Optical tweezers to measure the interaction between poly(acrylic acid) brushes

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ABSTRACT

Optical tweezers are employed to measure the forces of interaction within *single* pairs of poly(acrylic acid) (PAA) grafted colloids with an extraordinary resolution of ± 0.5 pN. Parameters varied are the concentration and valency of the counterions (KCl, $CaCl_2$) of the surrounding medium as well as its pH. The data are *quantitatively* described by a recently published model of Jusufi et al. [Colloid Polym Sci 2004; 282:910] for spherical polyelectrolyte brushes which takes into account the entropic effect of the counterions. For the scaling of the brush height a power law is found having an exponent of 0.25 ± 0.02 which ranges between the values expected for spherical and planar brushes. From the model the ionic concentration *inside* the brush is estimated in reasonable agreement with the literature.

1. Introduction

Polyelectrolyte brushes are formed when a dense layer of polyelectrolyte chains is grafted onto a solid surface [1]. Due to inter- and intra-molecular interactions the polyelectrolyte chains are stretched and elongated. Polyelectrolyte brushes are classified either according to the geometry of the substrate (as planar or spherical), or the chemical nature of the monomers (as strong or weak) [2,3]. In the latter a charge regulation mechanism takes place, which is controlled by the pH and the salt concentration of the surrounding medium.

Several factors are responsible for the interaction forces in polyelectrolyte brushes. The steric effect is controlled by the geometry and grafting density. The charge of the chain and the ionic strength of the medium play a decisive role in determining the electrostatic force. Other entropic details such as the translational entropy of the counterions and the elastic entropy of the chain control the space distribution of counterions and the conformation of the chain. The balance between all forces governs the brush conformation and its equilibrium length. Depending on the scaling law observed for the brush height, an osmotic, salted or collapsed brush (with increasing the salt concentration) can be observed by varying the salt concentration of the medium.

Optical tweezers [4] are experimental tools with extraordinary resolution in positioning a micron-sized colloid – without any mechanical contact – and in measuring the forces acting on it. This unique combination of experimental features made possible fascinating studies in biophysics [5–7], colloid- and polymer-science [8,9]. Other experimental techniques used for analysis of the polymer brushes include Surface Force Apparatus [10,11], AFM Colloidal Probe Technique [12–14], Ellipsometry [15], and Dynamic Light Scattering [16,17]. The strength of Optical Tweezers experiments in studying the interaction between polymer-grafted colloids can be traced back to three different roots of quite different origin: (i) Optical Tweezers enable one to move single colloids with nanometer precision and to measure forces acting on it in the range between 1 and $\sim$100 pN; (ii) experiments with Optical Tweezers can be carried out with single pairs of polymer-grafted colloids over extended periods of time (several hours). By changing the surrounding medium details of the scaling in dependence of separation between the colloids can be explored and effects of the variability of the colloids (in size, in grafting density etc.) are circumvented; (iii) last but not least are the preparative details to graft polymers on colloids worked out well.

Poly(acrylic acid) brushes (PAA) are pH responsive materials and the dissociation degree of its monomers varies with pH. Upon increasing the pH, a conformational transition from flexible to rigid chain takes place. The negative charge on the chain in a broad range of pH permits the interaction with positively charged counterparts, as for instance with proteins. This property has been used for reversible immobilization of proteins [18], an important task in many biotechnological and biomedical applications. PAA have been used in many studies with spherical brushes and planar systems [17,19,20].

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Recently – using optical tweezers – the forces of interaction between DNA-grafted colloids were measured in dependence on the ionic strength, on the surrounding medium, on the molecular weight of the grafted chains and its grafting density [21,22]. *Quantitative agreement* is found between the data and a model – originally developed for star polymers close to planar walls [23] – in which compression of the DNA-chains is assumed to be the dominating interaction. In the present work the experimental conditions are fundamentally different, the grafting density is about *thousand times* larger and the grafted (PAA)-chains are semiflexible. This means that interdigitation of arms becomes negligible and the forces of interaction are dominated by electrostatic, steric and entropic forces [24].

2. Materials and methods

2.1. Polymer brushes synthesis and characterization

Carboxyl-terminated poly(*tert*-butyl acrylate) (PtBA–COOH, $M_n = 42\,000$ g/mol, $M_w = 47\,000$ g/mol) synthesized by anionic polymerization, purchased from Polymer Source, Inc. Poly(glycidyl methacrylate) (PGMA) ($M_n = 84\,000$ g/mol) was synthesized by free radical polymerization of glycidyl methacrylate (Aldrich). Methanesulfonic acid (Fluka) was used without additional purification. Monodisperse silica particles with diameter of 1.55 μm, standard deviation of 0.04 μm were purchased in dry state from Microparticles GmbH (Berlin, Germany).

The 'grafting to' method was used to anchor polymer chains onto the surface of silica particles [25]. The synthetic procedure starts with adsorption of PGMA onto the particle surface. Before PGMA modification, particles were washed three times in dichloromethane followed by drying in a vacuum oven at 110 °C. PGMA was chemisorbed from a 2% chloroform solution. To remove non-adsorbed PGMA, the particles were washed and centrifuged several times in chloroform. For grafting of polymer onto the particle surface, PGMA modified particles were mixed with a 3% chloroform solution of carboxyl-terminated poly(*tert*-butyl acrylate) PtBA–COOH at room temperature during 24 h and then dried. The particle concentration in the solution was 3 wt%. The grafting process was performed at 150 °C during 15 h producing a dense polymer layer. Several cycles of washing in chloroform and centrifugation were needed to remove non-grafted polymers. The thickness of the polymer layer was ~10 nm (dry film) corresponding to a grafting density of ~0.12 chains/nm². The distance between grafting sites (~2.8 nm) is smaller than the radius of gyration (R_g) of PtBA polymer coils ($R_g \sim 5$ nm) in θ-conditions. In a good solvent the polymer chains are swollen and the $R_g \gg R_{g\,\theta\text{-conditions}}$. Consequently, the polymer-grafted film exposed to solvents can be considered as a brush-like layer [26]. Finally, PtBA was hydrolyzed with methanesulfonic acid for 5 min yielding polyacrylic acid (PAA).

Diffuse reflection infra-red (IR) spectroscopy was employed to control each step of the reaction (immobilization of PGMA onto the particle surfaces, esterification between terminating carboxyl groups of carboxyl-terminated PtBA–COOH and epoxy groups on the surface and hydrolysis of PtBA) and to determine the amount of grafted polymer. The latter was evaluated using calibration curves of the absorbance at 1493 cm⁻¹ made from different mixtures of polymer and particles. The result shows that about 4–5 mg/m² of polymer was grafted onto the particle surface, which corresponds to a total thickness of 5 nm. The grafting density of polymer was calculated to be $0.1 \pm .01$ chains/nm².

2.2. Optical tweezers set-up

For the optical trap an inverted microscope (Axiovert S 100 TV, Carl Zeiss, Jena, Germany) accomplished with a stabilized diode-pumped Nd:YAG laser (1064 nm, 1 W, LCS-DTL 322; Laser 2000, Wessling, Germany) was used. The beam was expanded and coupled into the back aperture of the microscope objective (Plan-Neofluor 100 1.30 Oil, Carl Zeiss, Jena, Germany). Video imaging and the optical position detection were accomplished at 20 frames per second by a digital camera (1M60CL, DALSA, Gröbenzell, Germany). The optical stage was positioned in three dimensions with nanometer resolution using piezoactuators (P-5173CD, Physik Instrumente, Karlsruhe, Germany). The sample cell consisted of a closed chamber that allows the flushing of solutions by a syringe pump. A custom-made micropipette with an inner tip diameter of 0.5 μm was inserted into the chamber to hold one colloid by capillary action. The whole experimental set-up was located in a temperature-controlled (298 ± 1 K) room. The calibration of the optical trap was made using Stokes' law as described in detail elsewhere [5]. A typical force constant for the trap was 0.043 pN/nm.

The experiments were performed with one grafted colloid fixed at the tip of a micropipette and the second one in an optical trap (see Fig. 1). The approach velocity was 0.4 μm/s. From the digital images, the displacement of the colloid in the optical trap out of the equilibrium position and the separation between the centers of the colloids were determined using a custom-made LabVIEW image analysis routine [9]. By that the separation between the two colloids could be determined with an accuracy of ±6 nm and the interacting forces with a resolution of ±0.5 pN.

Potassium chloride and calcium chloride were used as mono and divalent salts, respectively. The pH was regulated with HCl and KOH. The conductivity of the solutions was measured with a conductivity probe (EC-CONSEN91 W) with built-in temperature sensor (CyberScan PC 510 from EUTECH Instruments) in order to verify the concentration of the solutions.

3. Theory

The theoretical description of neutral planar brushes goes back to de Gennes and Alexander [27–29]. Scaling theories for charged brushes were later developed [30–38] and predictions were made concerning the dependence of brush height on the ionic strength in the surrounding medium, the grafting density or the molecular weight. Furthermore geometrical effects caused by the curvature of the underlying substrate were taken into account. Inspired by the original work of Pincus [31] and using as starting point a theory developed for star polymers [39], Jusufi and co-workers [24] reported a theoretical description of the interactions in spherical brushes. By means of molecular dynamics and mean field theory they have demonstrated that the main contribution to the interaction comes from entropic forces associated with the counterions inside the brush. In their approach the following assumptions were made: (i) the two brushes retract, and can be modeled as "chopped spheres"; (ii) the dominant term in the potential arises from the entropic contribution of the counterions inside of the brush; (iii) the electrostatic term is neglected. An effective potential (V_{eff}) for two identical spherical brushes which is function of the colloidal radius (R_c), the separation between the solid surfaces (D), the brush height (L) and the number of counterions inside the brush (Q/e) was obtained [24]. The repulsion force between two spherical brushes can be deduced from the derivative of the potential with respect to the position as:

$$F = -\frac{\partial V_{eff}}{\partial D} = k_B T (Q/e) \frac{\ln(D + 2R_c/2(L + R_c))(3D + 6L + 8R_c \ln(R_c/L + R_c) - 2(D - L + 3R_c)\ln(D + 2R_c/2(L + R_c)))}{[D + 2L - (D + 2R_c)(\ln((D + 2R_c)/2(L + R_c)))]^2} \qquad (1)$$
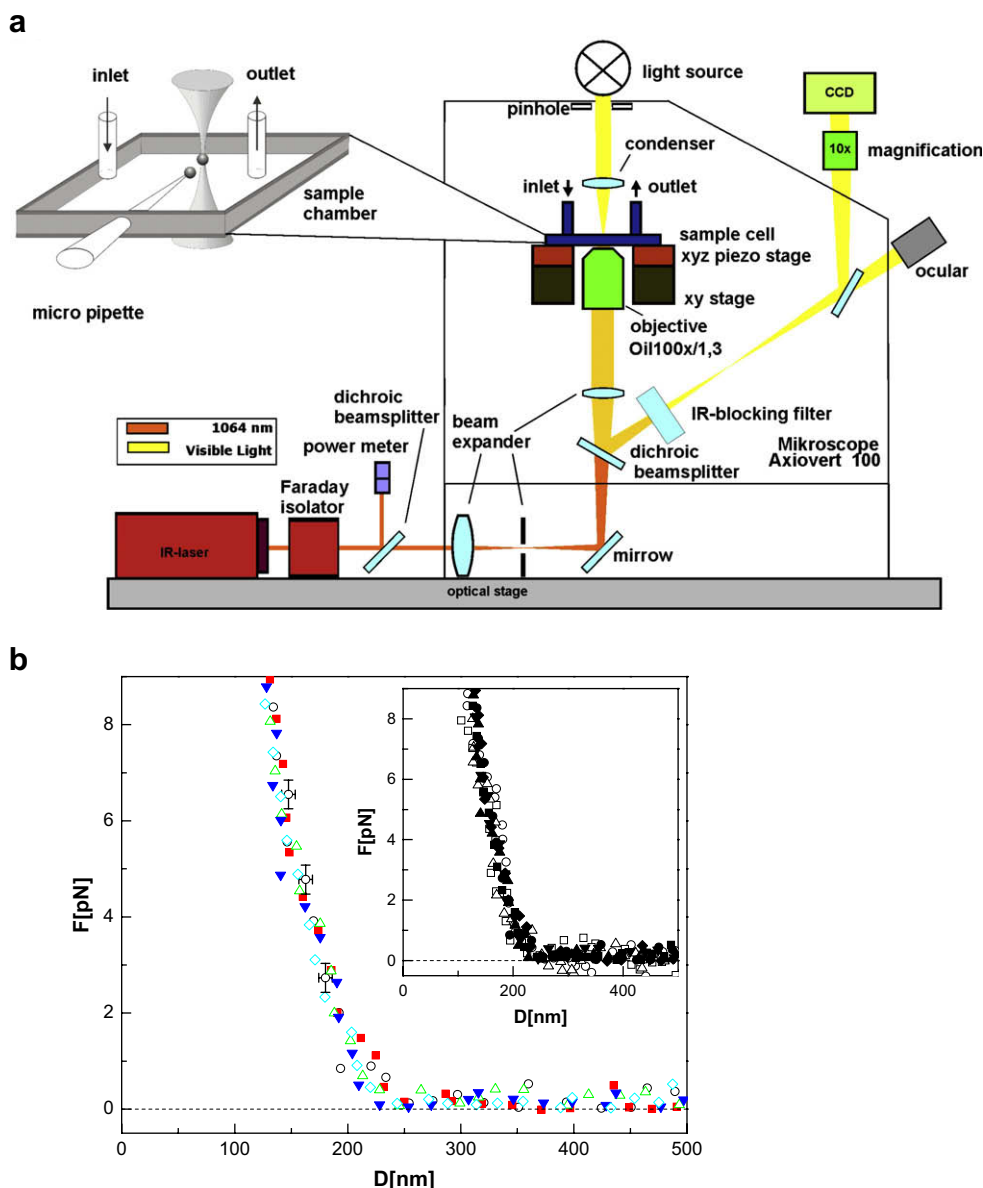
Fig. 1. (a) Scheme of the experimental set-up. One colloid is held with a micropipette due to the capillary action, the other is kept in an optical trap. The separation *D* between the colloids can be varied with nanometer precision by use of a *xyz* – piezostage. The forces of interaction between the two colloids are determined from the displacement of the colloid in the optical trap. (b) Force *vs.* separation within a *single pair* of colloids in a medium of 10^{-4} M KCl at pH 7. In order to demonstrate the experimental accuracy and reproducibility several runs are superimposed. The experimental uncertainty is indicated. In the inset, runs for *different* pairs of colloids are compared which were rescaled with respect to a common value at a force of 4 pN in 10^{-2} M KCl solution.

where k_B the Boltzmann constant, T the absolute temperature. Taking R_c as fixed and known, it is possible to calculate from the fits to the experimental data the brush height L and the number of counterions Q/e trapped inside the brush. From these parameters, the mean counterion concentration inside the brush can be estimated as:

$$C_{brush} = \frac{(Q/e)}{N_A (4/3)\pi \left((R_c + L)^3 - R_c^3 \right)} \qquad (2)$$

where N_A is the Avogadro number.

4. Results and discussion

Optical tweezers enable one to measure the forces of interaction within a *single* pair of colloids (Fig. 1a). Excellent reproducibility in

the force-separation curves is observed in subsequent runs under identical conditions (Fig. 1b). If different pairs of colloids are compared a variation of the particle radius of approximately $\pm 5\%$ has to be taken into account. To compare different pairs of colloids one can assume that at high salt concentrations the electrostatic repulsion of the grafted chains is screened and hence the polymer brushes are collapsed. By that it is possible to rescale the force–separation charts of different pairs of colloids with respect to a common value at a force of 4 pN. Following this procedure coinciding force–separation dependencies are found also for *different* pairs of colloids (inset of Fig. 1b).

The force–separation dependence (Fig. 2) as measured within a *single* pair of PAA-grafted colloids shows for varying KCl concentrations (at pH 7) a pronounced effect: With increasing ionic strength of the surrounding medium the potentials become steeper and hence the interaction extends to larger distances at lower ionic
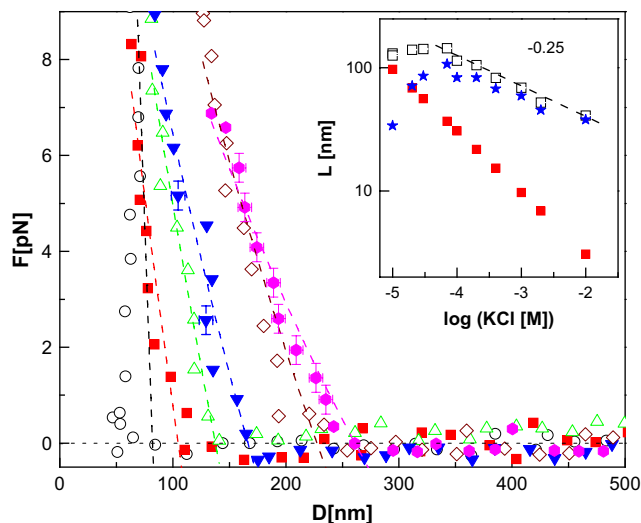
Fig. 2. Force *vs.* separation as measured for a *single pair* of PAA-grafted colloids in media of varying KCl concentrations: 10^{-2} M (open circles), 2×10^{-3} M (full squares), 10^{-3} M (open up-triangles), 4×10^{-4} M (full down-triangles), 10^{-4} M (open rhombus), 10^{-5} M (full hexagon) at pH 7. In order to ensure the experimental reversibility, at the end of a measurement cycle the force-separation dependence for the initial concentration was remeasured and proven to coincide within the experimental accuracy (± 0.5 pN). The dashed lines represent the fits according to Eq. (1). In the inset the resulting brush height L (open squares), Debye length (full squares) and the non-electrostatic term calculated as $L - L_{Debye}$ (full stars) in dependence of KCl concentration are shown.

Fig. 3. Force *vs.* separation as measured for the *identical pair* of PAA-grafted colloids of Fig. 2 in media of varying $CaCl_2$ concentrations: 10^{-3} M (open circles), 2×10^{-4} M (full squares), 10^{-4} M (open up-triangles), 4×10^{-5} M (full down-triangles), 2×10^{-5} M (open rhombus), and 4×10^{-6} M (full hexagon) at pH 7. At the end of the measurement cycle a 10^{-5} M KCl solution was flushed into the sample cell and it was found that the original force-separation dependence (form Fig. 2) is recovered, data not shown. The dashed lines represent the fits according to Eq. (1) In the inset the resulting brush height L (open squares), Debye length (full squares) and the non-electrostatic term calculated as $L - L_{Debye}$ (full stars) in dependence of the $CaCl_2$ concentration is shown.

strength. At the end of a measurement cycle the sample cell is flushed with medium of the initial (low salt) concentration and the force-separation is measured again in order to ensure the full reversibility of the ion exchange.

The data can be well described – within experimental uncertainty – by the Jusufi-model using Eq. (1). From the fits (dashed lines) the brush height L (corresponding to half of the separation at an extrapolated acting force of 0 pN) and the number of trapped ions *inside* the brush (Q/e) are obtained. The concentration dependence of the brush height (inset in Fig. 2) distinguishes the osmotic brush regime for KCl concentrations lower than 10^{-4} M from the salted brush regime in which a scaling with a slope of approximately -0.25 ± 0.02 is found. In order to determine the electrostatic contribution to the total repulsion between the colloids the Debye length, L_{Debye}, of the medium is calculated. A maximum for the non-electrostatic contribution calculated as $L - L_{Debye}$ is observed at a concentration of the order of 10^{-4} M.

For the *identical* pair of colloids in media of divalent $CaCl_2$ ions the forces scale similarly with the separation (Fig. 3) as for KCl, but shift to lower concentrations by one order of magnitude. The concentration dependence of the brush height, L, again follows a power law with an exponent of -0.23 ± 0.02. It ranges between $-1/6$ and $-1/3$ as predicted for spherical [40,41] and planar brushes, respectively. The ratio of the contour length (87 nm) of the polymers and the radius of the colloids (775 nm) is $\sim 1/9$, a value too high to consider the surfaces as planar but not large enough to treat them as spherical.

The force–separation dependence for varying pH (Fig. 4) at a (fixed) concentration of 10^{-3} M KCl shows close resemblance with Figs. 2 and 3. Again the Jusufi-model describes well (dashed lines) the data using Eq. (1). The brush height L as obtained from the fits (inset Fig. 4) shows a strong pH effect. It compares well with independent ellipsometric measurements. The increase in the brush height is caused by the pH-induced augment of the PAA dissociation and results in a stretching of the grafted chains. In order to separate the effects of ion concentration and pH the forces are represented as a function of the reduced distance (D/L) for
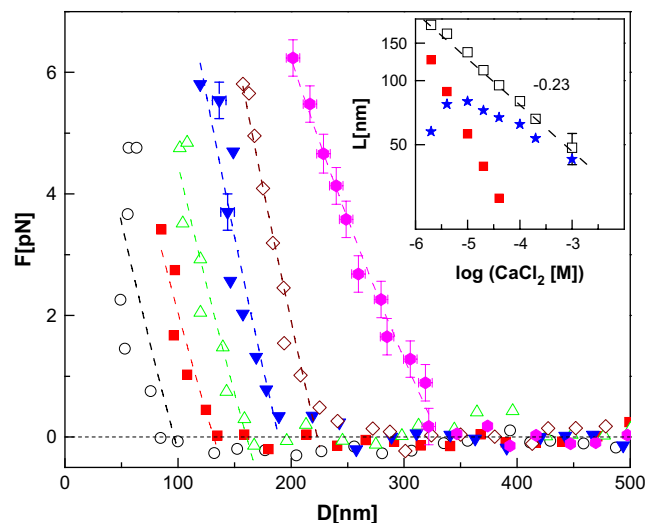
varying pH at a fixed ion concentration (Fig. 5) and *vice versa*. For the former case it is *not* possible to obtain a "master curve" in contrast to the latter (inset Fig. 5).

From the fits using Eq. (1) the number of counterions trapped in the brush Q/e is obtained and can be used to determine the ion concentration *inside* the brush (Eq. (2)). The comparison shows (Fig. 6) the extent to which it is higher than the ion concentration in the surrounding medium especially in the osmotic regime where the counterions are trapped inside the brush. It is important to mention that the model (Eq. (1)) assumes that only a small fraction of charges is outside the brush, so the electrostatic repulsion is
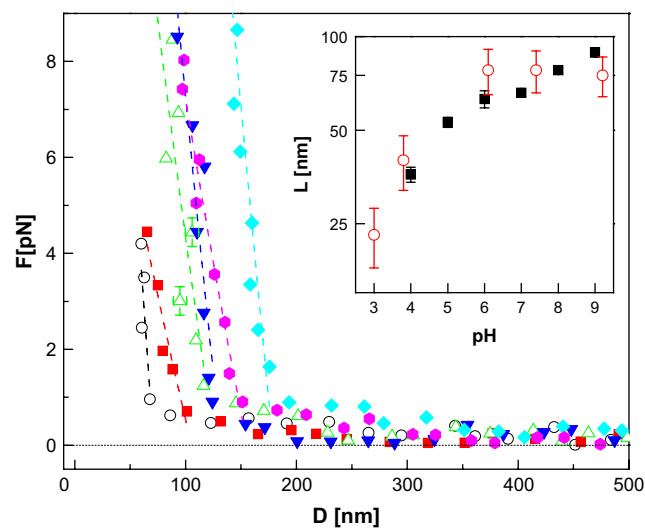

Fig. 4. Force *vs.* separation as measured for a *single pair* of PAA-grafted colloids in media of varying pH: 4 (open circles), 5 (full squares), 6 (open up-triangles), 7 (full down-triangles), 8 (full hexagon) and 9 (full rhombus) at 10^{-3} M KCl. The dashed lines represent the fit to the experimental data with Eq. (1). Inset: brush height L *vs.* pH at 10^{-3} M KCl obtained from analyzing the Optical Tweezers measurements using Eq. (1) (full squares) and as measured by Ellipsometry (open circles).
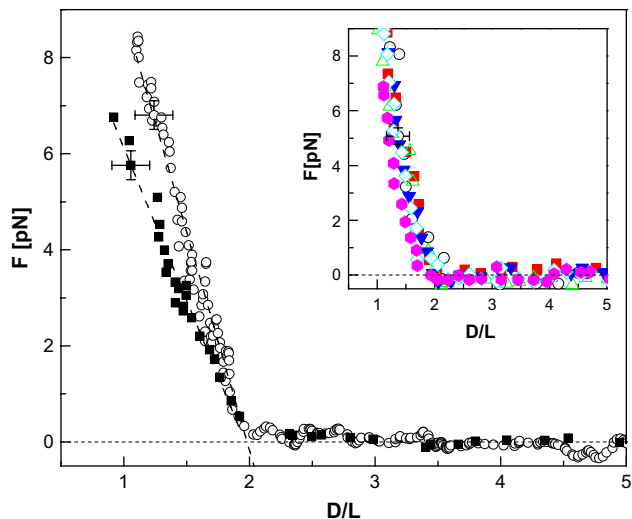
Fig. 5. Force *vs.* normalized separation (*D*/*L*) as measured for a *single pair* of PAA-grafted colloids in media at pH 8 (open circles) and pH 4 (full squares) at the same ionic strength (10^{-3} M KCl). In the inset, the force *vs.* normalized separation is shown in media of varying KCl concentration at pH 7: 2×10^{-3} (open circles), 10^{-3} (full squares), 4×10^{-4} (open triangles), 2×10^{-4} (full triangles), 10^{-4} (open rhombus), and 10^{-5} M (full hexagon).

much smaller than the entropic effect. This assumption is not fulfilled for salt concentrations lower than 10^{-4} M; with increasing ionic strength the concentration inside and outside of the brush tend to equalize. The ion concentration inside the brush shows a slight pH effect (inset of Fig. 6).

Using the theory developed by Hariharan et al. for strongly curved surfaces [42], Guo and Ballauff [16] have reported the salt concentration inside the PAA brushes as:

$$C_{\text{brush}} = \frac{1}{2} \sum_i \frac{n_i z_i^2}{N_A} = c_a \left[1 + \left(\frac{z \rho_f}{2e N_A c_a} \right)^2 \right]^{1/2} \quad (3)$$

where c_{brush} and c_a are the salt concentration inside the brush and in bulk, n_i is the number density of the ions of species i, z_i is the
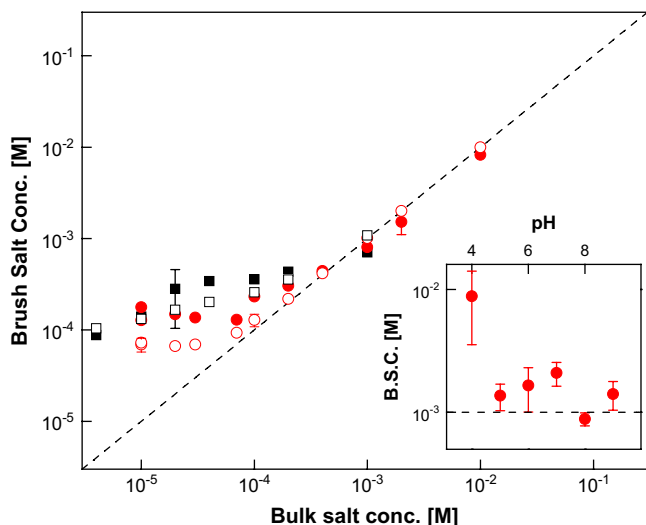

Fig. 6. Salt concentration *inside* the brush ("Brush salt concentration") *vs.* the salt concentration in the bulk solution of KCl (full circles) and $CaCl_2$ (full squares) at pH 7 calculated from Eq. (2). The dashed line indicates the equality of the salt concentration *inside* and *outside* the brush. Open symbols represent the salt concentration according to Eq. (3) for KCl (open circles) and $CaCl_2$ (open squares). Inset: brush salt concentration for 10^{-3} M KCl at varying pH.

valence of the ions, N_A the Avogadro number, e the electron charge and ρ_f the average charge density defined as:

$$\rho_f = - \sum_i e z_i n_i = \frac{3e R_c^2 \sigma L_c}{l_c \left[(R_c + L)^3 - R_c^3 \right]} \quad (4)$$

where σ is the grafting density, R_c the colloid radius, L_c the contour length and l_c the distance between the charges. The distance between the charges (l_c) is the Bjerrum length. This approach overestimates the salt concentration inside the brush as already discussed [43]. A discrepancy can be observed (Fig. 6) between the values calculated using the Hariharan and the Jusufi approaches at low salt concentration, and starting from 10^{-4} M good agreement between both is found. It should be noted that in the Jusufi-model electrostatic repulsion is neglected, which does not hold at low concentrations. On the other hand Eq. (3) is valid for highly curved surfaces a condition not fulfilled in our experiments.

A theoretical description for the interactions in weak polyelectrolytes brushes is reported by Biesheuvel [44]. The model enables one to quantify the effects of the chain conformation, excluded volume, and electrostatic interaction. It also includes the degree of dissociation of the weak polyelectrolyte chains. Unfortunately this model requires an "*arbitrary numerical pre-factor*" (in case of our experiments 1/5000, data not shown) in order to fit our data. (In Ref. [45] a "pre-factor" of 1/1000 has been used to apply this model.)

5. Conclusions

Optical Tweezers enable one to measure the forces *within* a *single* pair of colloids with an extraordinary resolution of ±0.5 pN. In combination with the well developed surface-chemistry techniques this offers an exciting chance to systematically study the interaction between polyelectrolyte brushes grafted onto colloids. Parameters varied are the concentration and the valency of ions in the surrounding medium and pH. Due to the fact that the measurements with *single* pairs of colloids can be carried out over extended periods of time, the inter-particle variability (variation in the diameter, the grafting density and the charge per colloid, etc.) is ruled out as a (often considerable) source of uncertainty.

In the present study the transition from an osmotic brush to a salted brush on varying the ionic strength and the valency of the surrounding medium is analyzed in detail. For the brush height a power law dependence with an exponent of $\sim -1/4$ is found for both, mono and divalent ions in the salted brush regime. This value ranges between those predicted for spherical and planar brushes which is reasonable due to the geometrical conditions. Increasing the pH results in an increase of the brush length because of the dissociation of the polyelectrolytes. The comparison between the brush lengths obtained from the fitting of the experimental data and the ellipsometric measurement are in quantitative agreement. In contrast to recent studies [21,22] with DNA-grafted systems (where the compression of the chain is responsible for the observed force), it is proven that in the case of PAA the interaction is dominated by entropic forces resulting from the counter-ion distribution *inside* the brush and can be estimated by means of the Jusufi approach [24]. Similar results are obtained from the Hariharan theory [42].

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