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ORIGINAL CONTRIBUTION

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Flocculation and stabilization of colloidal silica by the adsorption of poly-diallyl-dimethyl-ammoniumchloride (PDADMAC) and of copolymers of DADMAC with *N*-methyl-*N*-vinyl-acetamide (NMVA)

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Abstract The stabilization and flocculation behavior of colloidal silica-particles with cationic polyelectrolytes (PE) is investigated. The zetapotentials, diffusion coefficients and flocculation rate constants of silica particles have been measured as a function of the adsorbed amount of cationic polyelectrolytes 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 at different salt concentrations and pH-values. Very fast flocculation due to van der Waals attraction occurs if the zetapotential is small. At low ionic strength this condition occurs just below the plateau of the adsorption isotherms where the surface charges are screened by adsorbed polycations. Additionally with high molecular polycations slow mosaic flocculation is observed at lower PE concentrations. At high ionic strength fast flocculation takes place at low macroion concentration due to the screening of the surface charges by adsorbed polycations and salt ions. At medium concentrations of polycations below plateau adorption slow bridging flocculation is observed. At plateau adsorption the suspensions become stabilized up to high ionic strength. At low salt concentration charge reversal at full coverage with polycations results in electrostatic repulsion. At high ionic strength the particles are stabilized sterically due to the osmotic repulsion of the long adsorbed PE tails. Therefore macroions of high molar mass are necessary to stabilize the suspension at high ionic strength.

Key words Flocculation and stabilization – zetapotential – colloidal silica – poly(diallyl-dimethyl-ammonium chloride) – copolymers of diallyl-dimethyl-ammonium chloride and *N*-methyl-*N*-vinylacetamide – photon correlation spectrometry

Introduction

Important applications of polyelectrolytes (PE) are due to the adsorption of the macroions on surfaces [1]. Coulomb forces as well as other polar and apolar forces like van der Waals interactions are responsible for the binding. The structure of the adsorbed PE layer varies in dependence of ionic strength and pH of the solution, charge density and molar mass of the polyelectrolytes, charge density of the surface and chemical affinity between the macroions and the surface. The macroions develop an extended structure because of the mutual repulsion of the charged segments at low ionic strength of the aqueous solution. In this form they adsorb at solid surfaces dominantly influenced by the electrostatic attraction. Addition of salt ions leads to screening of the macroion charges. Therefore the macroions in solution take a coil conformation similar to that of uncharged polymers. At high ionic strength and at small amounts adsorbed polyelectrolytes adsorb in a flat structure like neutral macromolecules. With increasing coverage of the surface they form loops and tails. The adsorbed amounts in the plateau are determined by nonelectrostatic interactions. The influence of the charge densities of the macroions and of the surface is small.

Polyelectrolyte adsorption is applied for the coating of surfaces in order to protect them from external influences, e.g. electrostatic loading [1]. Additionally polyelectrolytes find use in the stabilization of colloidal systems, e.g. in food and pharmaceutical industries. The stability of macroion containing suspensions is due to the electrostatic repulsion of the polyelectrolyte covered particles and the electrostatic stabilization as well as to the increase of the viscosity.

Furthermore polyelectrolytes are applied for the flocculation of dispersions in order to separate the solid compounds from the dispersion medium [2, 3]. In these processes of phase separation Coulomb interactions play an important role but also polar and apolar forces have to be considered as driving forces.

Flocculation is observed if the surface charge of the particles is screened either by low molecular salt ions or by adsorbed macroions [2]. Especially linear polyelectrolytes with long chains and low charge densities can form polymer bridges between colloidal particles leading to bridging flocculation. Polyelectrolytes of high charge density and medium or high molar masses cause aggregation via patch or mosaik mechanism. Thereby parts of the surface of a particle change their charge signs because of the adsorption of polyelectrolytes and result in aggregation due to Coulomb-attraction between oppositely charged parts of the particle surfaces. The adsorbed macroions are then adsorbed on both particles.

Polyelectrolytes especially polyanions are used as flocculants, e.g. in waste water treatment [4] or in paper producing industries [5]. But usually the polyelectrolytes are added empirically. So we try to get rules for optimal dosages to obtain either stable suspensions or optimal flocculation, i.e. fast flocculation and large aggregates.

As model polyelectrolytes highly charged cationic poly(diallyl-dimethyl-ammoniumchloride) (PDADMAC) of different molar masses and copolymers of DADMAC with *N*-methyl-*N*-vinyl-acetamide (NMVA) of various compositions and charge densities are investigated. As substrate precipitated colloidal silica is applied which is suspended by ultrasonication. In this study the influence of the coverage of the silica surface by the cationic PE and by PNMVA at various salt concentrations and pH-values is reported. The changes of the zetapotential are compared with the state of flocculation and with the flocculation kinetics measured by the diffusion coefficients of the colloidal particles.

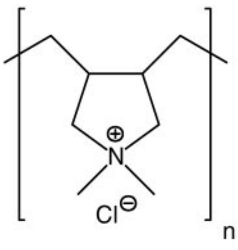
Experimental part

Materials

Precipitated silica particles are prepared by the method of Stöber et al. [6]. The characterization is carried out by photon correlation spectroscopy (PCS) [7] (Table 1), where D_{90} and D_0 are the diffusion coefficients at scattering angles of 90° and 0°, d_{90} and d_0 are the diameters of the particles calculated from D_{90} and D_0 by the Einstein–Stokes equation respectively, ρ is the density of the particles. The second moment of the distribution of the D-values is also included.

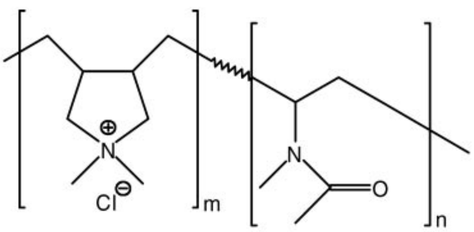
The preparation of the silica suspensions is described elsewhere [8].

Poly(diallyl-dimethyl-ammonium-chloride) (PDADMAC) **1**, copolymers of DADMAC and *N*-methyl-*N*-vinyl-acetamide (NMVA) **2**, and poly(*N*-methyl-*N*-vinyl-acetamide) (PNMVA) **3** are produced by radical polymerization [9].



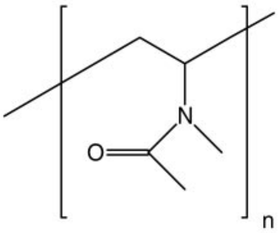
PDADMAC

1



P(DADMAC-co-NMVA) (m:n)

2



PNMVA

3

Table 1 Characterization of precipitated silica

D_{90} $[10^{12}\ \mathrm{m^2 s^{-1}}]$	D_0 $[10^{12}\ \mathrm{m^2 s^{-1}}]$	d_{90} [nm]	d_0 [nm]	Second moment [%]	ρ $[\mathrm{g\,cm^{-3}}]$
3.37	2.8	140	175	6	2.05

Their characteristics are given in Tables 2 and 3, where $[\eta]$ is the intrinsic viscosity, $\bar{M}_\mathrm{n}$ and $\bar{M}_\mathrm{w}$ are the numbers and the weight averages of the molar mass of the polymers, respectively.

All chemicals are of the highest purity grade commercially available and are used without further purification. Solutions are prepared with doubly distilled water. NaCl is employed as supporting electrolyte. The bulk pH is adjusted using either chloride acid or sodium hydroxide. The pH is measured using a Metrohm pH Meter, Model 691, equipped with a Metrohm pH Electrode, No. 6.0239.100.

Procedures

The microelectrophoretic mobilities of the silica particles are measured 15 min after addition of the silica suspension to a solution of the polyelectrolyte as described for the measurements of the adsorption isotherms [8] using a Zetamaster (Malvern Instruments). The zeta potentials (ζ) are calculated from the measured electrophoretic mobilities (μ_e) of the particles with Eq. (1), according to Henry [10]:

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

where ε is the dielectric constant, ε_0 the dielectric permittivity of vaccum, κ the Debye–Hückel screening parameter and a the radius of the particles.

For $f(\kappa a)$ we use Oshimas [11] approximation (Eq. (2)), which agrees within 1% with the exact values over the entire range of κa provided ζ is not too high.

$$f(\kappa a) = 1 + \frac{1}{2}\left(1 + \frac{2,5(1 + 2\exp(-\kappa a))}{\kappa a}\right)^{-3}. \tag{2}$$

Table 2 Molecular characterization of PDADMAC **1**

Polymer	$[\eta]$[a] $[\mathrm{ml\,g^{-1}}]$	$\bar{M}_\mathrm{n}$[b] $[10^3\ \mathrm{g\,mol^{-1}}]$	$\bar{M}_\mathrm{n}$[c] $[10^3\ \mathrm{g\,mol^{-1}}]$	$\bar{M}_\mathrm{w}$[c] $[10^3\ \mathrm{g\,mol^{-1}}]$	$\bar{M}_\mathrm{w}$[d] $[10^3\ \mathrm{g\,mol^{-1}}]$
PDADMAC 428.000	320	373	428	643	709
PDADMAC 372.000	324		372	580	574
PDADMAC 117.000	118	101	117	162	143
PDADMAC 30.000	33	31	30	44	45
PDADMAC 5.000	12	5[e]			

[a] Determined at 30 °C in 1 M NaCl.
[b] Determined by membrane osmometry.
[c] Determined by size exclusion chromatography; solvent: 0.5 M $NaNO_3$ in water.
[d] Determined by light scattering.
[e] Determined by viscosimetry.

Table 3 Molecular characterization of P(DADMAC-co-NMVA) (m:n) **2** and of PNMVA **3**

Polymer	content [mol%]	$[\eta]$[a] $[\mathrm{ml\,g^{-1}}]$	$\bar{M}_\mathrm{n}$[b] $[10^3\ \mathrm{g\,mol^{-1}}]$	$\bar{M}_\mathrm{n}$[c] $[10^3\ \mathrm{g\,mol^{-1}}]$	$\bar{M}_\mathrm{w}$[c] $[10^3\ \mathrm{g\,mol^{-1}}]$
	DADMAC:NMVA				
P(DADMAC-co-NMVA) (3:1)	75:25	73	71	74	107
P(DADMAC-co-NMVA) (1:1)	53:47	63	58	66	98
P(DADMAC-co-NMVA) (1:3)	24:76	64	51	65	92
P(DADMAC-co-NMVA) (17:83)	17:83	67		76	100
P(DADMAC-co-NMVA) (14:86)	14:86	74	79	83	121
P(DADMAC-co-NMVA) (6:94)	6:94	73		87	116
PNMVA 120.000	0:100	124	111	124	201
PNMVA 260.000	0:100	187	269	260	349

[a] Determined at 30 °C in 1 M NaCl.
[b] Determined by membrane osmometry.
[c] Determined by size exclusion chromatography; solvent: 0.5 M $NaNO_3$ in water.

To investigate the flocculation of the particles a continuous measurement of the diffusion coefficient is started straight after mixing the silica suspension with the polyelectrolyte solution at a certain pH and ionic strength. The resulting silica concentration is 0.05 g/l. Because of the small particle concentration it can be assumed that the adsorption process is much faster than the aggregation. Adsorption is finished before the particles begin to flocculate. Therefore no difference in the results is observed by changing the sequence of adding the substances.

The diffusion coefficient of the suspended particles, measured 40 min after mixing, are discussed as characteristic parameters for the state of flocculation. Small diffusion coefficients are standing for large aggregated particles.

The flocculation rate constants based on Smoluchowski second order aggregation theory [12, 13] are calculated with the method of Versmold and Härtl [14]. The calculation program is described elsewhere [15].

Results and discussion

In Fig. 1 the zetapotential of silica is shown as function of the concentration of PDADMAC 428.000. The marks at the abscissa axis indicate the PDADMAC concentrations which correspond to the plateau-values of the related adsorption isotherms. The isotherms have been obtained by polyelectrolyte titration [8].

The amount of the zetapotential of the bare silica decreases with increasing salt concentration because of the screening of the surface charges. The adsorption of the polycation also results in a decrease of the amounts of the zetapotentials with increasing concentration PDADMAC. The isoelectric point is reached at about 0.05 mg/l PDADMAC at any ionic strength. Higher polyelectrolyte concentrations change the charge sign of the polyelectrolyte covered particles. The amount of the zetapotential increases until plateau adsorption.

Theoretical treatments [16] show that at low surface coverage polyelectrolytes adsorb in a flat conformation at any ionic strength. The shear plane of the polyelectrolyte covered particles should then be outside of the adsorbed layer. Just below plateau adsorption the adsorbed macroions assume a more extended conformation depending on the salt concentration with the shear plane outside the loops but inside the tails. For all salt concentrations the isoelectric point is reached at the same polyelectrolyte concentration. Therefore we conclude that the macroions displace the low molecular salt ions. At low surface coverage the zetapotential is determined by the adsorbed amounts of polycations.

With increasing ionic strength the adsorbed amounts in the plateau rise because of the formation of loops and tails. Therefore the plateau-values of the zetapotentials increase. At very high salt concentration ($c_{\mathrm{NaCl}} = 0.1$ M) we observe a very flat zetapotential curve and a decrease of the zetapotential plateau in comparison to 0.01 M NaCl. This is attributed to the screening of the polyelectrolyte charges by the salt ions.

With PDADMAC 5.000 the zetapotential curves are similar to those with PDADMAC 428.000 (Fig. 2). This is expected because the adsorbed amounts in the plateau are

Fig. 1 Zetapotentials of silica as a function of the added concentration of PDADMAC 428.000 for various salt concentrations at pH 5.8. The open marks at the abscissa axis indicate the concentrations which correspond to the adsorption plateau

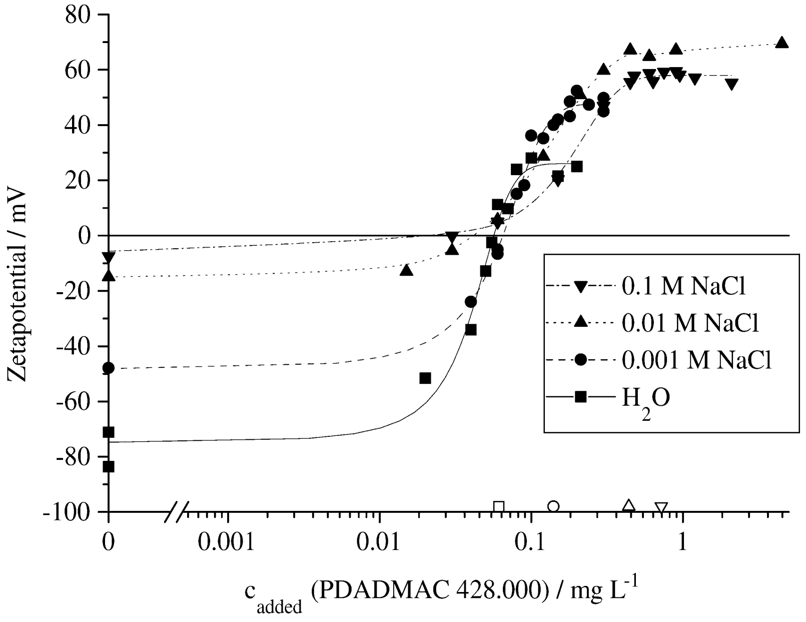
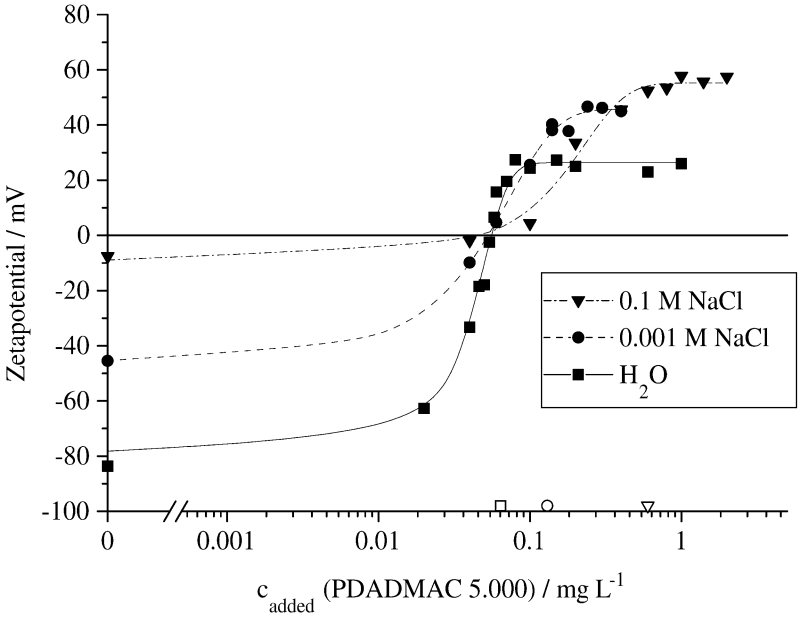


Fig. 2 Zetapotentials of silica as a function of the added concentration of PDADMAC 5.000 for various salt concentrations at pH 5.8. The open marks at the abscissa axis indicate the concentrations which correspond to the adsorption plateau



nearly the same up to an ionic strength of about 0.1 M NaCl. At any salt concentration the isoelectric point is observed at the same macroion concentration as with PDADMAC 428.000.

In 0.1 M NaCl the plateau value of the zetapotential is reached at the same concentration of PDADMAC 5.000 as with PDADMAC 428.000. For PDADMAC 5.000 this is the saturation concentration whereas for PDADMAC 428.000 this value belongs to about 70% of the plateau amount. The adsorbed amount of PDADMAC 428.000 increases beyond that due to the formation of longer tails while the zetapotential is not effected because of the screening of the additional charges by the salt ions.

In Fig. 3 the zetapotential of silica is shown as a function of the concentration of P(DADMAC-co-NMVA) (1 : 3) for various salt concentrations at pH 5.8. The shapes of these curves are similar to those observed with the silica covered with PDADMAC. As with PDADMAC 428.000 and 5.000 the isoelectric point (i.e.p.) is independent of the ionic strength. At the i.e.p. values of silica covered with copolymer and homopolymer the same amount of charges is adsorbed.

Especially at high ionic strength the zetapotential plateau values of silica covered with the copolymer 1 : 3 are smaller than those of silica covered with PDADMAC. This is attributed to the smaller amount of adsorbed charges of the adsorbed copolymers in comparison to those of PDADMAC at a certain salt concentration [8].

The adsorption of the neutral polymer PNMVA 120.000 leads to a slightly smaller value of the negative zetapotential due to the shift of the shear plane by the adsorbed layer (not shown).

In Fig. 4 the diffusion coefficients of the covered silica particles are plotted as a function of the concentration of PDADMAC 428.000 for various salt concentrations at pH 5.8. Again the open marks at the abscissa axis indicate the concentrations which correspond to the adsorbed amounts in the plateau. Up to an ionic strength of about 0.01 M NaCl the bare and with small adsorbed amount covered silica particles are stable. In water without any added salt the particles aggregate at an adsorbed amount of about 50% of the plateau value [17]. Because of the already large zetapotential of −50 mV we suppose a mosaic flocculation mechanism. With increasing adsorbed amount the polycation covered silica particles change their charge signs, and the zetapotentials become positive. At plateau adsorption the suspension is stabilized electrostatically due to the positively charged PDADMAC layer around the colloids. The same behaviour is found in 0.001 M NaCl.

At 0.01 M NaCl the suspension is destabilized at a much lower PDADMAC concentration, when the zetapotential value is smaller than 20 mV. At higher ionic strength the bare silica particles aggregate due to the screening of their surface charges by the salt ions.

With increasing PDADMAC adsorption the zetapotential becomes positive. But the suspensions are not stabilized until the adsorption plateau is reached. Bridging flocculation is supposed to be the mechanism in this case.

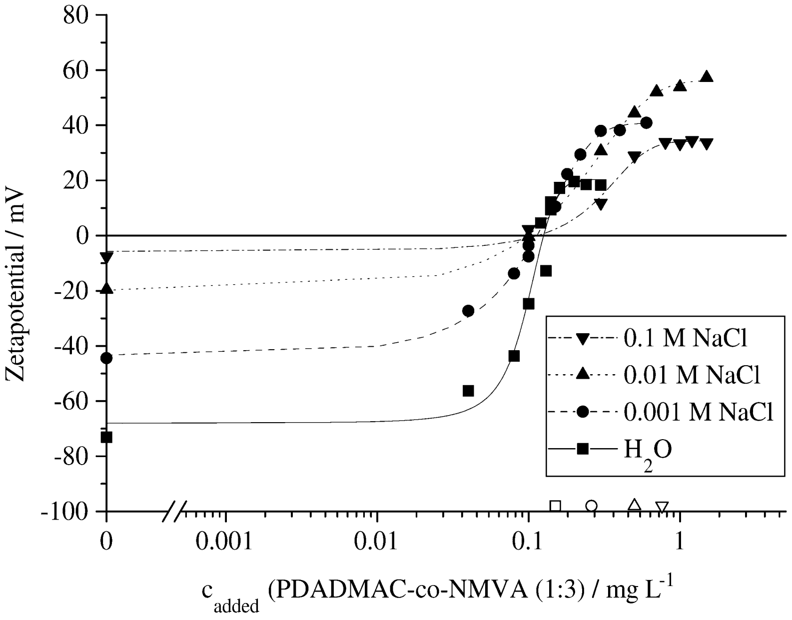


Fig. 3 Zetapotentials of silica as a function of the added concentration of P(DADMAC-co-NMVA) (1 : 3) for various salt concentrations at pH 5.8. The open marks at the abscissa axis indicate the concentrations which correspond to the adsorption plateau

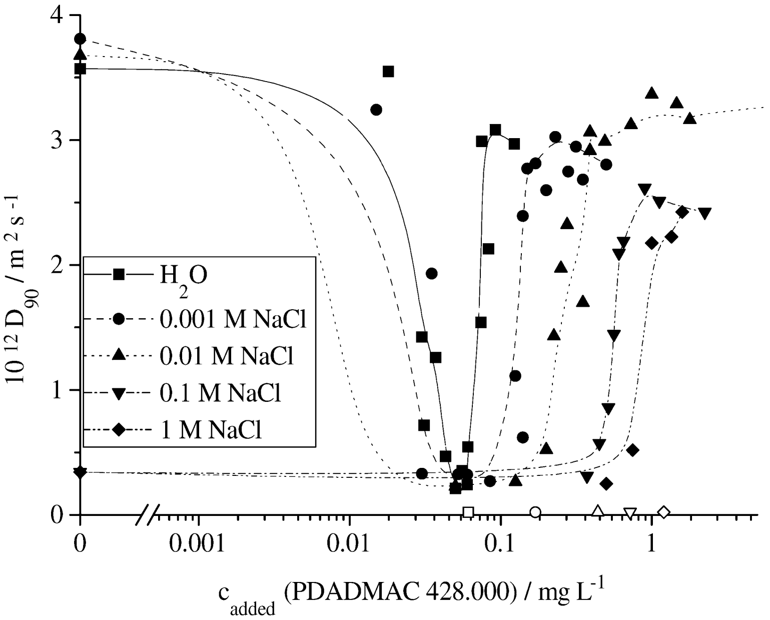


Fig. 4 Diffusion coefficients of silica as a function of the added concentration of PDADMAC 428.000 for various salt concentrations at pH 5.8. The open marks at the abscissa axis indicate the concentrations which correspond to the adsorption plateau

At plateau adsorption bridging flocculation is prevented because there is no free surface available and the osmotic repulsion of the screened polyelectrolyte segments becomes effective. The particles are stabilised sterically.

At medium ionic strength especially in 0.01 M NaCl transition from electrostatic to sterical called electrosterical stabilization might be existing [18].

The flocculation and stabilization behavior of the silica particles caused by PDADMAC 117.000 is similar to that caused by PDADMAC of the higher molar mass (Fig. 5).

In water without any added salt the flocculation range is narrower with PDADMAC 117.000 than with PDADMAC 428.000. There seems to be no mosaic flocculation with PDADMAC of the low molar mass because of the distribution of the adsorbed macroion charges over the whole solid surface [19]. Therefore flocculation due to van der Waals attraction occurs in water without any added salt at a concentration of PDADMAC 117.000 equal to about 80% of the adsorption plateau at a low amount of the zetapotential, smaller than 20 mV.

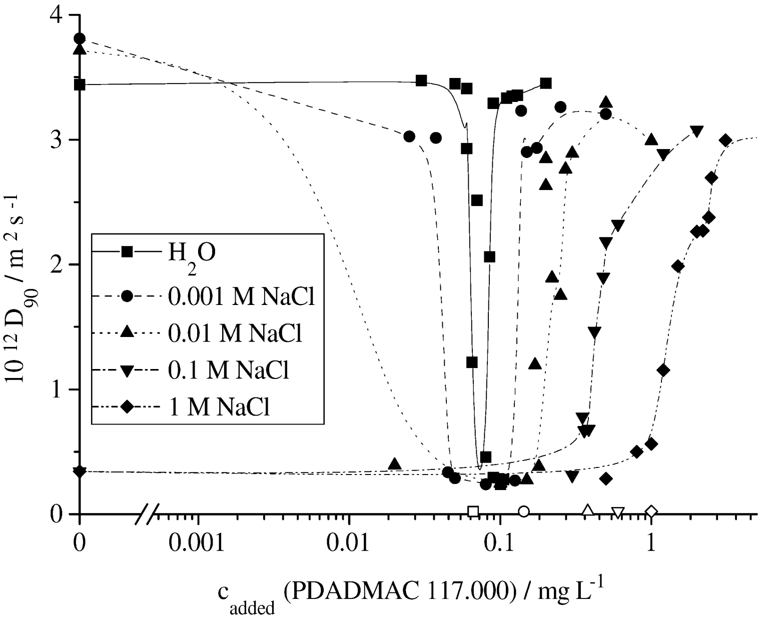


Fig. 5 Diffusion coefficients of silica as a function of the added concentration of PDADMAC 117.000 for various salt concentrations at pH 5.8. The open marks at the abscissa axis indicate the concentrations which correspond to the adsorption plateau

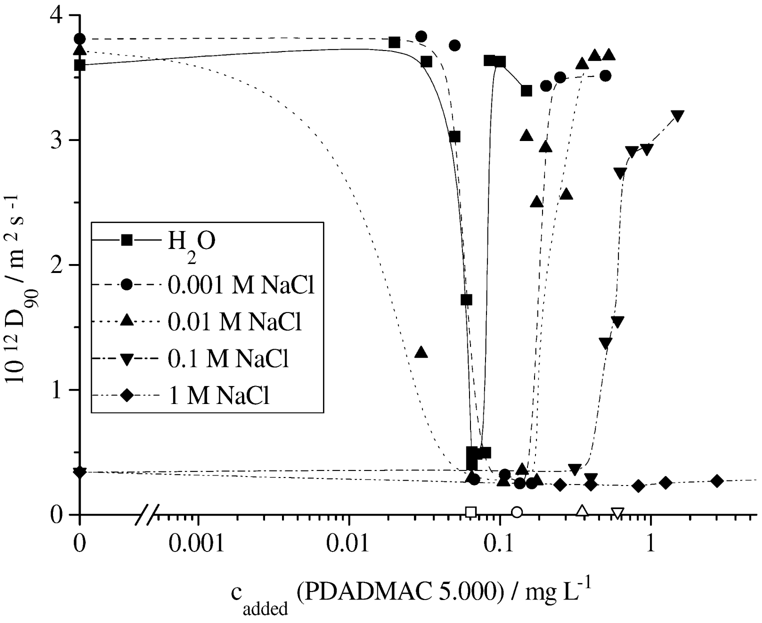


Fig. 6 Diffusion coefficients of silica as a function of the added concentration of PDADMAC 5.000 for various salt concentrations at pH 5.8. The open marks at the abscissa axis indicate the concentrations which the adsorption plateau

At an ionic strength of 0.01 M NaCl the suspension is restabilized by a PDADMAC concentration of about 70% of the adsorption plateau at a zetapotential of 40 mV.

At this potential the approximation of two particles is insufficient for the formation of bridges by the relatively short tails. So the suspension is stabilized electrosterically. In contrast to the stabilization by PDADMAC 428.000 in 1 M NaCl PDADMAC 117.000 does not stabilize the suspension by plateau adsorption but by a large excess of polyelectrolyte in solution. This might be due to a change in the structure of the adsorbed layer. At a large excess the competition of the macroions for the surface sites may lead to the formation of longer loops and tails and therefore to sterical stabilization. Additionally the increasing viscosity obtained by the larger PDADMAC concentration could prevent particle collisions and aggregation.

Similar behavior is observed with PDADMAC 31.000 (not shown). With PDADMAC 5.000 the reported trends become more efficient (Fig. 6). In 1 M NaCl the suspension

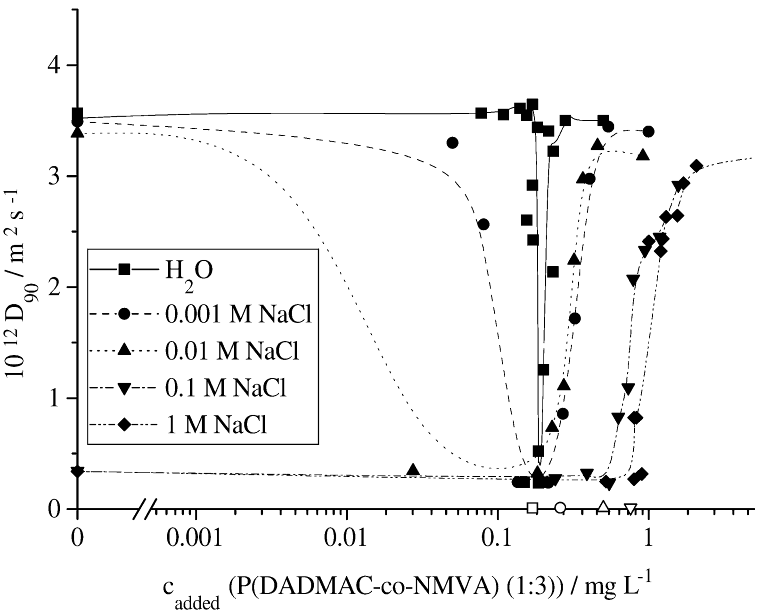


Fig. 7 Diffusion coefficients of silica as a function of the added concentration of P(DADMAC-co-NMVA) (1 : 3) for various salt concentrations at pH 5.8. The open marks at the abscissa axis indicate the concentrations which correspond to the adsorption plateau

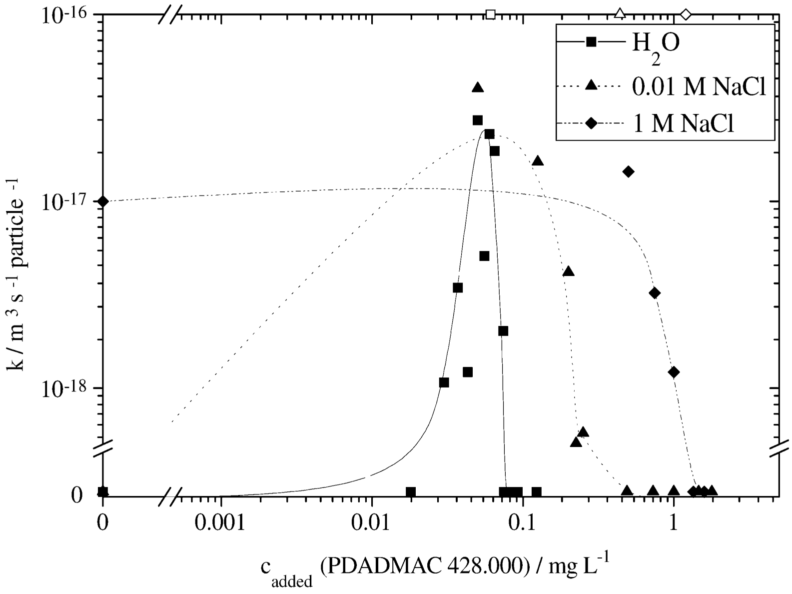


Fig. 8 Flocculation rate constants of silica as a function of the added concentration of PDADMAC 428.000 for various salt concentrations at pH 5.8. The open marks at the upper abscissa axis indicate the concentrations which correspond to the adsorption plateau

is unstable even with a very high excess of PDADMAC 5.000. The tails of this adsorbed polycation of low molar mass are not long enough to prevent flocculation by osmotic repulsion [8].

The flocculation and stabilization behavior of silica suspensions covered with P(DADMAC-co-NMVA) (1 : 1) (not shown) and (1 : 3) (Fig. 7) is very similar to that observed with PDADMAC 117.000 of nearly the same molar mass.

In water without any added salt the flocculation region is very small. At any salt concentration flocculation occurs if the amount of the zetapotential is smaller than 20 mV due to the screening of the surface charges by the adsorbed copolymer. At high salt concentrations bridging of the macroions between silica particles leads to flocculation at zetapotentials also higher than 20 mV.

In 0.01 M NaCl the particles are stabilized electrostatically at 50% of saturation, at higher ionic strength sterical stabilization is caused by osmotic repulsion of the copolymer tails at plateau adsorption.

Similar trends are observed with the copolymers 14 : 86 and 6 : 94 (not shown).

Fig. 9 Flocculation rate constants of silica as a function of the added concentration of PDADMAC 5.000 for various salt concentrations at pH 5.8. The open marks at the upper abscissa axis indicate the concentrations which correspond to the adsorption plateau

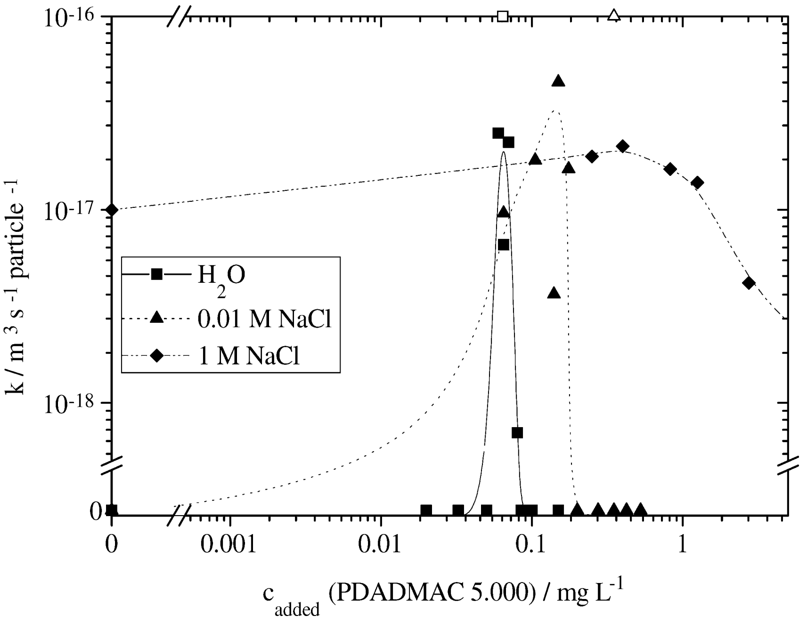
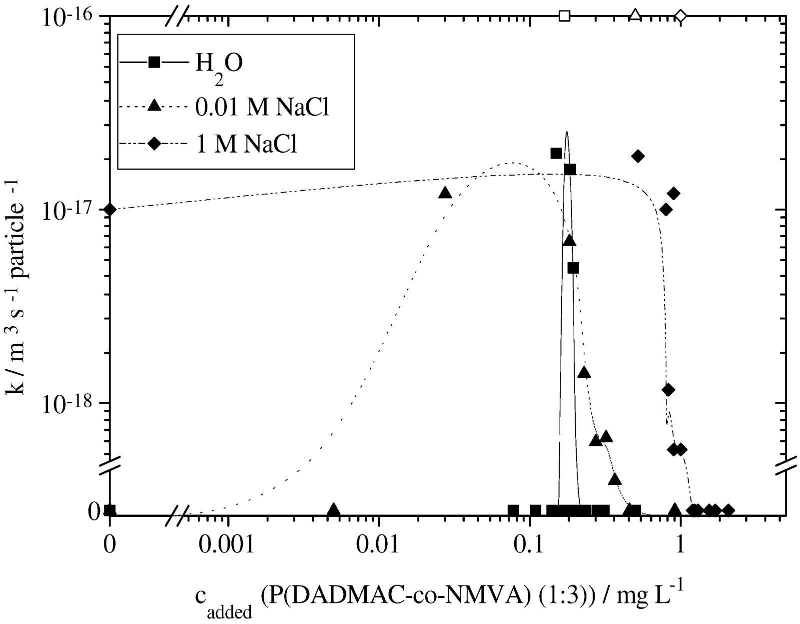


Fig. 10 Flocculation rate constant of silica as a function of the added concentration of P(DADMAC-co-NMVA) (1:3) for various salt concentrations at pH 5.8. The open marks at the upper abscissa axis indicate the concentrations which correspond to the adsorption plateau



Suspensions containing the neutral polmers PNMVA 120.000 and 260.000 are stable at any polymer concentration up to a salt concentration of 0.01 M NaCl due to the electrostatic repulsion of the particle surface charges (not shown). At higher ionic strength the particles flocculate at coverages below plateau adsorption because of the screening of the surface charges by the salt ions. At plateau adsorption the suspensions are stabilized sterically.

Figures 8–10 show the flocculation rate constants of the silica particles as a function of the concentration of PDADMAC 428.000, 5.000 and of the copolymer P(DADMAC-co-NMVA) (1:3), respectively, at different ionic strengths and pH 5.8. At the top abscissa axis the PE concentrations corresponding to the adsorption plateaus at different salt concentration are marked.

At those polyelectrolyte concentrations where the flocculation is accomplished by van der Waals attraction, i.e. at a zetapotential value between -20 and $+20\,\mathrm{mV}$, the flocculation is very fast and the evaluated flocculation rate constant is larger than the maximal flocculation constant predicted by Smoluchowski with 6×10^{-18} m^3 s^{-1} particle^{-1}. In the physical sense such high rates of flocculation seem to be produced by erroneous evaluation of the experimental data. The PCS measuring device and the evaluation procedure is not suited perfectly for aggregation processes of very large rate [20]. Fast flocculation is observed in water by adsorption of PDADMAC at about 80% of plateau adsorption and in 1 M NaCl below plateau adsorption due to the screening of the surface charges. At full coverage with PDADMAC of high molar mass and with copolymer the suspensions become stable also in 1 M NaCl.

In 1 M NaCl strong screening of the surface charges should lead to very fast aggregation. At plateau adsorption a sharp decrease of the flocculation rate is observed due to sterical stabilization. Only with low molar mass PDADMAC 5.000 no stabilization occurs because the osmotic repulsion of the short tails is too weak. With an excess of PDADMAC 5.000 in the solution the aggregation rate becomes smaller. This can be explained by the increase of the viscosity of the suspension and the resulting decrease of collisions of the particles.

If the flocculation is caused by mosaic like adsorption, e.g. with PDADMAC 428.000 in water without added salt at 50–80% of plateau adsorption, or by bridging flocculation, e.g. in 0.01 M NaCl at PE concentrations resulting in zetapotentials larger than 20 mV, the aggregation rate becomes much smaller than the Smoluchowski value.

A similar flocculation and stabilization behavior with the same trends is observed at any explored pH value (pH 2, 5.8 and 10.5).

Conclusions

The zetapotentials, diffusion coefficients and rates of flocculation of silica suspension are investigated as a function of added polyelectrolyte concentration and of amount adsorbed, of ionic strength and of pH in order to get an insight into the flocculation and stabilization behavior.

The amounts of the negative zetapotentials of the silica particles decrease with increasing salt concentration as well as 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 ionic strength and of the charge density of the adsorbed polyelectrolyte. The plateau value of the zetapotential is reached at plateau adsorption. This zetapotential plateau rises with increasing salt concentration due to the increasing adsorbed plateau amounts. At high ionic strength the zetapotential plateau decreases due to the screening of the charges of the adsorbed macroion segments.

The state of flocculation of the silica suspension is determined by the diffusion coefficient of the silica particles measured by photon correlation spectroscopy. Aggregation is observed if the amount of the zetapotential is smaller than 20 mV at screening of the surface charges either by the salt ions or by the adsorbed polyelectrolytes. Additionally at low ionic strength mosaic flocculation can be observed at about 50–80% of surface saturation with macroions of long chain length. At high ionic strength flocculation can occur at zetapotentials higher than 20 mV by bridging. In the adsorption plateau the suspensions are stabilized electrostatically at low ionic strength, electrosterically at medium ionic strength and sterically at high ionic strength. The steric stabilization by osmotic repulsion of the tails of the adsorbed polyelectrolytes needs macroions of long chain length.

The aggregation is very fast and diffusion controlled at macroion adsorption resulting in very low zetapotentials and in flocculation by van der Waals attraction. Bridging and mosaic flocculation are much slower because repulsive potentials between the particles exist.

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