xie et al. [5] studied the adsorbed amount of PDADMAC with molecular weight 400-500 kDa different conditions of IS, obtaining a value of about 0.3 mg/m^2 in a 10 mM solution and roughly 0.35 mg/m^2 in a 400 mM solution. These results are of the same order of magnitude of results presented here and obtained at pH 10 in a 3 mM solution and a 250 mM solution. Furthermore, they showed the same increasing trend upon increase of IS. By in situ optical reflectometry, Popa et al. [19] studied the effect of the ionic strength on the adsorption at a PDADMAC at a concentration of 10 mg/L. They used PDADMAC with molecular weights of 400-500 kg/mol and KCl solution to change the IS. Their experiments showed an adsorbed dry mass of about 0.05 mg/m^2 at pH 4 and IS of 1 mM. Increasing the IS to 100 mM, the adsorbed PDADMAC increased to 0.3 mg/m^2, approximately. In solutions of the same IS but at pH 9, the adsorbed amount was about 0.2 mg/m^2 and about 0.35 mg/m^2, respectively. In our experiments with a 3 mM NaCl solution and pH 2.5 the adsorbed wet mass of PDADMAC with high molecular weight was about 0.15 mg/m^2, while in a 250 mM NaCl solution and pH 2.5 it increased to 1.3 mg/m^2. The results achieved with QCM-D are larger because this instrument registers the mass of the adsorbent together with the solvent that couples with the adlayer while reflectometry probes only the dry mass. However, the results are consistent and suggest the same trends. Bauer et al. [23] investigated the influence of PDADMAC with different molecular weight on the stability and flocculation of dispersed particles. In the adsorption process at pH 5.8 and with a 3 mM solution the adsorbed amount of PDADMAC with a molecular weight of 117 kg/mol was about 0.3 mg/m^2. This result is almost equal to the quantity of adsorbed PDADMAC observed in our experiments in a 3 mM solution at unadjusted pH.

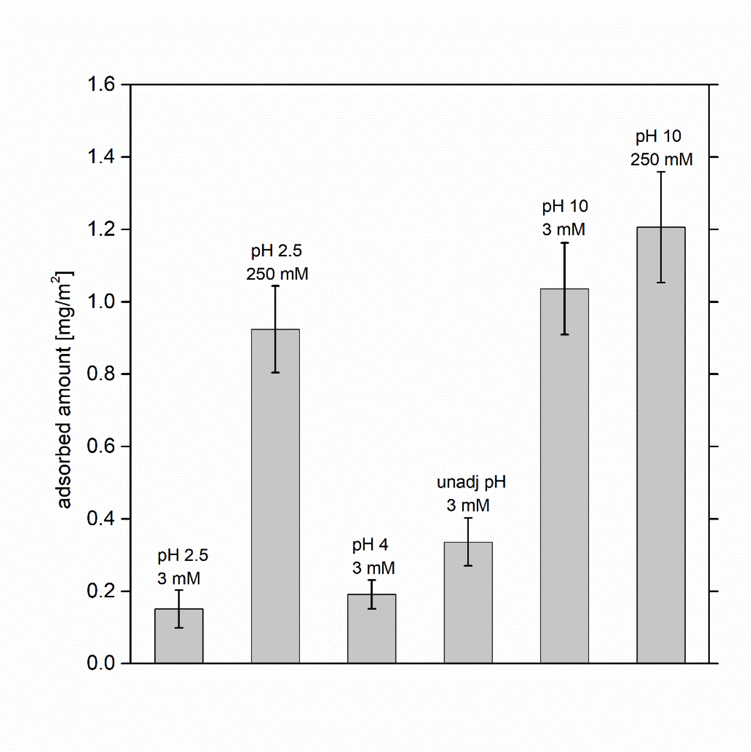

Figure 3.1.1.1 Adsorbed amount of PDADMAC with low molecular weight in different conditions of pH and IS.

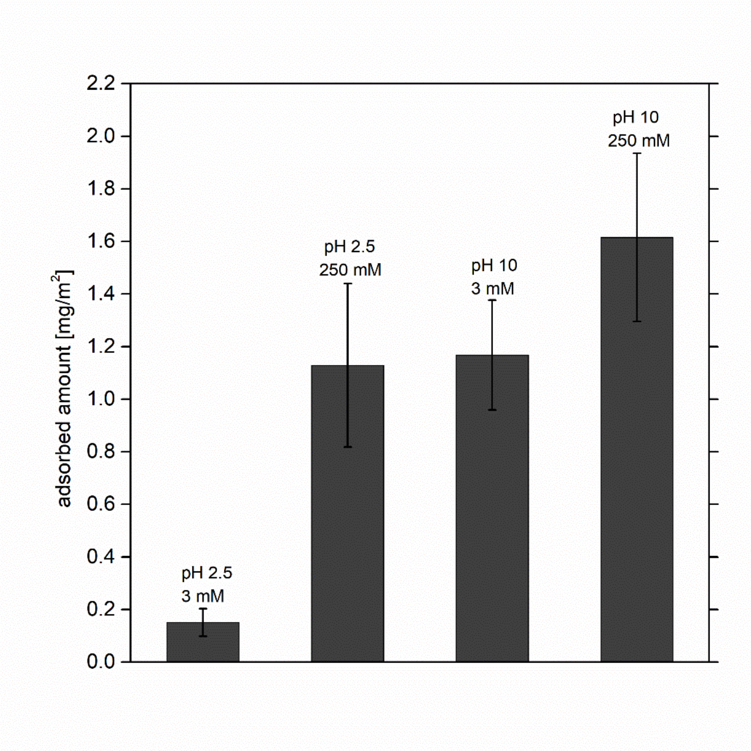

Figure 3.1.1.2 Adsorbed amount of PDADMAC with high molecular weight in different conditions of pH and IS.

3.1.2 Desorption of previously adsorbed mass of PDADMAC on flat silica surfaces

Results of desorption experiments, whose protocol was reported in the paragraph 2.3.1, was obtained by introducing in the system a polymer-free solution of different IS and/or pH after pre-deposition of a saturated PDAMAC layer and until steady-state was reached in the QCM-D signal. Finally, the initial background solution (polymer-free solution with the same chemistry of that employed during pre-deposition) was again introduced in the system in order to compare the final signal upon polymer desorption with that following initial adsorption. Considering the results shown in the previous chapter, one can deduce that an increase in pH and/or IS leads to an increase of adsorbed mass at saturation, so to induce desorption of the adsorbed PDADMAC, it is necessary to decrease one of the two parameters or both parameters. Thus, desorption experiments were conducted to investigate the influence of changes in pH and IS, but also to evaluate how the pathway or the initial conditions of the adsorption process can influence the final adsorbed amount.

Figure 3.1.2.1 shows the desorption results obtained with a change in solution pH employing PDADMAC with low molecular weight. Initially, PDADMAC was adsorbed in 3 mM NaCl at pH 10 until saturation. The value of mass was then normalized to 1, in order to more easily compare the effects of changes in pH on adsorbed amounts. After the adsorption process, using a solution with unadjusted pH (roughly 6) to induce desorption, the normalized amount of adsorbed substance became roughly 0.55 (55% of the amount pre-adsorbed), thus it was reduced of about 45%, while the fraction of mass adsorbed was about 0.38 passing directly from pH 10 to 4. Finally, the figure shows that changing the solution pH from 10 to 2.5, desorption reduced the adsorbed PDADMAC of about 77%. Accordingly, these results suggest that lowering the pH of the desorbing solution renders the desorption process more effective due to the resulting decrease in the magnitude of the diffuse-layer potential of the surface in the case where this potential was of opposite sign to that of the polyelectrolytes. This phenomenon leads to increased repulsion between deposited chains due to a smaller concentration of counterions at the solid/water interface.

Dejeu et al. [24] studied the influence of post-treatment rinsing after the formation of self-assembled polyelectrolyte films made with the weak base poly(allylamine hydrochloride) (PAH). A single layer of PAH was adsorbed on silica at pH 9, and then a polymer-free solution at different pH values was circulated in the cell. The polymer desorbed partially in more acidic solutions: the lower the pH, the more it desorbed, fully in accordance with what was achieved in our results. Their results even showed that at pH 3 the adsorbed mass was completely desorbed. Likely, this behavior was caused by the lower charge of the PAH than the PDADMAC, which implies lower electrostatic interaction with the underlying negatively charged surface.

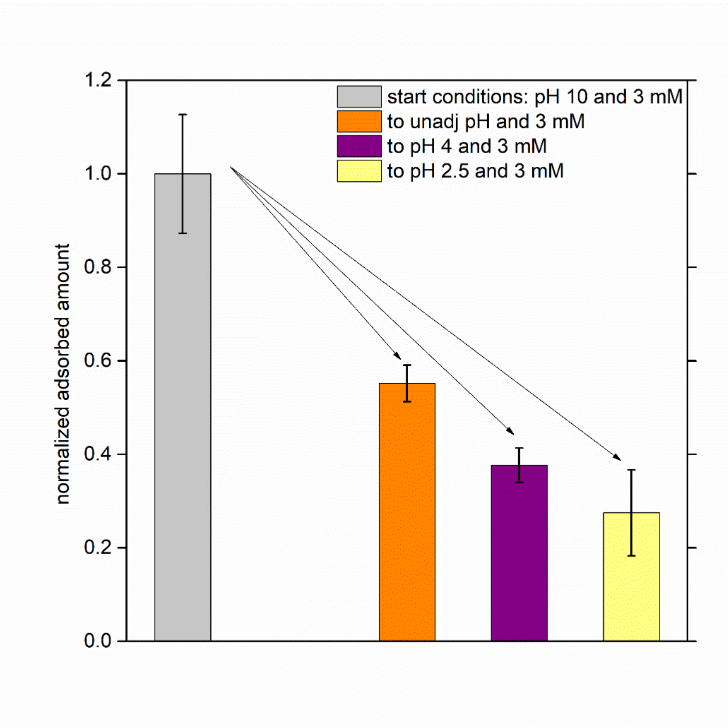

Figure 3.1.2.1 Effects of change in pH on the desorption process of PDADMAC with low molecular weight.

Figure 3.1.2.2 summarizes the effect of change in IS on the desorption process of PDADMAC with molecular weight < 100 kg/mol. In the first case, after the adsorption process was carried out in 250 mM NaCl solution at pH 10, the IS was reduced to 3 mM at fixed pH and the adsorbed amount, equal to about 1.3 mg/m^2, decreased of a small amount to 1.23 mg/m^2, approximately. In other experiments, the adsorption process was conducted in a 250 mM NaCl solution at pH 2.5 and, in this situation, the same change of IS produced a more important desorption of PDADMAC with the adsorbed mass passing from 0.92 mg/m^2 to 0.49 mg/m^2.

Larger ionic strengths enable closer deposition of the charged molecules due to reduced chain−chain electrostatic repulsion, and due also to a decrease in the electrostatic double-layer repulsion between like-charged polyelectrolytes and surfaces. On the contrary, when the salt amount is decreased, the repulsion of the electric double layers becomes increasingly long ranged, which leads to desorption of part of the adsorbed polymer from the surface. Furthermore, this figure suggests how the surface-polyelectrolyte interactions leading to adsorption are at high pH. The same IS change, in fact, halves the adsorbed amount at pH 2.5, while the reduction at pH 10 is negligible. At pH 10 the surface was highly charged and the presence of counterions allowed close packing of PDADMAC chains even after a momentous reduction of ionic strength. At acidic pH, the interchain repulsion became dominant and drove desorption when ionic strength was no longer sufficient to screen this repulsion.

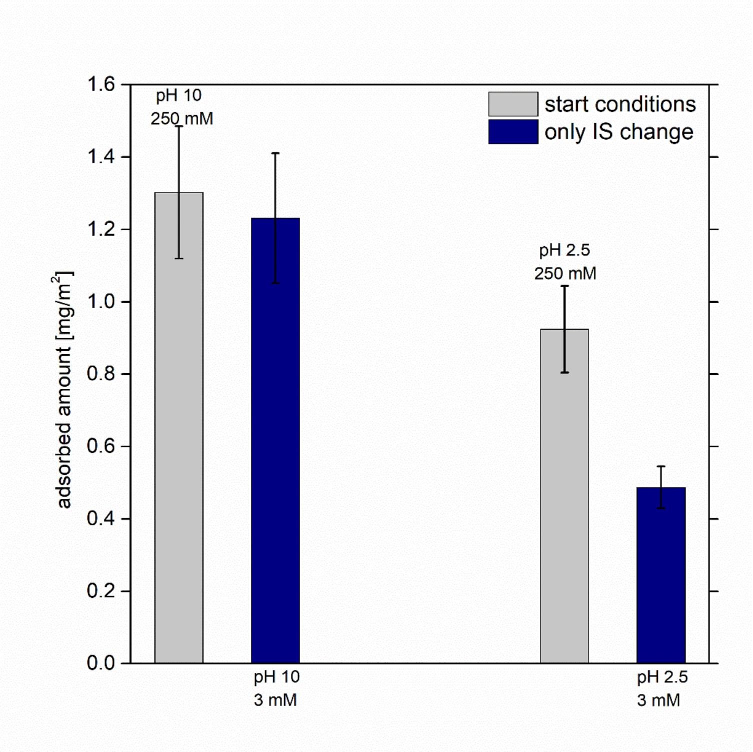

Figure 3.1.2.2 Effects of change in IS on the desorption process of PDADMAC with low molecular weight.

Figure 3.1.2.3 summarizes the effect of pathway following pH reduction to induce desorption of previously adsorbed PDADMAC. It is interesting to understand if the desorption process is more effective reaching the final pH directly or if it is more effective by reaching the final pH by intermediate steps. In Figure 3.1.2.3, the grey bar represents the adsorbed mass of PDADMAC of lower molecular weight obtained in 3 mM NaCl solution at pH 10, normalized to 1. The effects of the pathway was investigated by reducing, in all experiments, the solution pH from 10 to 2.5, but in different ways, e.g., through steps, continuously (seamlessly by adding small amount of acid for the entire duration of the desorption step), or in one single step, and also by going first through an increase of ionic strength.

Reducing directly the solution pH into the system to the final condition, the adsorbed mass decreases about 73%; by inducing this change slowly (last bar on the right) or by steps we observed a 77% reduction, approximately. The quantity of adsorbed mass is roughly 0.24 in the case the pH went from 10 to 2.5 but at a high salt concentration of 250 mM, and then returning to a 3 mM solution (yellow bar). These results would suggest that the pathway is not particularly important in the desorption process and that the initial and final conditions are the parameters that govern the desorption process.

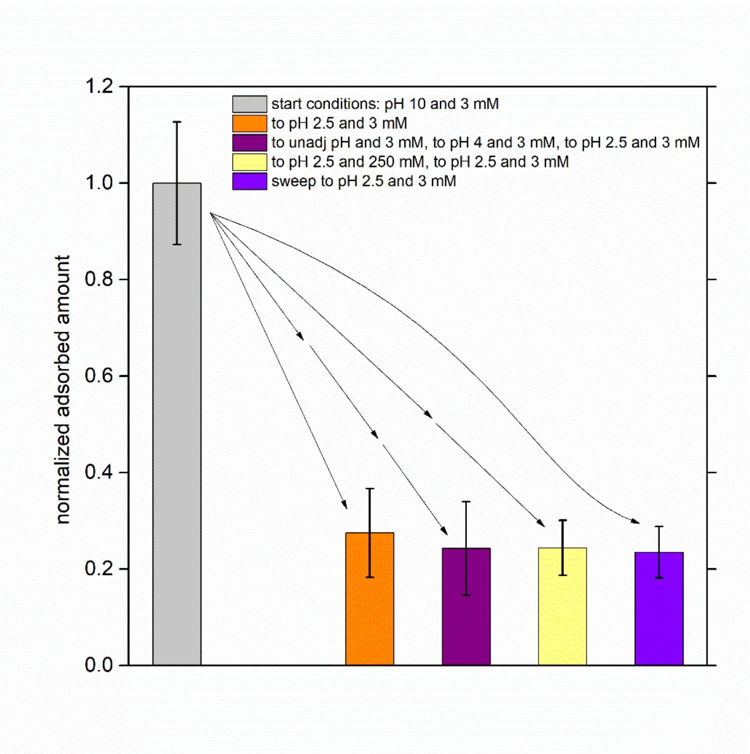

Figure 3.1.2.3 Effects of pathway on the desorption process of PDADMAC with low molecular weight.

Based on the results discussed above about the influence of pH and IS on the desorption process, it is helpful to compare the effects of these two parameters. To do this, it is also necessary to realize some experiments including changes of both pH and IS but in the opposite direction, i.e., decreases of pH and increases of IS, and vice versa. In Figure 3.1.2.4, the remained adsorbed mass after the desorption process was graphed with green bars in the case desorption was obtained by changes of pH only, blue bars for changes of IS only, whereas wine-red bars were used when both chemical parameters were changed in the desorption process. In the first set of tests already shown above, the mass of adsorbed polymer in a 250 mM NaCl solution at pH 10, equal to about 1.3 mg/m^2, was subjected to two different desorption processes:

- only a IS reduction from 250 mM to 3 mM, resulting in a reduction of adsorbed mass down to about 1.2 mg/m^2;
- only a pH reduction from 10 to 2.5, which led to a final adsorbed PDADMAC of roughly 0.85 mg/m^2, approximately.

In the second set of tests, the mass of adsorbed PDADMAC in a 3 mM NaCl solution at pH 10 was halved after a molarity increase from 3 mM to 250 mM and a simultaneous pH reduction from 10 to 2.5. In this situation, considering the results graphed in Figure 3.1.2.2, the IS increase should thwart the desorption process and this partly happens, since the adsorbed amount is higher than what is shown in the last bar, displaying that the PDAMDAC layer mass was reduced of roughly 75% after the pH was reduced and the IS was kept at 3 mM. All these results may suggest that a pH decrease is more effective to induce desorption with respect to IS changes. Obviously, the reduction of both parameters leads a greater desorption.

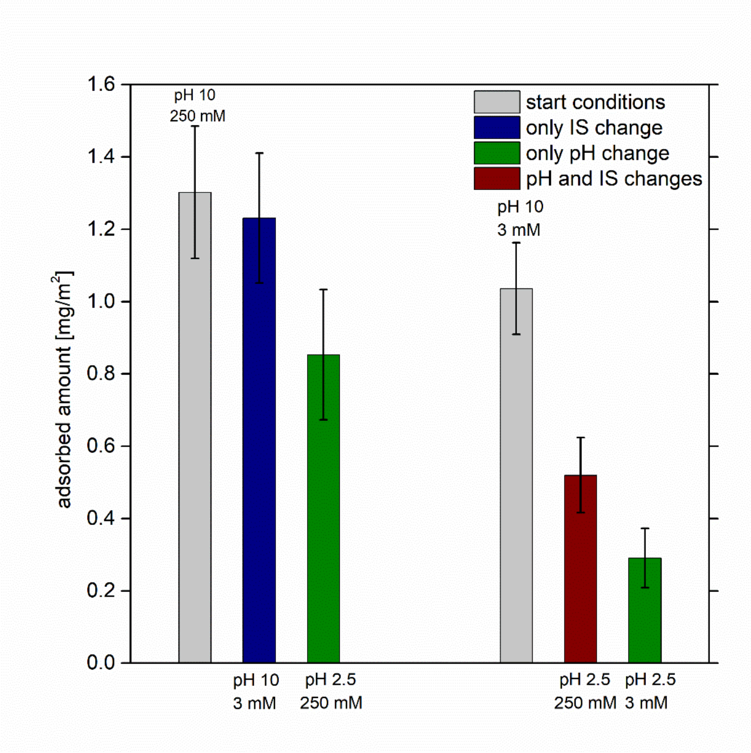

Figure 3.1.2.4 Dispute between pH and IS on the desorption process of PDADMAC with low molecular weight.

The same type of experiments was conducted with PDADMAC with molecular weight < 400-500 kg/mol, in order to investigate any differences in behavior due to a different molecular weight. As seen above, the adsorption was greater with this polymer. In principle, the desorption process is expected to be less efficient in this case. Results are shown in Figure 3.1.2.5. In the first set of experiments, the mass of adsorbed polymer in a 250 mM NaCl solution at pH 10 was equal to about 1.61 mg/m^2 and it decreased of about 28% following a pH change from 10 to 2.5 (the reduction was 35% for lower molecular weight PDADMAC). In the second set of experiments, only the salt concentration was changed from 250 mM to 3 mM and the pH was kept at a value of 2.5. The presence of a lower number of ions in solution led to a reduction of the quantity of adsorbed PDADMAC of 42%, approximately (the same experiments using PDADMAC of lower molecular weight showed a reduction of roughly

50%). In the last set of experiments, the mass of adsorbed PDADMAC in a 3 mM solution at pH 10 was subjected to two different desorption processes:

- pH and IS changes, from 10 to 2.5 (inducing desorption) and from 3 mM to 250 mM (thwarting desorption), respectively, resulting in a decrease of adsorbed mass of roughly 35% (50% for low MW PDADMAC);
- only a pH reduction from the initial conditions to 2.5, by which led to an adsorbed PDADMAC reduction of 80% down to 0.24 mg/m^2 (75% for low MW PDADMAC)

These results suggest the same trends of desorption, regardless of molecular weight. The absolute amounts of adsorbed PDADMAC with high molecular weight were always larger than those obtained with PDADMAC with molecular weight < 100 kg/mol, even after desorption. That being said, no clear influence of molecular weight was observed on desorption magnitude. Generally, it seemed that larger molecular weight makes desorption slightly less favorable, but this different was not significant for the ranges of MW investigated in this study.

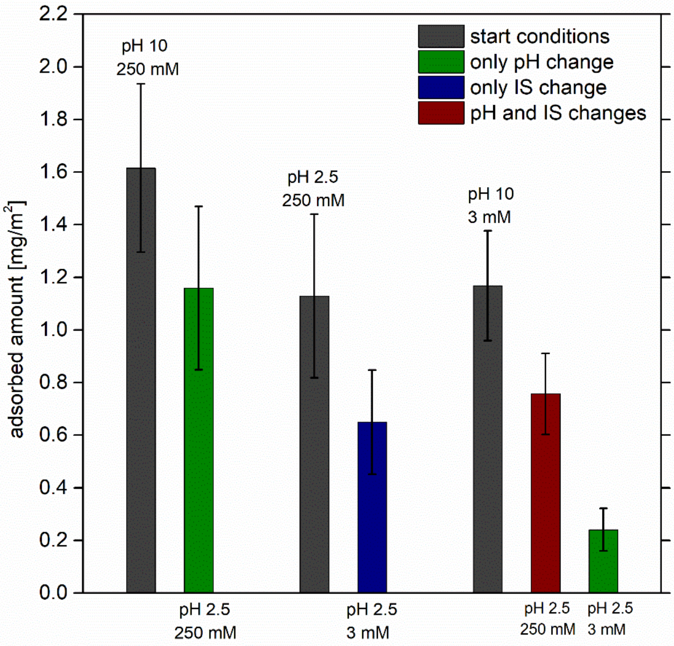

Figure 3.1.2.5 Dispute between pH and IS on the desorption process of PDADMAC with high molecular weight.

One of the main question that this study should answer is whether the adsorbed amount of polymer under a certain condition is the same or different in the case where this condition is reached upon a change in solution chemistry and it follows desorption of some pre-deposited polyelectrolyte or in the case this condition is the one under which adsorption has occurred. Or, analogously, if starting from systems at different conditions promotes or inhibits desorption of an adlayer. Understanding this allows us better engineer adsorption processes and to predict the behavior of systems subject to sudden changes of solution chemistry, e.g., following floods, infiltration, or drainage in porous media.

Figure 3.1.2.6 summarizes all the desorption results presented earlier together with other experiments, all plotted in a way to attempt answering the question of the previous paragraph. In the figure, the four conditions of the x axis (pH 2.5 3 mM, unadjusted pH 3 mM, pH 4 3 mM, or pH 10 3 mM) are the chemical conditions of the solutions used to induce desorption (as such, of the final condition). The different bars overlying each of these four conditions represent the adsorbed amounts upon desorption when the polymer was pre-adsorbed in different solution chemistries, indicated next to each of the bars. The white bar represents adsorption and desorption under the same condition (thus, no desorption occurring) and are the benchmark of comparison of the other bars, which instead are plotted according to same colour code as above. If these bars are higher than the white bar, this means that desorption was not sufficient to lead to the same adsorbed amount that would be obtained if the system had always only seen the final condition.

All these data imply the important role of the initial conditions under which the adsorption process occurred. Desorption did not have the ability to completely remove the entire amount of extra PDADMAC adsorbed on the substrate compared to the adsorption that would be observed at the final condition. For this reason, the blue and green bars are always higher that white bars. This is always the case and it is especially true when desorption was achieved by changes of IS only, compared to changes of pH.

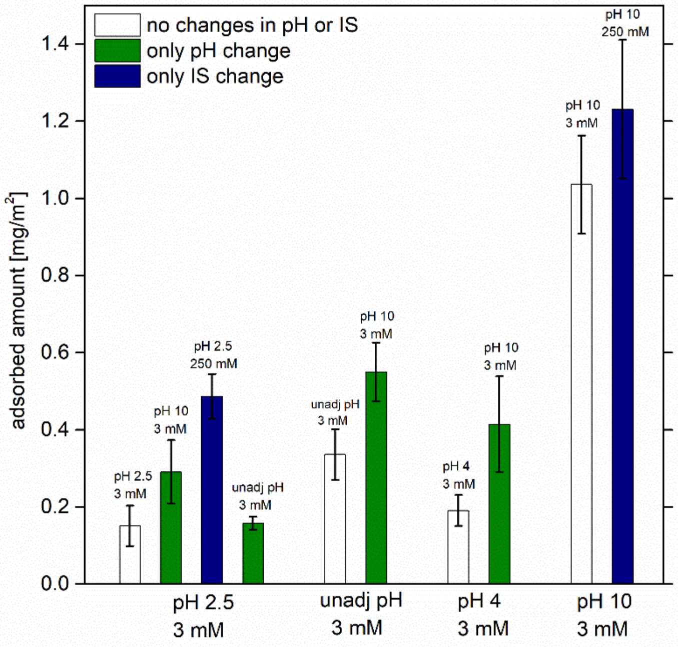

Figure 3.1.2.6 Effects of initial adsorption on the final adsorbed amount of PDADMAC with low molecular weight.

Figure 3.1.2.7 displays the results of similar experiments just described, but in the case of PDADMAC with molecular weight < 400-500 kg/mol. These results have the same trend of previous ones, that is, desorption did not restore the condition observed while adsorbing PDADMAC directly at the final condition (the blue and green bars are always higher that white bars). This behavior has an important influence in the engineering applications of PDADMAC as a flocculant, in which the adsorbed mass on the surface enhances the aggregation power.

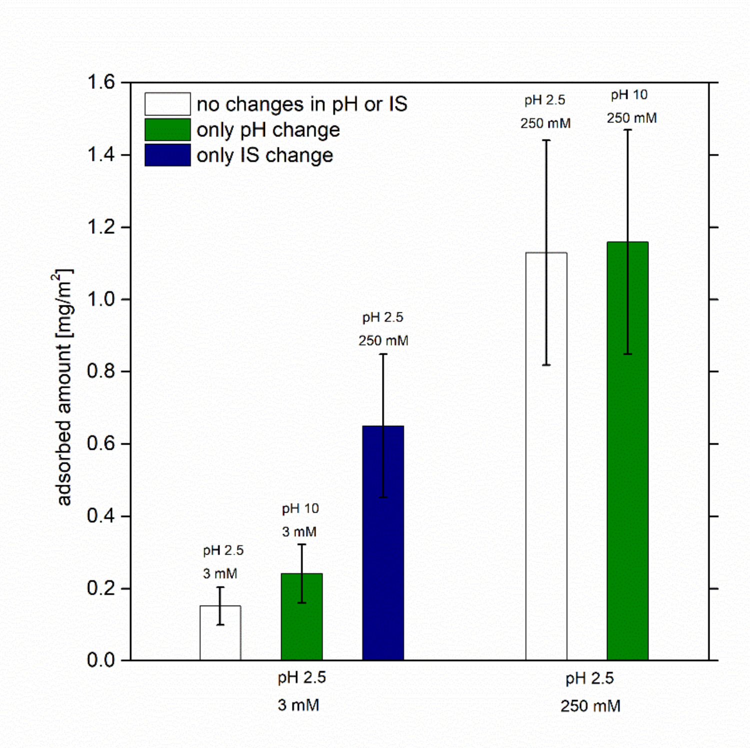

Figure 3.1.2.7 Effects of initial adsorption on the final adsorbed amount of PDADMAC with high molecular weight.

Summarizing, the adsorption and desorption experiments with QCM-D were conducted with 10 mg/L of PDADMAC of two different molecular weights. The adsorption rate increased strongly with increasing ionic strength due to the progressive screening of the electrostatic repulsion between the adsorbing polyelectrolyte chains. Moreover, the adsorbed amount further increased with increasing pH due to the increase of the surface charge of the silica substrate. Under the same conditions, the adsorption was slightly larger with PDADMAC with higher molecular weight.

Partial desorption of previously adsorbed PDADMAC chains was obtained thanks to a solution with desired IS and pH injected in the system following pre-deposition at a different condition of IS and/or pH. The reduction of adsorbed mass due to a pH change was caused by the resulting decrease in the magnitude of the diffuse-layer potential given by the charges of the underlying surface. This phenomenon leads to increased repulsion between deposited chains due to a smaller concentration of counterions at the solid/water interface. However, the pathway followed to decrease the pH was not so important in the desorption process. When the salt level was decreased, the repulsion among deposited chains became increasingly long ranged, which also led to desorption of part of the adsorbed polymer from the surface. Our experimental results suggested that a pH decrease is more effective to promote desorption process with respect to IS changes. Obviously, the reduction of both parameters can lead to more significant desorption than that obtained by changing only one parameter. Finally, from a conditions of high adsorbed amount and through desorption induced by changes in solution chemistry, one cannot reach the value of adlayer mass that would be obtained by adsorbing a polymer directly under the final condition; the mass observed under the final condition upon desorption is usually significantly larger, suggesting that desorption occurs only if an energy barrier is overcome, likely due to the large density of interaction sites between the polyelectrolyte chains and the surface. In fact, this conclusion seems to be truer for polyelectrolytes of larger molecular weight, although our results in this case are not conclusive. The two polymers had molecular weight distanced by a factor of roughly five; probably, results would be more telling if polymer had molar masses of different orders of magnitude.

Our results have important implications for environmental or engineering processes. For examples, they suggest that, for example:

- floods or infiltration of low IS water in a system is not as effective as expected in desorbing polyelectrolytes previously adsorbed on oppositely charged surfaces;
- saline intrusion may induce adsorption of polyelectrolytes that would be later difficult to desorb when normal conditions are restored;

- a process that aims at maximizing the mass of adsorbed polyelectrolyte on a surface (for functionalization or to promote flocculation) could be performed under conditions in which adsorption is more favorable compared to the actual process conditions, as only a partial amount of polyelectrolyte would desorb upon the change in chemistry.

3.2 Electrophoretic mobility experiments with DLS

The zeta potential is the potential generated as a result of the formation of an electrical double layer and it is responsible for the electrokinetic phenomena and the stability of the colloids. Since particles of similar charge will repel each other, those with high charges will resist flocculation and aggregation for longer periods making such samples more stable. This means that the stability can be modified by altering the pH, the IS, the type of ions and by using additives such as surfactants and polyelectrolytes. The zeta potential of particles and molecules is determined by measuring their velocity while they are moving due to electrophoresis. Particles and molecules that have a zeta potential will migrate towards an electrode if a field is applied. The speed they move is proportional to the field strength and their zeta potential. If we know the field strength, we simply measure the speed of movement using for example DLS, and then apply established theories to calculate the zeta potential [21]. However, in order to avoid the application of these theories, our experimental results were graphed in terms of electrophoretic mobility. All these experiments were conducted with suspensions of 300 mg/l of LUDOX TM-50 colloidal.

3.2.1 Influence of pH on electrophoretic mobility of bare silica particles and of particles with saturated layer of PDADMAC

The effect of pH was studied by varying this parameter between 2 and 9 in two different conditions of ionic strengths, 3 mM NaCl and 250 mM NaCl (Figure 3.2.1.1). For bare particles, the electrophoretic mobility was negative at all pH values because the charge of bare silica is negative and the pK of silanol groups is low. The mobility value increased from pH 2 to basic pH, reaching a maximum value of about -2.5 μmcm/Vs at pH 9 in the first case and of roughly -1.2 μmcm/Vs at pH 7 in the second case. Increasing the pH allows more quantitative deprotonation of the silanol groups of the bar silica. Also, IS leads to a reduction of the silica electrophoretic mobility, due to the compression of the electric double layer. Bauer et al. [17] investigated the zeta potentials of silica for various salt concentrations at pH 5.8. They obtained these values of mobility for the bare silica: -3.92 μmcm/Vs, -1.37 μmcm/Vs and -0.78 μmcm/Vs in a 1 mM, 10 mM and 100 mM NaCl solution, respectively. It can be seen how these results are consistent with those obtained in this study with the DLS, also considering the effect of IS.

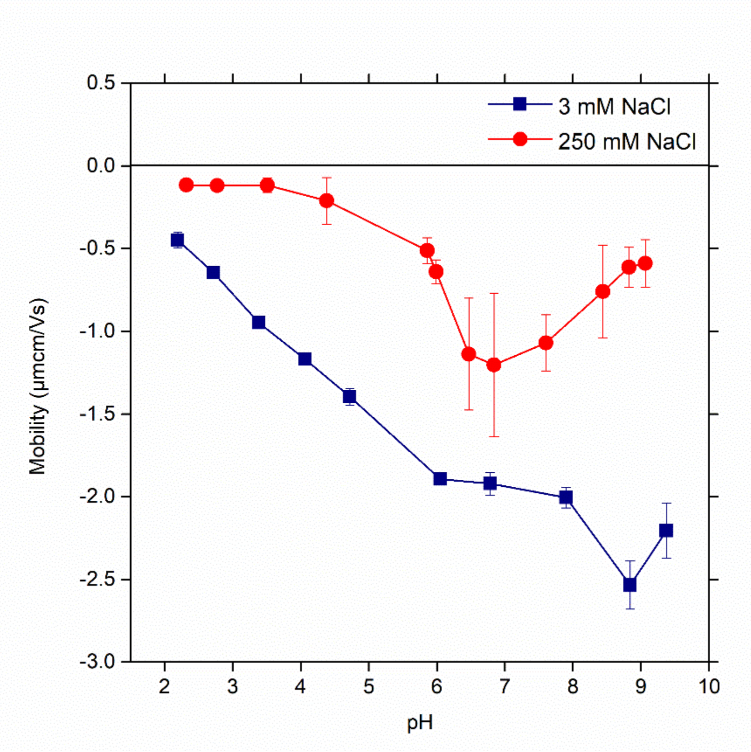

Figure 3.2.1.1 Sweep of pH in a 3 mM (black) and in a 250 mM (red) NaCl solution with 300 mg/l of LUDOX TM-50.

Then, the effects of pH on the silica electrophoretic mobility (Figure 3.2.1.2) was investigated with an excess of PDADMAC in solution in the same two different values of IS. The choice of 30 mg/l as concentration of PDADMAC, which correspond a PDADMAC dose of 100 mg/g, was done after several tests, thanks to which it was shown that this concentration is the lowest allowing particle surface saturation across the entire pH range and for both ionic strengths investigated.

The presence of PDADMAC in solution yielded a positive value of the mobility because the polyelectrolyte adsorbed on the silica particles leading to overcharging, as discussed above. Therefore, positive maximum values of roughly 3 μmcm/Vs in 3 mM and of about 1.5 in 250 mM were reached at pH 7. Also in these tests, the increase of IS reduced the magnitude of particle mobility, validating the effects showed in the figure 3.2.1.1. Michna et al. [1] measured the electrophoretic mobility of mica particles modified with a layer of PDADMAC with a molecular weight of 101 kg/mol for various ionic strengths using laser doppler velocimetry (LDV). The mobility decreased with ionic strength from 4.2 μmcm/Vs (for 1 mM) to 2.7 μmcm/Vs (for 150 mM) at pH 5.8. These results follow the trend shown in the figures below, their values are similar to our results but of higher magnitude due to the different particles used in the experiments and to lower ionic strengths.

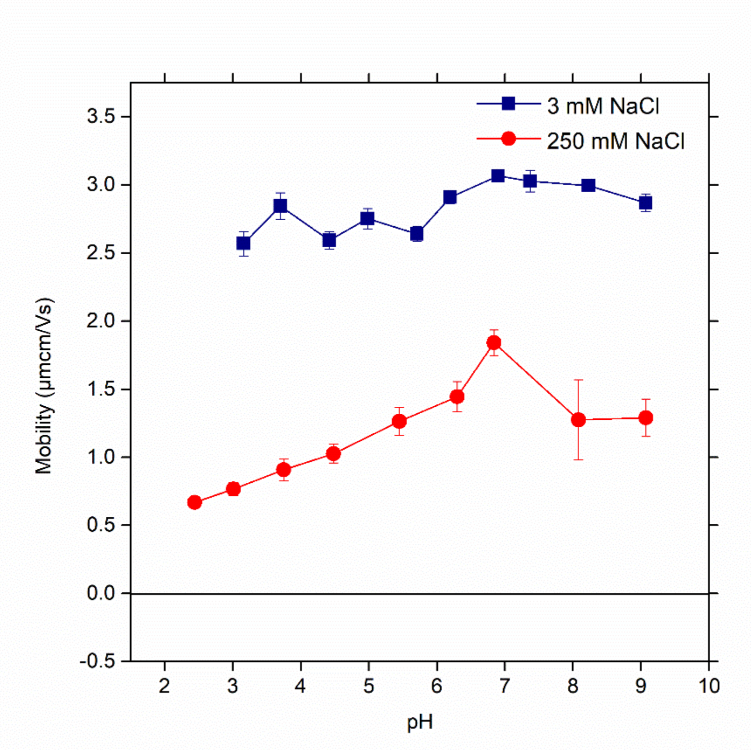

Figure 3.2.1.2 Sweep of pH in a 3 mM (black) and in a 250 mM (red) NaCl solution with 300 mg/l of LUDOX TM-50 and 30 mg/l of PDADMAC with molecular weight < 100 kg/mol.

As seen in the two figures just above, pH has an important influence on the silica mobility when it changes from acid to basic conditions. pH values larger than 9 renders the silica unstable and it is possible that this effect is enhanced in solutions of higher ionic strength.

3.2.2 Influence of PDADMAC dose on the electrophoretic mobility of silica particles

The amount of the adsorbed polyelectrolyte regulates the overall particle charge and the latter parameter can be correlated to many suspension properties, such as colloidal stability and particle adhesion characteristics [7]. At low polyelectrolyte dose, the electrophoretic mobility is negative, which reflects the negative charge of the silica particles. Due to the increase of the polyelectrolyte dose, the electrophoretic mobility increases because the adsorption of the positively charged PDADMAC neutralizes the silica charge, thus reaching the isoelectric point (IEP). Increasing the dose further, the mobility becomes positive since the adsorption process remains favorable although the particles are now positively charged. Further addition of PDADMAC beyond the point leads to saturation, at which the adsorbed amount is steady, and the surplus polyelectrolyte remains dissolved in solution. On the contrary, below saturation, the adsorption of the polyelectrolyte is quantitative [18]. This behavior is typical of polyelectrolytes adsorbing to oppositely charged substrates [2].

The experiments as a function of PDADMAC dose where conducted at two different pH values (4 and 8) in a 3 mM NaCl solution and at three different pH values (4, unadjusted, and 8) in a 250 mM NaCl solution. In the first case, in a 3 mM NaCl solution at pH 4, the IEP was reached with about 10 mg/g of PDADMAC dose, while the adsorption process reached saturation (roughly 3 μmcm/Vs) when the dose of PDADMAC was 50 mg/g, approximately. One observes the typical charge reversal of the negatively charged silica particles by the positively charged PDADMAC polyelectrolyte. In Figure 3.2.1.1, it is possible to note that the mobility of bare silica at this pH and IS conditions is about -1 μmcm/Vs. For this reason, the IEP value was reached with a relatively low dose of PDADMAC.

In the literature, similar experiments are reported at pH 4, but with different IS and PDADMAC of different molar mass. Hierrezuelo et al [2] investigated the sulfate-terminated latex particles in the presence of PDADMAC with molecular weight of 450 kg/mol at pH 4.0 in aqueous KCl electrolyte solutions by dynamic light scattering and electrophoresis. The disadvantage is that the technique averages the signal of all particles in solution, and thus leads to a relatively poor resolution. In a 1 mM solution, they obtained a typical curve of charge with the IEP at about 3 mg/g of polymer and the saturation mobility of 3 μmcm/Vs at roughly 10 mg/g of PDADMAC. Their other experiments were performed in a 10 mM KCl solution at pH 4 and with three different concentrations of particles: 0.8 mg/l, 8 mg/l and 80 mg/l, respectively. The three different curves pass by the IEP with the same polymer dose (about 5 mg/g) and reach an equal saturation mobility (roughly 4 µmcm/Vs). The same results of Hierrezuelo et al. were achieved by Vaccaro et al. [25] using negatively charged colloidal latex particles in a 10 mM KCl solution. This discrepancy between these results and ours is undoubtedly due to the different molecular weight of the polymer, but also to the different particles utilized. However, the range of mobility values is rather similar.

In Figure 3.2.2.1 the electrophoretic mobility of silica particles is also shown as a function of the polyelectrolyte dose in 3 mM NaCl solution at pH 8. Based on the results shown in Figure 3.2.1.1, where a more basic pH yields to a higher mobility of bare silica, it is normal to expect a larger dose of PDADMAC to neutralize the silica negative charge. In fact, at low PDADMAC dose, the mobility is more negative and the IEP was shifted to the right and it was reached with about 9 mg/l of polymer, which corresponds to a dose of roughly 30 mg/g. The value of mobility at saturation, instead, does not depend on the pH, in fact, it is always about 3 µmcm/Vs and it is reached at pH 8 with a PDADMAC dose of around 60 mg/g. Finally, the results shown below highlight that at higher pH the charge reversal curve is steeper because there is an increase in the electrostatic interaction between PDADMAC and silica and so the adsorption process is accelerated.

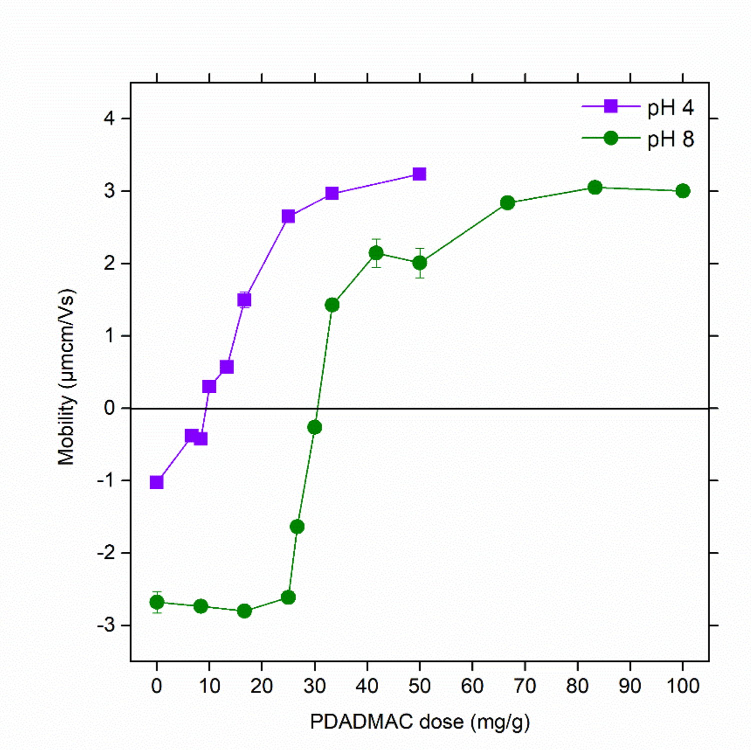

Figure 3.2.2.1 Sweep of PDADMAC with low molecular weight in a 3 mM NaCl solution at pH 4 and at pH 8 with 300 mg/l of LUDOX TM-50.

Then, the same type of experiments was conducted in a 250 mM NaCl solution, so we have a wider point of view of the influence of PDADMAC dose on the electrophoretic mobility. Based on the results reported in the paragraph 3.2.1, it is expected that the increase of IS yields to a reduction of the particles mobility due to the screening of the surface charges. Furthermore, the results reported in the literature have shown how the variation of the ionic strength usually moves to higher values the dose of polyelectrolyte at which the IEP is reached.

In Figure 3.2.2.2, the electrophoretic mobility of silica particles is shown as a function of the PDADMAC dose in 250 mM NaCl solution at pH 4, 8, and at an unadjusted value of roughly 6. At pH 4, the mobility values are close to zero with low polyelectrolyte dose, and the IEP is reached with a PDADMAC dose of about 10 mg/g, as already seen in Figure 3.2.2.1 for experiments performed at lower IS. However, the shape of this curve is flatter than that in a 3 mM NaCl solution and the mobility at saturation is about 2 μmcm/Vs, confirming the mobility reduction due to larger IS. Hierrezuelo et al [2] reported results comparable with those of the figure below. However, they worked with sulfate-terminated latex particles and with 1 M and 100 mM KCl solutions. In the first case, they obtained a curve with the same saturation value as ours, but with a different shape, in fact, the plateau is reached with lower PDADMAC dose. In a 100 mM KCl solution, instead, the mobility at saturation is about 4 μmcm/Vs and the curve have the same shape of that in the figure below. In general, the IEP was reached at lower doses in the experiments by those authors.

At unadjusted pH and at low PDADMAC dose, the mobility is steady around -1 μmcm/Vs, consistent with the results achieved for bare particles as a function of pH in a 250 mM NaCl solution and shown above. The point at which the mobility is close to zero is achieved with a PDADMAC dose lower than 40 mg/g and the plateau of the curve, on the other hand, is around 2 μmcm/Vs, as also seen at pH 4. Bauer et al. [17] performed similar tests but using PDADMAC with molecular weight of 428 kg/mol and a 100 mM NaCl solution. They obtained the IEP with a PDADMAC dose of 2 mg/g and the value of mobility at saturation was, instead, equal to 3.92 in a 100 mM NaCl solution. Comparing these results with those of figure 3.2.2.2, it is observed values of mobility at saturation are comparable, but a higher molecular weight allows to reach the IEP at lower dose, confirming what was seen previously.

Lastly, tests as a function of PDADMAC dose with low molecular weight were also performed at pH 8. The results shown in the Figure below agree with previous trends and considerations. There is, in fact, a further shift of the IEP to higher dose of PDADMAC and the mobility values change in a range between – 2 μmcm/Vs and 2 μmcm/Vs. As shown before in 3 mM NaCl, the values of mobility at high dose of PDADMAC are largely independent of pH. Compared to those experiments performed at lower IS, the dose of PDADMAC needed to reach the IEP is generally larger, consistent with literature reports.

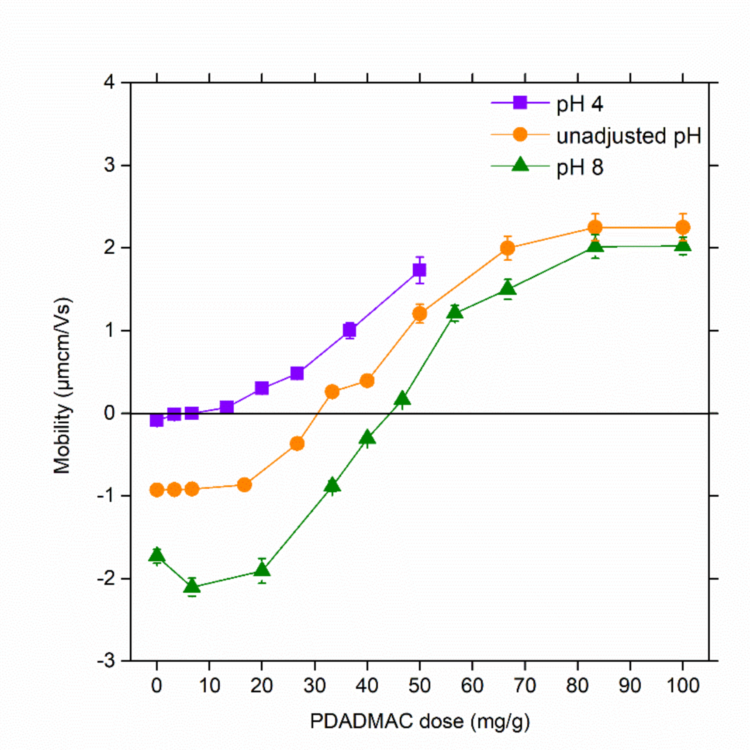

Figure 3.2.2.2 Sweep of PDADMAC with low molecular weight in a 250 mM NaCl solution at pH 4, at unadjusted pH and at pH 8 with 300 mg/l of LUDOX TM-50.

Finally, the results already shown in Figures 3.2.2.1 and 3.2.2.2 were graphed in a different way to highlight the effect of IS, on the electrophoretic mobility of the silica particles as a function of PDADMAC dose. The charge reversal curves, obtained at pH 4, were plotted in Figure 3.2.2.3, while in Figure 3.2.2.4 the curves refer to sweep of PDADMAC conducted at pH 8. These graphs better illustrate two additional characteristics for such polyelectrolyte–particle systems. The first is the decrease of the magnitude of the electrophoretic mobility with increasing salt level, including the value of the mobility at surface saturation. This phenomenon gives a flatter shape at the curve and it is connected to the reduction of the surface potentials with increasing salt level. The second feature, instead, is that the dose necessary to reach the IEP is equal or larger if ionic strength is higher. This may be due to a different configuration of the PDADMAC chains, which adsorb on silica surface in a less flat configuration. Also, all the results suggest that, below the saturation point, PDADMAC adsorbs completely and the amount added corresponds to the adsorbed amount. One can see that the electrophoretic mobility is independent of the particle concentration when plotted versus the polymer dose, above all at acid pH. If the polyelectrolyte would partition between the dissolved and adsorbed state, one would necessarily observe a different dependence on the polyelectrolyte dose at different particle concentrations. This behavior was equally reported in other system [2] [8] [23].

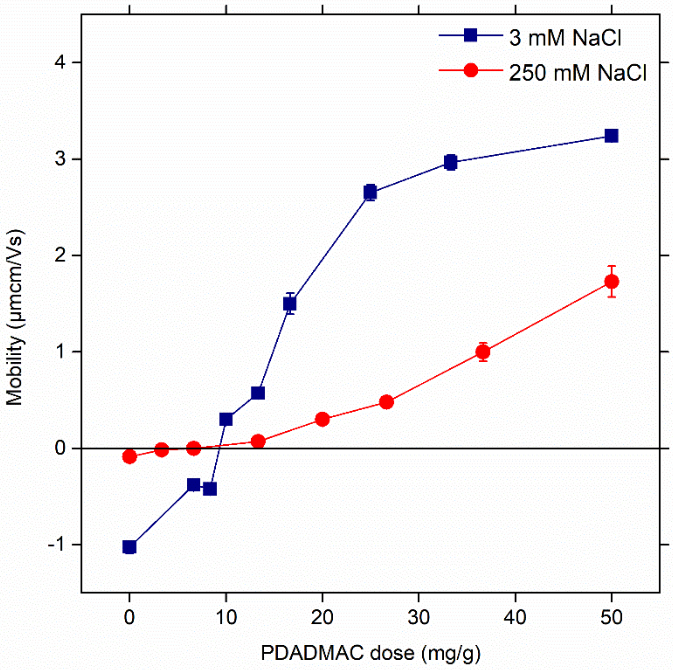

Figure 3.2.2.3 Sweep of PDADMAC with low molecular weight in a 3 mM NaCl and in a 250 mM NaCl solution at pH 4 with 300 mg/l of LUDOX TM-50.

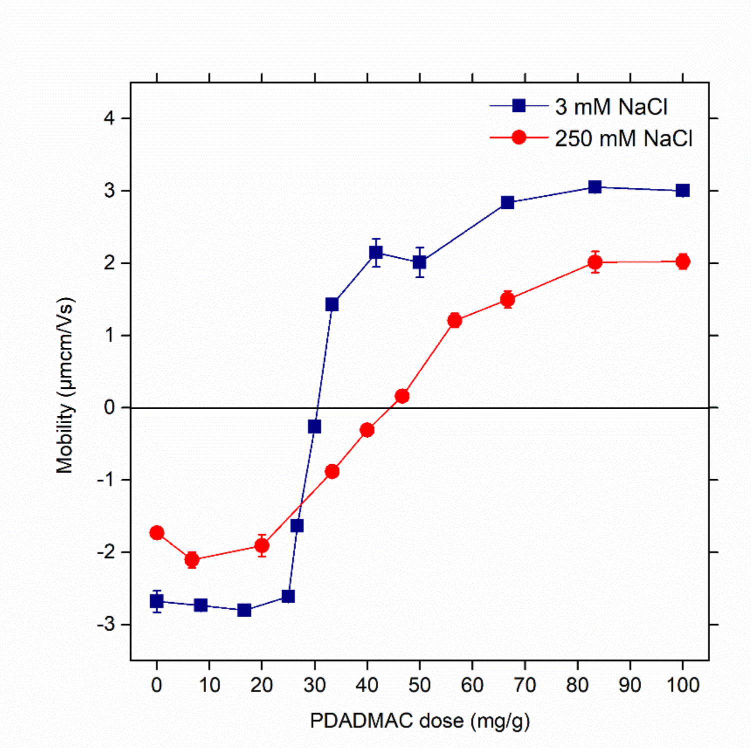

Figure 3.2.2.4 Sweep of PDADMAC with low molecular weight in a 3 mM NaCl and in a 250 mM NaCl solution at pH 8 with 300 mg/l of LUDOX TM-50.

To sum up, the adsorbed polyelectrolyte determines the overall particle charge and the graphs of this paragraph show the typical charge reversal of the negatively charged silica particles due to the adsorption of the cationic polymer. The point in with the overall potential is zero, called isoeletric point, was reached with different PDADMAC doses. However, it is possible to conclude that (i) increasing IS the IEP is shifted to higher dose. Similar trends were equally observed in other systems containing negatively charged particles systems and cationic polyelectrolytes [8] [17] [23]. Furthermore, one observes that (ii) the values of mobility at saturation was influenced by IS but not by pH. Finally, (iii) the shape of the charge reversal curves become steeper at more basic pH values due to the increase in the electrostatic interaction between PDADMAC and silica as silica is more charged at higher pH, and flatter in a solution with high IS due to the screening of the surface potentials.

3.3 Size experiments with DLS

The classical theory of Derjaguin, Landau, Verwey, and Overbeek (DLVO) about the aggregation processes of colloidal particles has established the importance of the attractive van der Waals forces and repulsive electrostatic double layer forces. However, it was recognized recently that these forces are probably the same to drive the aggregation of charged particles in the presence of oppositely charged polyelectrolytes, such as PDADMAC. This mechanism is important since adsorbed polyelectrolytes lead to charge neutralization and charge reversal, as already seen in the results of the previous paragraph.

The aggregation rate increases when the adsorption of oppositely charged polyelectrolytes reduces the overall particle charge and consequently the electrostatic repulsion is weakened. At the isoeletric point (IEP), where the particle charge is neutralized by the adsorbed polyelectrolyte, the aggregation process reaches the maximum efficiency. Beyond this point, the adsorbed density of the polyelectrolyte increases further, leading to a reversal of the particle charge. In this regime, called overcharging, the suspension is again stabilized and dominated by electrostatic repulsion [26]. The results of our size experiments, reported in this chapter, were conducted with the DLS and at a concentration of silica particles of 100 mg/l (LUDOX TM-50 silica)

As already reported in chapter 2.4.1, these experiments were divided in five plus one steps:

1. size measurement at the initial chemical condition (A) in the absence of PDADMAC;
2. addition of the PDADMAC dose to reach IEP to promote aggregation (known from previous electrophoresis experiments);
3. size and electrophoretic measurement with this “IEP dose” at the initial condition (A);

4. change of solution chemistry to reach the new condition (B);

5. electrophoretic mobility and size measurements under the new condition (B);

5+1. Also, electrophoretic mobility and size measurements were conducted directly under condition B and upon addition of the “IEP-dose” related to condition A. In this case, condition B was not reached upon a change in chemical condition.

All the results obtained during these experiments and presented in this chapter were graphed as bars with three different colours: green, wine-red and blue. Green column indicates the size value determined at initial conditions A (step 3 of the protocol), wine-red column represents particles size after the change solution chemistry from condition A to B (step 5 of the protocol), and the blue column reports the size of the particles measured directly under condition B (step +1 of the protocol). The background value, instead, is the size of bare silica particles under condition A, i.e., the size measurement conducted at initial condition A before addition of PDADMAC, and it must be considered as a benchmark to appraise whether aggregation has occurred upon addition of PDADMAC.

Particle size is related to aggregation, which is a direct consequence of the surface potential and thus of the amount of PDADMAC adsorbed on the particle. As such, there is a strong correlation between PDADMAC adsorption and particle size. The purpose of these experiments is to assess whether some of the mechanisms discussed above lead to an interesting aggregation/disaggregation behavior. Specifically, our experiments were designed to observe any eventual disaggregation upon changes of solution chemistry in systems comprising particles and PDADMAC at doses lower than the saturation dose: as a matter of fact, step 2 of our protocol promotes aggregation as it is conducted to reach the system IEP. Under such condition A, and based on the assumption of irreversibility of polymer adsorption, all PDADMAC chains are adsorbed onto the particle surface and none is left in solution. This condition is the most favorable one to induce coagulation, as electrostatic repulsion is cancelled. This condition also allows investigation of how subsequent pH or IS change to reach condition B can influence the zeta potential and the possible disaggregation.

All the size values obtained from these experiments are referred to the size average value (Z-avg), which was graphed as the base-10 logarithm in the figures that follow. Figure 3.3.1 shows the results of the first experiment, in which condition A is 3 mM NaCl pH 8 and condition B is 3 mM pH 4. The background particle size value in the absence of PDADMAC at pH 8 is 47.8 nm, which correspond to 1.68 on a base-10 logarithm scale; from previous experiments, it was determined that 2.8 mg/L (28 mg/g of PDADMAC dose) is the concentration with which the potential is about 0 μmcm/Vs at pH 8. The size measurement, conducted with this concentration, gave value of about 2157 nm. Therefore, as expected, there was an increase in size due charge neutralization. Changing the pH solution from 8 to 4, the mobility becomes positive increasing to 2.68 μmcm/Vs and this result was predictable given the results presented in a previous chapter showing that the isoeletric point (IEP) was reached with a higher dose of polymer at pH 8 compared to pH 4. This implies "overcharging" and the main consequence of this phenomenon is some disaggregation of the silica particles coated with an excess of PDADMAC and leading to a reduction of the size value from about 2157 nm to roughly 166 nm. If a fresh solution is prepared directly at pH 4 with addition of 28 mg/g of PDADMAC dose in solution with final conditions, aggregation does not occur significantly because the particles are positively charged and electrostatic repulsion are important and the size of these aggregates is small: 112 nm although the mobility is 2.11 μmcm/Vs, lower than that related to the middle bar in Figure 3.3.1. The small discrepancy between the size measurements implies that the initial condition influences the adsorbed amount of PDADMAC on silica particles. This result suggests that, similar to what discussed above regarding the desorption of previously adsorbed chains on a surface, here there is a barrier to disaggregation that needs to be overcome, such that already aggregated particles will have difficulties disaggregating even for aqueous conditions under which aggregation would not be promoted in the first place.

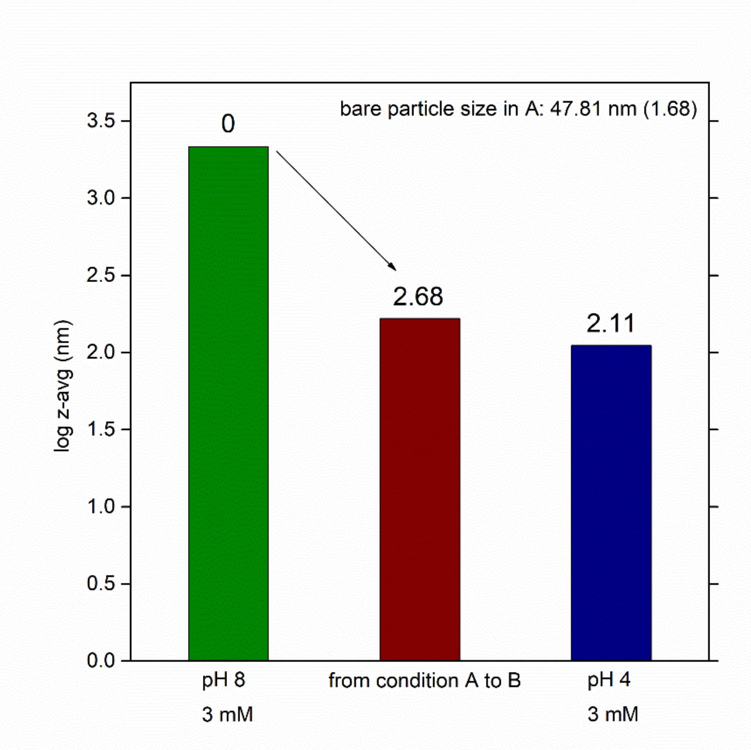

Figure 3.3.1 Size and mobility measurements in 3 mM NaCl solution at pH 8, from pH 8 to 4 and at pH 4 with 100 mg/l of LUDOX TM-50.

A similar experiment was conducted reversing the pH and the results were graphed in Figure 3.3.2. The size of bare particles was 40 nm, consistent with the test discussed just above. However, the silica electrophoretic mobility at pH 4 is lower (see Figure 3.2.1.1) the PDADMAC dose used to reach IEP was roughly 5 mg/g which led to an increase of the particles size value up to about 1528 nm. Increasing the pH to 8, the mobility decreased because silica charges ionize and the current amount of adsorbed PDADMAC is no longer sufficient to reach the IEP. The negative charge is expected to promote disaggregation. As a matter of fact, the particle size was reduced to 471 nm. However, also in this case disaggregation was not sufficient to return to the smaller particle size observed if the same PDADMAC dose were added directly to the suspension under condition B (pH 4).

Summing up, the main finding of the results represented in the two figures just above is that the disaggregation of already aggregated particles does occur upon changes of solution chemistry but needs to overcome an energy barrier. This is summarized as the particle sizes displayed in the wine-red middle columns are larger than those related to the last blue column, although in the second situation the lower absolute value of electrophoretic mobility should in principle promote more aggregation.

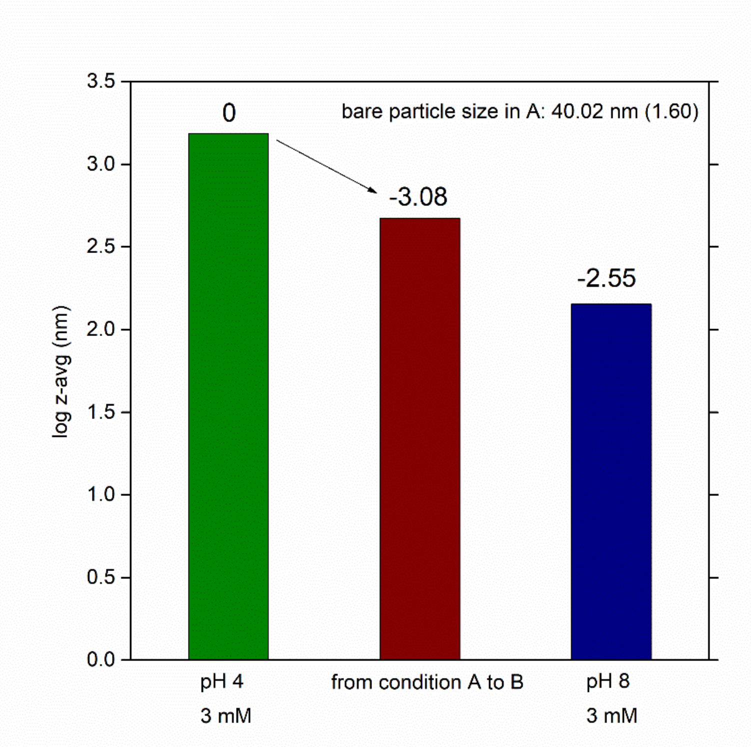

Figure 3.3.2 Size and mobility measurements in 3 mM NaCl solution at pH 4, from pH 4 to 8 and at pH 8 with 100 mg/l of LUDOX TM-50.

Subsequently, similar experiments were performed in a solution of 250 mM NaCl and the results are presented in Figure 3.3.3 and 3.3.4. Contrary to what discussed above, in these cases the increase in the magnitude of electrophoretic mobility did not result in any observable particle disaggregation (i.e., the middle column is at least as high as the left green column). Certainly, this behavior is due to the high number of ions dispersed in solution whose effect on particle stability is dominant compared to other phenomena.

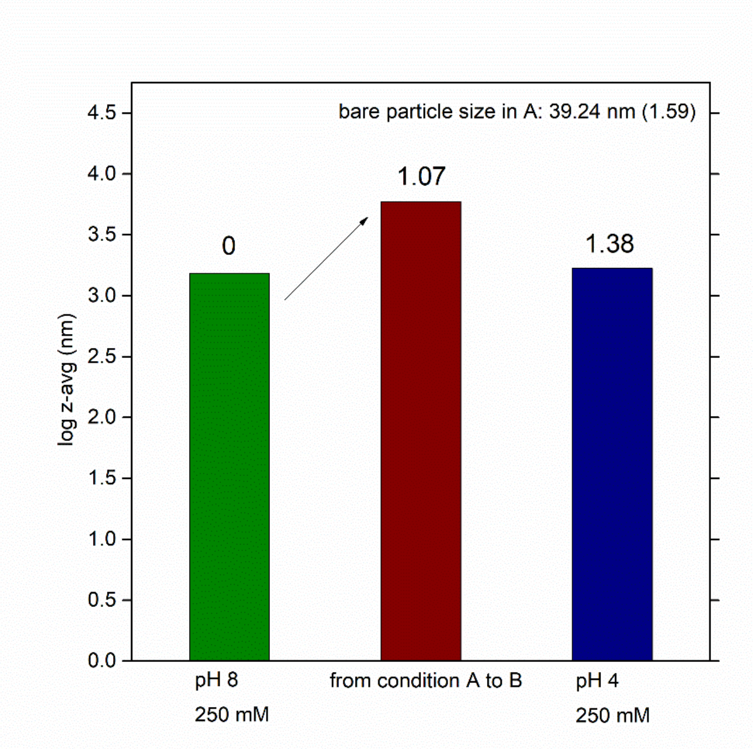

Figure 3.3.3 Size and mobility measurements in 250 mM NaCl solution at pH 8, from pH 8 to 4 and at pH 4 with 100 mg/l of LUDOX TM-50.

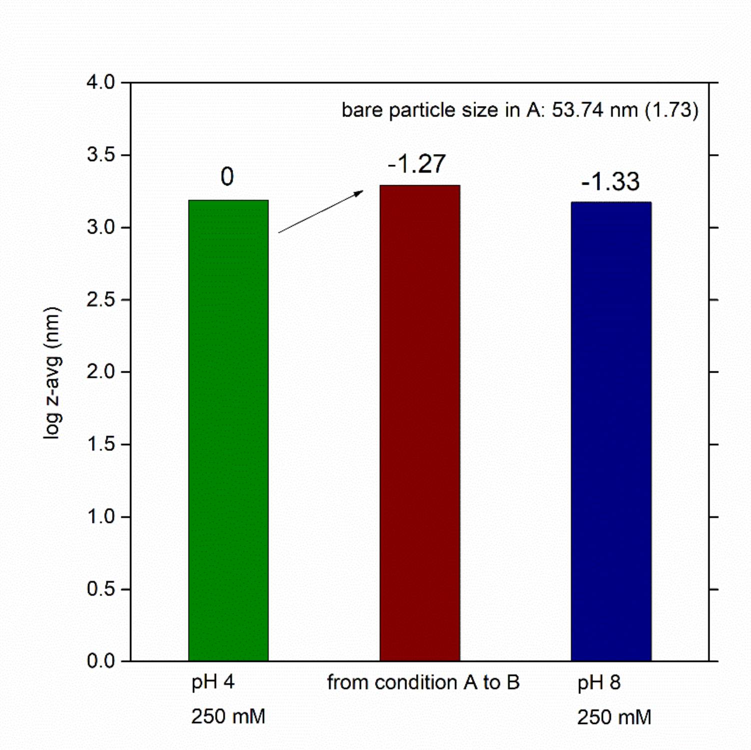

Figure 3.3.4 Size and mobility measurements in 250 mM NaCl solution at pH 4, from pH 4 to 8 and at pH 8 with 100 mg/l of LUDOX TM-50.

Just to confirm the observations just discussed, about the dominance of high IS on particle stability behavior, the last sets of experiments were conducted to investigate the influence of the IS increase at constant pH. Firstly, pH 4 was considered and the results are plotted in Figure 3.3.5. At this pH value, the change in IS did not significantly change the mobility, according to the statement above that at pH 4 the IEP does not depend strongly on the concentration of the PDADMAC (see Figure 3.2.2.3). Accordingly, no significant change in particle size was observed upon addition of IS.

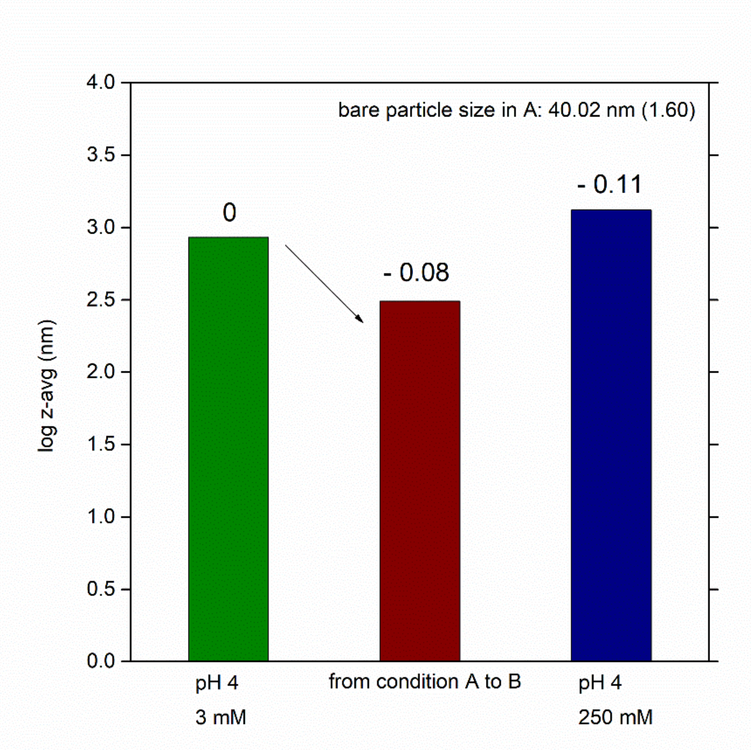

Figure 3.3.5 Size and mobility measurements at pH 4 in 3 mM NaCl solution, from 3 to 250 mM NaCl solution and in 250 mM NaCl solution with 100 mg/l of LUDOX TM-50.

On the contrary, in the last test at pH 8, the expected increase in mobility upon IS increase did not result in disaggregation. See results in Figure 3.2.2.4. The particle size was the same for the tests relative to all the three bars in Figure 3.3.6, confirming that a high IS causes aggregation and thwarts disaggregation in the presence of PDAMAC regardless of the way in which the solution is prepared or the final condition is achieved. It is important to underline that no significant aggregation was observed for bare particles, even in solutions of high ionic strength, even at relatively low values of mobility. On the other hand, aggregation was observed in the presence of PDAMAC also for mobility absolute values of 1 µmcm/Vs or higher. This observation suggests that phenomena are occurring during PDADMAC addition to the system at high IS that may promote aggregation during the adsorption process, or that forces other than DLVO forces might be at play in these systems. Regardless, the conclusions discussed above about disaggregation upon changes of solution chemistry stand under all circumstances.

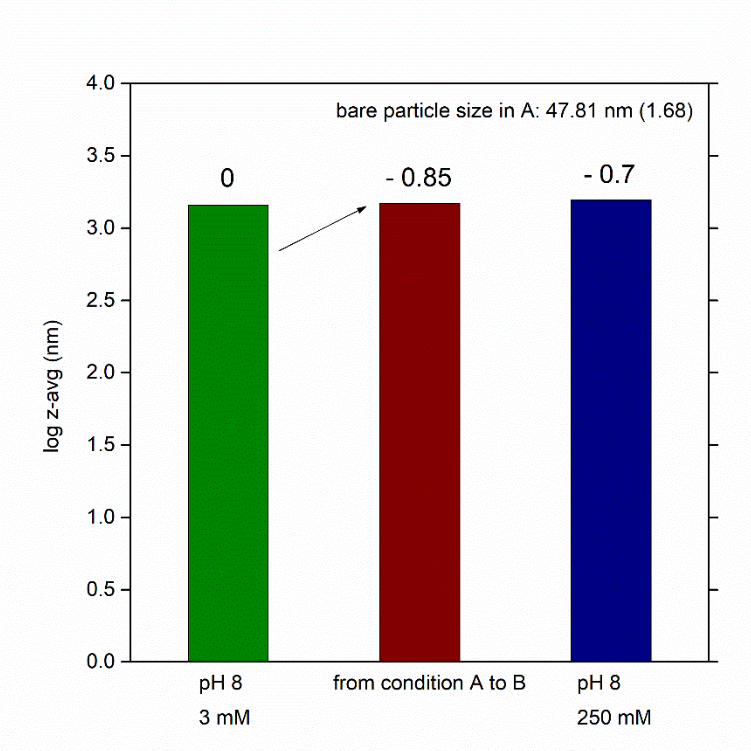

Figure 3.3.6 Size and mobility measurements at pH 8 in 3 mM NaCl solution, from 3 to 250 mM NaCl solution and in 250 mM NaCl solution with 100 mg/l of LUDOX TM-50.

Conclusions

The adsorption and desorption of PDADMAC on silica was investigated by combining the QCM-D, in which flat silica was utilized, and DLS, employed to study the aggregation and disaggregation behavior of silica nanoparticles.

The adsorption amount and the plateau value of mass at saturation increased strongly with increasing ionic strength and this effect is caused by the progressive screening of the electrostatic repulsion between the adsorbing polyelectrolyte chains. The adsorbed amount further increased with increasing pH and this effect is likely caused by the corresponding increase of the surface charge of the silica substrate. Both results are consistent with the trends reported in the literature. Furthermore, under the same conditions, the adsorbed mass was slightly higher with PDADMAC with high molecular weight in solution.

Partial desorption of previously adsorbed chains of PDADMAC on silica was achieved thanks to solution with lower IS and/or pH placed in contact with the adlayer. The reduction of adsorbed mass layer due to a pH decrease is caused by the resulting decrease in the magnitude of the diffuse-layer potential exerted by the silica surface that can no longer neutralize the positively charged PDADMAC chains, some of which tend to return in solution to minimize the energy of the system. When the salt level is decreased, instead, the repulsion of the interchain electric double layers becomes increasingly long ranged, which leads to desorption of part of the adsorbed polymer from the surface. However, desorption was always partial and, interestingly, the adsorbed mass at steady-state achieved by adsorbing PDADMAC under one condition was always lower than the mass achieved under the same condition but upon a desorption process starting from an adlayer of large mass. This result suggests that the barrier for desorption is relatively high and significant changes of solution chemistry are needed to trigger re-suspension of previously deposited chains. These mechanisms have important implications for engineering applications of the PDADMAC as flocculant, where the greater adsorbed layer strongly influences the filtering power.

Moreover, the amount of the adsorbed PDADMAC also regulates the overall particle charge, and the latter parameter can be correlated to many suspension properties, such as colloidal stability. The presence of PDAMAC in a suspension of silica particles results in neutralization of the electric potential and then overcharging as the dose of polyelectrolyte increase, consistent with literature observation. The IEP, the point in with the electric potential is zero, was shifted to higher doses when the pH increased, since the larger amount of ionized silanol groups necessitated higher doses of polyelectrolyte to reach the neutralization of the potential. Furthermore, the value of electrophoretic mobility at surface saturation decreased with increasing IS but was not influenced by pH. The shape of the charge reversal curves became steeper at more basic pH values, due to the increase in the electrostatic interaction between PDADMAC and silica, and flatter in a solution with high IS due to the screening of the charges.

Finally, the particle size measurements highlighted that disaggregation of the previously aggregated particles can be promoted by changes of solution chemistry but is also thwarted by an energy barrier. Disaggregation was only observed in solutions of relatively low ionic strength, while at high IS aggregation was always favoured in the presence of PDADMAC regardless of the solution chemistry.

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