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ORIGINAL CONTRIBUTION

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Adsorption of polyelectrolytes on colloidal latex particles, electrostatic interactions and stability behaviour

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Abstract The stabilization and flocculation behaviour of colloidal latex particles covered with cationic polyelectrolytes (PE) is studied with photon correlation spectroscopy and zetapotential measurements. Diffusion coefficients, flocculation rate constants and zetapotentials have been determined as a function of adsorbed amount of cationic poly-(diallyl-dimethyl-ammoniumchloride) (PDADMAC) of different molar masses and of statistic copolymers of DADMAC and *N*-methyl-*N*-vinyl-acetamide (NMVA) of various compositions in water and at high ionic strength. Flocculation by van der Waals attraction can be observed if the zetapotential is low. This occurs, if the surface charge is screened by the oppositely charged cations. Furthermore, in the case of adsorption of high molecular polycations mosaic flocculation occurs if the adsorbed amount is low. At high ionic strength, flocculation takes place if the adsorbed amount is below the adsorption plateau. If the adsorption plateau is reached the suspensions become stabilized. In water the charge reversal at full coverage leads to electrosteric stabilization both with low and high molar mass polycations. At high ionic strength only polycations with high molar mass are able to stabilize the suspension. If a certain molar mass of the polycation is exceeded, steric stabilization of the suspension occurs due to the formation of long adsorbed PE tails and their osmotic repulsion. The layer thicknesses are determined as a function of the molar mass.

Key words Photon correlation spectroscopy · Zetapotential · Colloidal latex · Stability · Flocculation · Polyelectrolyte · Poly-(diallyl-dimethyl-ammonium-chloride) · Poly-(*N*-methyl-*N*-vinyl-acetamide)

Introduction

Many industrial processes including papermaking, mineral processing and water treatment include operations in which aqueous colloids are aggregated by synthetic water-soluble polymeric flocculants [1]. Another new development is the self assembling of polyelectrolytes in the presence of colloidal templates, e.g. for the encapsulation of drugs with controlled drug release [2]. The adsorptive behaviour of polyelectrolytes causes the modification of solid surfaces and interfaces by polyelectrolyte based coatings and adhesives [3–5]. To influence the stability of colloidal particles by adsorbed polymer and polyelectrolyte layers is therefore of great scientific and technological significance [6, 7]. The stabilization and flocculation of colloidal suspensions depends mainly on the conformation of the adsorbed macromolecules on the particle surface [8]. The most promising method to obtain information on layer extensions are hydrodynamic methods like diffusion, sedimentation and electrophoresis. With photon correlation spectroscopy (PCS) the diffusion coefficients of the colloidal particles, bare or covered, can be measured. Additionally, with electrophoretic measurements the zetapotential and the charge of the polyelectrolyte particles can be determined.

In this study we demonstrate that flocculation and stabilization of a colloidal polystyrene latex suspension depend strongly on the molar mass, the charge density of the polyelectrolyte and the ionic strength of the solution. In some cases the hydrodynamic layer thicknesses of the adsorbed polyelectrolytes can be determined. As polyelectrolyte cationic poly(diallyl-dimethyl-ammoniumchloride) (PDADMAC), copolymers of DADMAC with *N*-methyl-*N*-vinyl-acetamide (NMVA) with different molar ratio and the neutral homopolymer of NMVA are used. The colloidal stability of the latex polyelectrolyte system under different conditions is evaluated. Parallel to the stability investigations the electrophoretic properties of polyelectrolyte covered colloidal particles are investigated.

Experimental

As substrate, colloidal polystyrene latex samples with negative surface charge (prepared by Dr. Jaeger, Fraunhofer Institut für Angewandte Polymerforschung Teltow, Germany) were used without any further purification. The spherical latex particles were synthesized by emulsion polymerization of styrene with the initiator potassium peroxidisulfate and exclusively sulfate groups are located on the smooth surfaces. The characteristic data are given in Table 1.

As flocculants, cationic poly-diallyl-dimethyl ammoniumchloride (PDADMAC), poly-*N*-methyl-*N*-vinyl acetamide PNMVA of different molar mass and copolymers of DADMAC with NMVA poly(DADMAC-*co*-NMVA) of comparable molar masses were applied. The homopolymers and the statistic copolymers were prepared by radical polymerization with the initiator 2,2′-azobis-(2-amidinopropane) in aqueous solution. Details of the latex samples and the molecular characterization parameters for the polymers and the polyelectrolytes are published elsewhere [9, 10].

Zetapotential measurements were accomplished in a Malvern Zetamaster at room temperature (23 ± 1 °C). The Zeta potentials ζ were calculated from the measured electrophoretic mobilities μ_e of the particles by applying the Henry equation [11]:

$$\mu_e = \frac{2\zeta\varepsilon\varepsilon_0 f(\kappa a)}{3\eta} \tag{1}$$

where ε is the dielectric constant, ε_0 the dielectric permittivity of vacuum, κ the Debye Hückl screening parameter, a the radius of the particles and η the viscosity of the solution.

At an ionic strength below or equal to 0.001 mol/l, $f(\kappa a)$ is assumed to be 1.0. In all other cases $f(\kappa a)$ is set to 1.5. The latex concentration was about 0.050 g/l.

Table 1 Characterization of polystyrene latex sample

Latex sample	d_{EM} [nm]	d_{PCS} [nm]	Charge density [μC/m^2]	Polydispersity [%]
PS 85/86	210–215	228	−7.4	< 5

Dynamic light scattering (DLS), also known as photon-correlation-spectroscopy (PCS), was used to determine the state of flocculation as a function of time as well as the thickness of the adsorbed polymer layer. All light scattering measurements were accomplished with an autocorrelator (System 7400, Malvern Instruments, Spring Lane, Worcestershire, UK), equipped with an argon ion laser (Model 2016, Spectra Physics) at a wavelength of 514.4 nm at a scattering angle of 90° in a water bath at 25 °C. Details of the method with respect to the investigation of colloidal particles covered with polymers can be found in [12–14].

Immediately after mixing the latex polyelectrolyte suspension with the salt solution of a certain ionic strength, the measurements of the diffusion coefficient were made with an interval distance of about 4 min. The resulting latex concentration was about 0.050 g/ml.

Changes in the sequence of adding the substances gave no effects within the experimental error. Due to the small particle concentration, the collision process is very slow compared to the adsorption process. So adsorption could take place before the particles began to flocculate.

The diffusion coefficient measured at a time of 40 min after mixing is used as characteristic parameter for the state of flocculation. Small diffusion coefficients are related to large aggregates of the latex particles. Based on the Smoluchowsky theory for the aggregation of colloidal particles [15, 16], the rate constants of aggregation are determined with a method of Versmold and Härtl [17] by evaluating ten diffusion coefficients obtained in a time dependent measurement.

The hydrodynamic layer thickness was measured at 25 °C 1 h after the addition of 1 ml of a latex suspension to 1 ml of a solution of polyelectrolyte and salt. The resulting latex concentration was 0.005 g/l. The amount of added polyelectrolyte exceeded under all conditions at least three times the plateau concentration of the adsorption isotherm.

The hydrodynamic radius a of the suspended particles was obtained by applying the Stokes-Einstein equation (Eq. 2) to the diffusion coefficient D:

$$a = \frac{kT}{6\pi\eta D} \tag{2}$$

where k is the Boltzmann constant, T the Temperature in K and η the dynamic viscosity of the suspension. The hydrodynamic layer thickness is obtained from the difference of the radii of covered and bare particles.

To ensure that the hydrodynamic layer is not superimposed by any flocculation process, all layer thickness measurements were made under stable conditions, confirmed by the angle and time dependence of the diffusion coefficients [12–14].

Furthermore, scanning micrographs at different ionic strengths and different polyelectrolyte coverage were made to visualize the states of aggregation. The dispersion (300 μl of a sample with an effective latex concentration of about 0.005 g/l) was filtered at a reduced pressure of about 900 mbar through a homoporous ceramic filter (Anodisc Filter, Fa. Whatman) with a pore diameter of 100 nm. The deposed particles were washed twice with 200 μl bidistilled water, dried at 30 °C for 3 h and vapour deposited with gold before imaging by REM.

Results and discussion

Flocculation behaviour of the pure latex suspension in the presence of salt

Measurements of the diffusion coefficient of bare latex at different ionic strengths (not presented) show a critical coagulation concentration (ccc) of about 0.3 mol/l

NaCl. This corresponds to a Zetapotential of −25 mV (not shown). The screening of the surface charge by the added electrolyte ions reduces the electrostatic repulsion of the particles and the suspension begins to coagulate. According to the PCS measurements, electron micrographs of bare latex particles without any added salt show single particles (Fig. 1), while at a ionic strength of 1 mol/l only clusters of aggregated latex particles are found (Fig. 2).

Flocculation and stabilization behaviour under different conditions

All adsorption isotherms of PDADMAC and the copolymers onto polystyrene latex are published elsewhere [10].

Flocculation behaviour in presence of PEs at low ionic strength

Figure 3 shows the diffusion coefficients of the latex particles as a function of added PDADMAC of different molar mass normalized to $c_{saturation}$ in water. $c_{saturation}$ corresponds to plateau adsorption. Latex samples covered with high molar mass PDADMAC 428.000 and PDADMAC 372.000 (not shown here) begin to flocculate at about 60% of saturation. The electron micrograph in Fig. 4 shows the aggregated system at a level of 70% of saturation. On the other hand, low molar mass PDADMAC 5.000 destabilizes the suspension at a coverage of about 80%. The zetapotential in Fig. 5 shows in the case of PDADMAC 428.000 at 60% of saturation a value of about −50 mV. Therefore the suspension should be stabilized electrostatically. The reason for the observed destabilization can attributed to the formation of patches and a mosaic like charge compensation between two covered particles [18]. This is in evidence with investigations by Horn et al. [19], who showed patches of adsorbed polyethyleneimine onto a polystyrene latex surface visualized with atomic force microscopy (AFM).

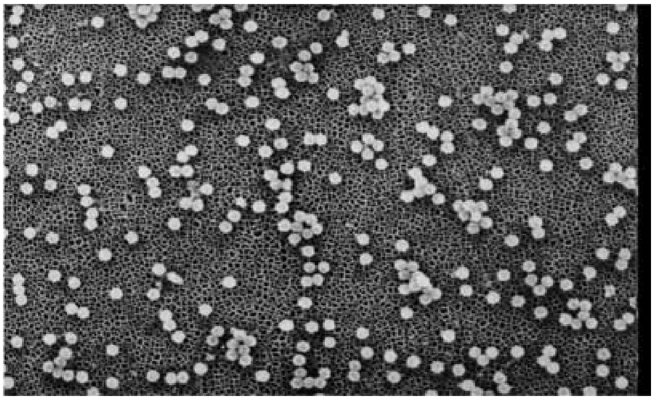

Fig. 1 Electromicrograph of bare latex without addition of salt

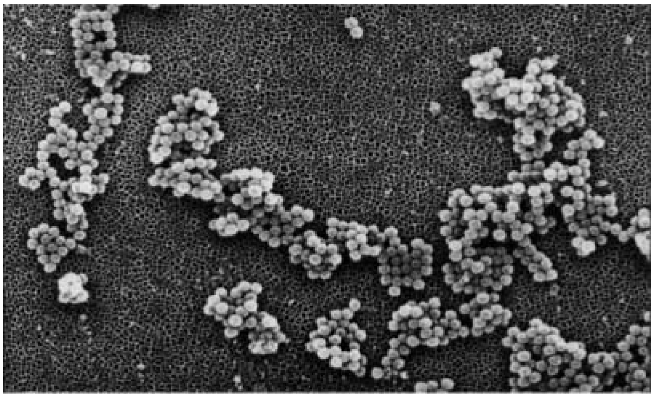

Fig. 2 Electromicrograph of bare latex in 1 mol/l NaCl

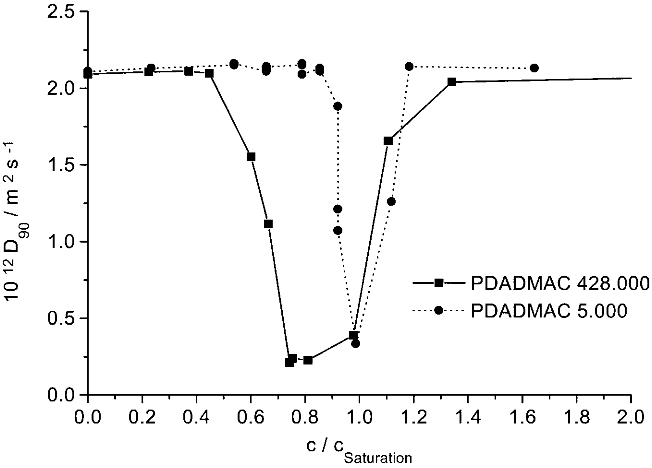

Fig. 3 Diffusion coefficient of latex as a function of coverage with PDADMAC without salt

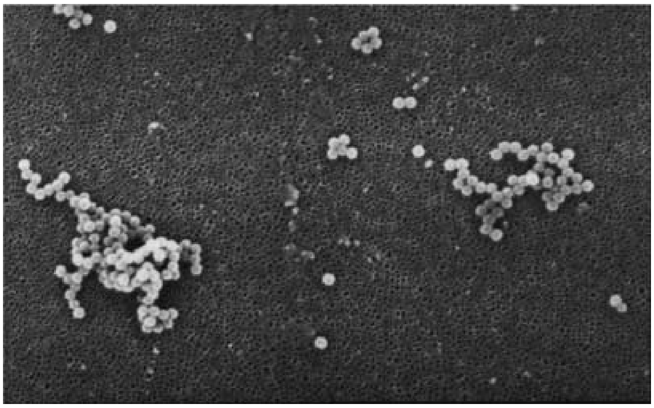

Fig. 4 Electromicrograph of latex covered to 70% with PDADMAC without salt

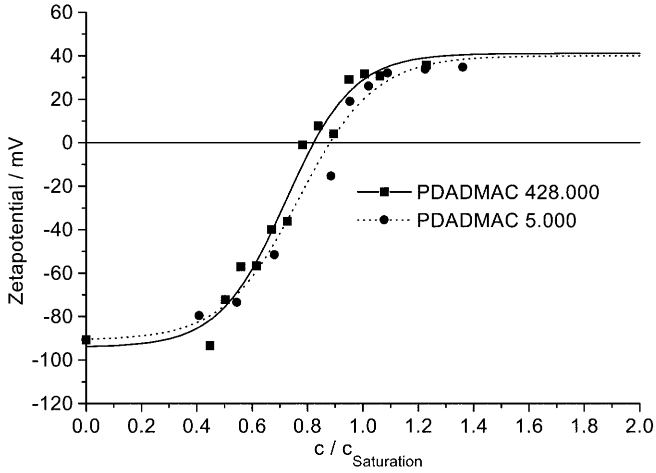

Fig. 5 Zetapotential of latex as a function of coverage with PDADMAC without salt

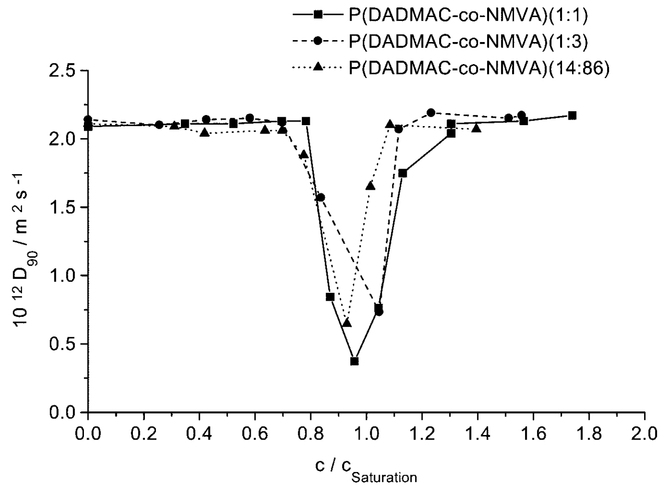

Fig. 6 Diffusion coefficient of latex as a function of coverage with P(DADMAC-*co*-NMVA) different stoichiometric composition without salt

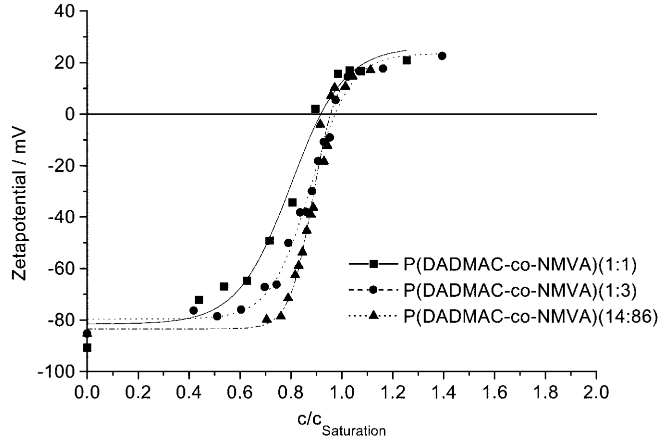

Fig. 7 Zetapotential of latex as a function of coverage with P(DADMAC-*co*-NMVA) different stoichiometric composition without salt

In the case of low molar mass PDADMAC 5.000 the polyelectrolyte chains become distributed more homogeneously onto the particle surface. Patch structures do not seem to be plausible. This is supported by the low zetapotential of −20 mV in the case of PDADMAC 5.000 at a level of saturation of 80%. The electrostatic repulsion is not sufficient to stabilize the system and therefore flocculation by van der Waals attraction occurs.

In both cases increasing adsorbed amounts lead to a decreasing negative zetapotential and an electrokinetic charge reversal at about 80% of saturation. At the adsorption plateau $c/c_{saturation} = 1$ the plateau value of the reversed zetapotential is reached. The zetapotential becomes independent of the polyelectrolyte concentration. At polyelectrolyte concentrations higher than $c_{saturation}$ the suspension is restabilized due to the electrostatic repulsion between the reverse charged colloidal particles. The diffusion coefficient reaches values similar to those of bare latex particles.

The flocculation behaviour of P(DADMAC-*co*-NMVA) in water shows similar behaviour. Flocculation starts at a level of saturation of about 85% (Fig. 6) and the corresponding zetapotential is about −25 mV (Fig. 7). The reduced charge density as well as the low molar mass of the adsorbed copolymer result in a homogeneous distribution of the charges onto the particle surface. This leads to flocculation by van der Waals attraction due to missing electrostatic repulsion. Increasing adsorbed amounts result in a decreasing negative zetapotential. As stated above, electrokinetic charge reversal appears at a level of about 80% of saturation. At the adsorption plateau $c/c_{saturation} = 1$ the zetapotential about +20 mV would be not sufficient to stabilize the suspension electrostatically. But the reduced charge density of the adsorbed copolymers leads to a high chain flexibility and the resulting extended polymer layer together with the zetapotential of about +20 mV restabilizes the suspension electrosterically [20]. The adsorption of the neutral polymers PNMVA 120.000 and 230.000 shows no flocculation (not shown here). The zetapotential of about −80 mV is independent of the adsorbed amount (not shown here). Therefore the suspension is stabilized electrostatically.

Flocculation behaviour and stabilization of the PE covered suspension at high ionic strength

Polyelectrolytes with high molar mass (PDADMAC 428.000) at high ionic strength stabilize the suspension sterically in the plateau region of the adsorption isotherm while low molar mass polyelectrolytes (PDADMAC 5.000) cannot stabilize the suspension at all electrolyte concentrations (Fig. 8). Due to the short chain length, the formation of a polymer layer consisting of loops and tails of sufficient length is impossible and steric stabilization at high ionic strength does not occur.

Figure 9 shows the flocculation rate constants for latex as a function of the concentration of PDADMAC 5.000 and PDADMAC 428.000 at an ionic strength of 1 mol/l. The strong screening of the surface charges leads to very fast aggregation with kinetic constants close to the theoretical Smoluchowsky value of 6 × 10^{-18} m^3 s^{-1} $particle^{-1}$. In the case of PDADMAC 428.000 the flocculation rate drops to zero if the plateau adsorption is reached and the suspension becomes stabilized sterically. In the case of PDADMAC 5.000, no stabilization is achieved and the flocculation rate stays close to the theoretical Smoluchowsky value. At higher PDADMAC 5.000 concentrations the reaction rate decreases gradually. This is a result of the increasing viscosity of the suspension, which reduces the number of collisions between the particles.

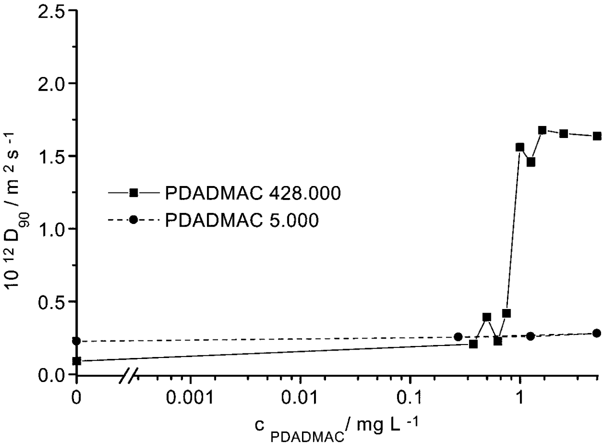

Fig. 8 Diffusion coefficients of silica as a function of the added concentration of PDADMAC at a salt concentration of 1 mol/l NaCl

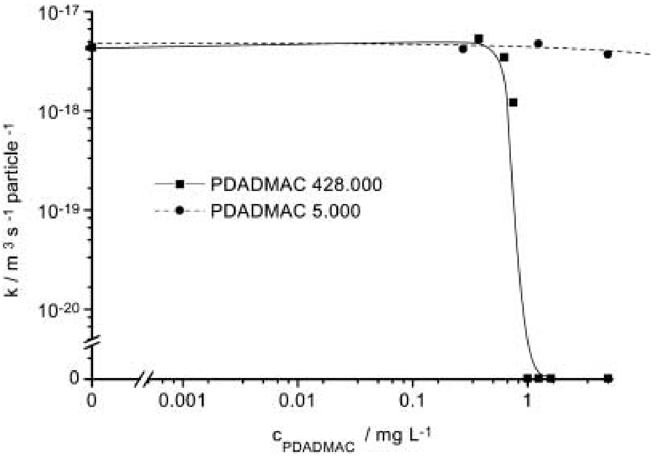

Fig. 9 Flocculation rate constants of latex as a function of the added concentration of PDADMAC at a salt concentration of 1 mol/l NaCl

The flocculation and stabilization behaviour of hydrophobic latex and hydrophilic silica suspensions in presence of electrolytes of different ionic strength are published in detail elsewhere [9, 21, 22].

Hydrodynamic thicknesses of polyelectrolyte layers

Figure 10a–c shows the electron micrographs of latex particles covered with PDADMAC 428.000, PDADMAC 5.000 and PNMVA 120.000 at large electrolyte concentrations. Particles fully covered with high molar mass PDADMAC 428.000 (Fig. 10a) show at all electrolyte concentrations, especially at 1 mol/l, isolated particles, while particles covered with PDADMAC 5.000 (Fig. 10b) at a ionic strength of 1 mol/l lead to big clusters of aggregated particles. This is in accordance with results of the diffusion coefficient as a function of the scattering angle of PDADMAC 428.000 covered particles (Fig. 11). Even after 24 h in 1 mol/l NaCl solution no significant change in the diffusion coefficient can be observed, demonstrating that no flocculation occurs. Therefore it is possible to measure hydrodynamic layer thicknesses in the plateau of the adsorption isotherms. Figure 12 shows the polymer layer thickness as a function of the electrolyte concentration by changing the way of preparation of the suspension. Within the experimental error no differences appear, indicating that the adsorption process is fast compared to the flocculation process in diluted suspensions. The suspension becomes stabilized in all cases. Furthermore the polymer layer thickness is independent from the latex concentration in the concentration range from 1 mg/l to 50 mg/l (not shown here), supporting the derived conclusions.

Figure 13 shows the hydrodynamic layer thickness in the plateau region of the adsorption isotherm of PDADMAC of different molar mass covered particles as a function of the ionic strength. At low ionic strength the hydrodynamic layer thickness is small and increases with ionic strength. Screening of the polyelectrolyte charge by small ions leads to the formation of loops and tails. At high salt concentration longer tails are formed by the polymers of higher molar masses. This leads to an increase of the hydrodynamic layer thickness with the chain length of the adsorbed PDADMAC. Repeated measurements of the layer thickness result in different values of about 20%. This might be related to the fact that slight formation of small aggregated clusters occurs, when preparing the suspension. DLS is a mass weighting

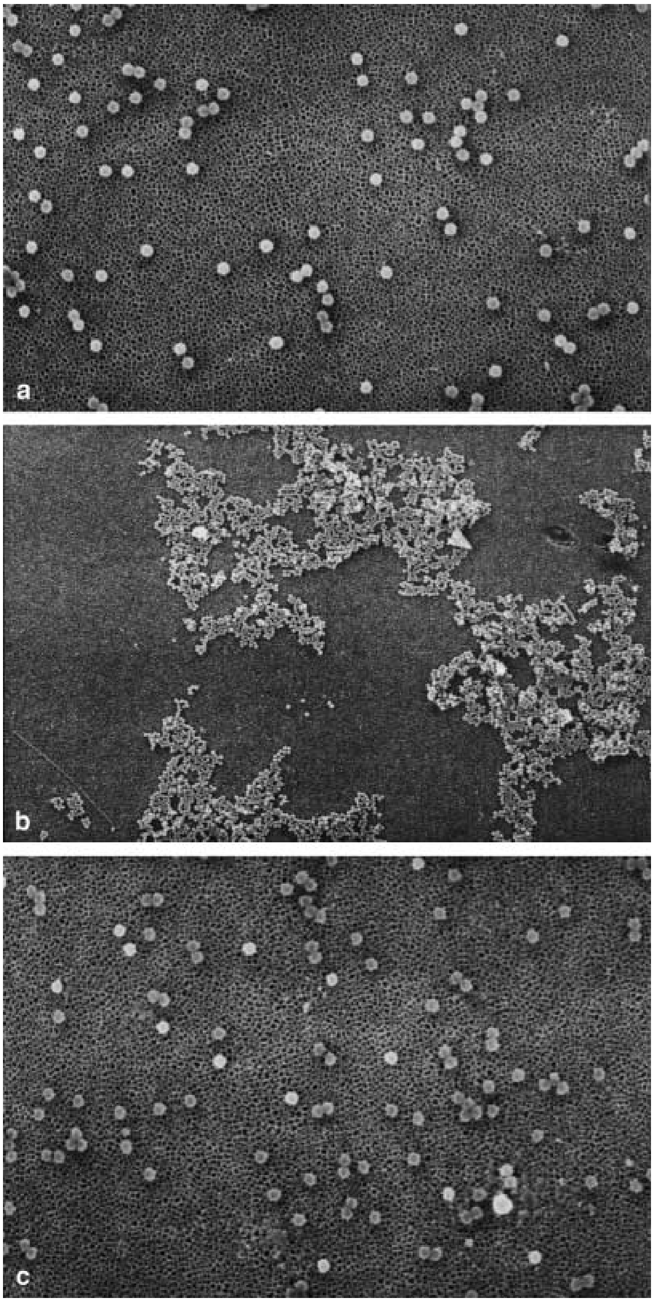

Fig. 10 **a** Electromicrograph of latex fully covered with PDADMAC 428.000 in 1 mol/l NaCl. **b** Electromicrograph of latex fully covered with PDADMAC 5.000 in 1 mol/l NaCl. **c** Electromicrograph of latex fully covered with PNMVA 120.000 in 0.1 mol/l NaCl

method and therefore some small particle aggregates influence the measured diffusion coefficient.

This behaviour can also be observed in the case of copolymers of P(DADMAC-*co*-NMVA) of different charge densities (Fig. 14).

The neutral homopolymers PNMVA (Fig. 15) show a small linear increase in hydrodynamic layer thicknesses

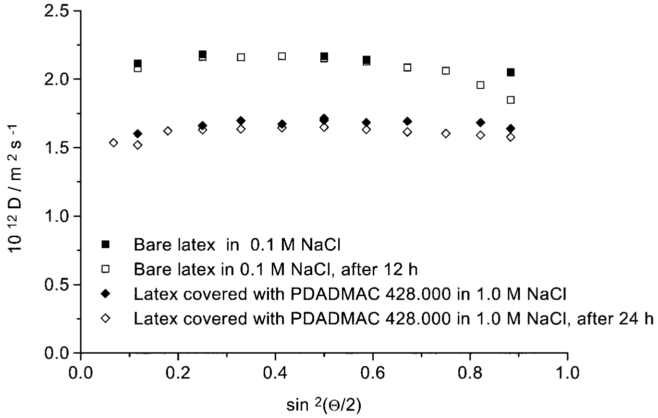

Fig. 11 Dependence of the diffusion coefficient D on scattering angle θ of latex fully covered with PDADMAC 428.000 in 1 mol/l NaCl. For comparison purposes the results are also shown for bare latex

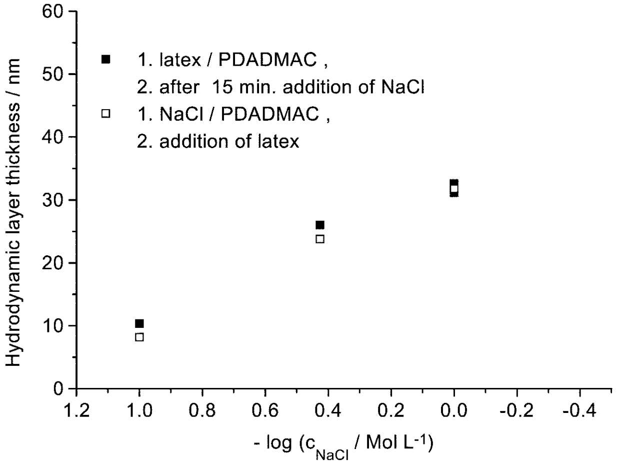

Fig. 12 Layer thickness of latex samples fully covered with PDADMAC 428.000 in 1 mol/l NaCl prepared by changing the preparation sequence

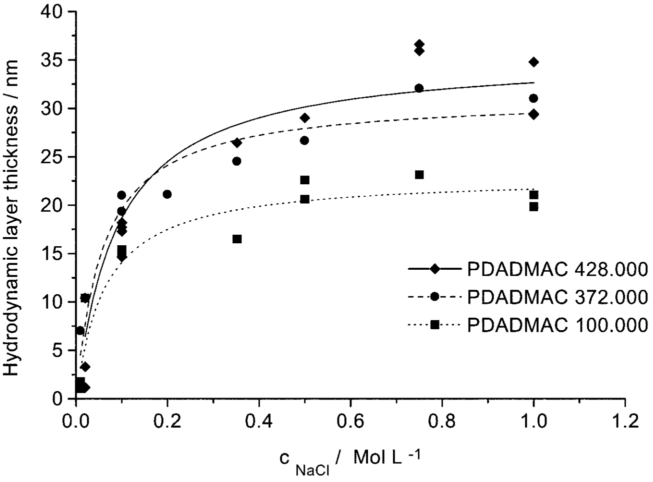

Fig. 13 Hydrodynamic layer thicknesses of adsorbed PDADMAC of different molar mass on latex as a function of the NaCl concentration

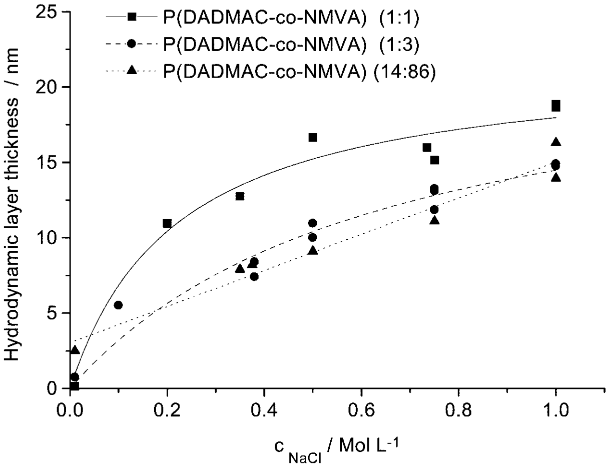

Fig. 14 Hydrodynamic layer thickness of adsorbed P(DADMAC-*co*-NMVA) of different charge density on latex as a function of the NaCl concentration

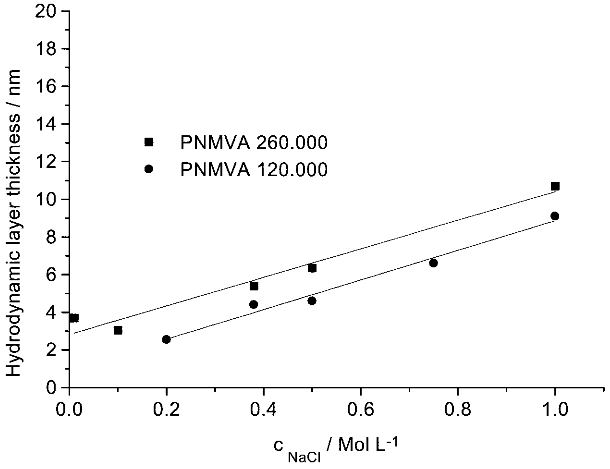

Fig. 15 Hydrodynamic layer thickness of PNMVA layers of different molar mass on latex as a function of the NaCl concentration

with increasing ionic strength. This might be due to the displacement of adsorbed polymer segments by competing electrolyte ions at high ionic strength.

Conclusions

Diffusion coefficients and zetapotentials of latex suspensions are investigated as a function of added polyelectrolyte and of ionic strength to get an insight into the flocculation and stabilization behaviour. The amounts of the negative zetapotential of the latex particles decrease with increasing polyelectrolyte concentration because of screening of the surface charges. The isoelectric point is reached at the same amount of adsorbed charges regardless of the charge density of the adsorbed polyelectrolyte. The zeta potential plateau value corresponds to the plateau adsorption. The state of flocculation of the latex particles is measured by photon correlation spectroscopy and shows flocculation if the amount of the zetapotential is smaller than 25 mV by screening of the surface charges by the adsorbed macroions.

If the surface coverage is small, mosaic flocculation can be observed. In the adsorption plateau the suspension is stabilized electrostatically in water or at low ionic strength.

At high ionic strength the charges of the adsorbed polymer chains are screened. The suspension becomes stabilized sterically by osmotic repulsion of the tails of the adsorbed macroions if the PEs are of high molar mass.

At the plateau adsorption layer thicknesses of the adsorbed polyelectrolyte layer can be measured. With increasing ionic strength, the thickness of the adsorbed layer increases in the case of PDADMAC and copolymers of P(DADMAC-*co*-NMVA) due to screening of the polymer charge and the formation of loops and tails. The homopolymers of NMVA show a small increase in layer thickness with increasing ionic strength. This might be due to the displacement of adsorbed polymer segments by competing electrolyte ions.

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