Macromol. Symp. ***126,*** *173–188 (1997)*

POLYELECTROLYTE ADSORPTION AND STABILIZATION OF SILICA-SUSPENSIONS

Doris Bauer, Erwin Killmann*

Lehrstuhl für Makromolekulare Stoffe, Institut für Technische Chemie,
TU München, Lichtenbergstraße 4, D-85747 Garching

Abstract: The adsorption of cationic polyelectrolytes on colloidal silica-particles is investigated. The polyelectrolytes poly(diallyl-dimethyl-ammoniumchloride) PDADMAC of different molar mass have been used. The adsorbed amount is influenced by the ionic strength and pH of the suspension and the molar mass of the macromolecule. The adsorption determines the zetapotential of the covered particles. The electrostatic interaction between the particles as well as the structure of the adsorbed polyelectrolytes play an important role in the stabilization and flocculation behaviour of the polyelectrolyte covered suspensions.

INTRODUCTION

To influence the stability of colloidal particles by adsorbed polymers and polyelectrolyte layers is of great scientific and technological significance. Polyelectrolytes are widely used, e.g., as flocculants in water treatment, in the processing of ores or as stabilizers of dye-dispersions (Ref. 1,2). The adsorption of polyelectrolytes onto charged surfaces depends not only on the chemical and molecular structure of the macroions but also on their electrochemical character and the surface charge density of the substrate (Ref. 3). Electrostatic interactions between the polymer segments and the adsorbent and between the polymer segments themselves, which are strongly dependent on the ionic strength and on the pH of the solution, influence the conformation of the adsorbed macromolecules and the thickness of the adsorbed layer (Ref. 4). The structure of this layer and the electrostatic charge of the polymer covered particles determine the interaction between them and as a result of this the flocculation behaviour (Ref 5,6,7).

© 1998 Hüthig & Wepf Verlag, Zug CCC 1022-1360/98/$ 10.00

In this work we investigate the influences of the molecular weight of highly charged cationic poly(diallyl-dimethyl-ammonium-chloride) (PDADMAC), of the ionic strength and of the pH of the solution on the adsorption on negatively charged colloidal silica particles. We compare this results with flocculation characteristics and zetapotential data in order to get insight into the stabilization and flocculation mechanism of the investigated system.

EXPERIMENTAL PART

Materials

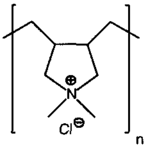
Precipitated silica particles were prepared by the method of Stöber et al. (Ref. 8). The characterization was carried out by photon correlation spectroscopy (PCS) (see Tab. 1), where D_{90} and D_0 are the diffusion coefficients at a scattering angle of 90° and 0°, d_{90} and d_0 are the diameters of the particles calculated from D_{90} and D_0 by the Einstein-Stokes-equation (Eq. 1), ρ is the density of the particles. The surface charge density was measured by potentiometric titration as well as by polyelectrolyte adsorption (see Fig. 2 and the following discussion).

Tab. 1. Characterization of precipitated silica

D_{90} $10^{12}\cdot m^2s^{-1}$	D_0 $10^{12}\cdot m^2s^{-1}$	d_{90} nm	d_0 nm	second moment %	ρ $g\,cm^{-3}$
3,37	2,8	140	175	6	2,05

To prepare a 1 g/L silica suspension, 50 mg of precipitated silica were weighed into a 100-mL beaker and 30 mL of doubly distilled water were added. After ultrasonification for 15 min the suspension was filled into a 50-mL glass measuring flask and shaken by hand. After standing for about 16 hours in order to let metall particles settle down, adsorption, flocculation or zetapotential measurements were accomplished.

The poly(diallyl-dimethyl-ammonium-chloride)s (PDADMAC)s **1** were produced by Dr. W. Jaeger of the Fraunhofer Institut für Angewandte Polymerforschung, Teltow.



1

Their characteristics are given in Tab. 2, where [η] is the intrinsic viscosity, M_n and M_w are the number and the weight average of the molar mass of the polymers respectively.

Tab. 2. Molecular characterization of PDADMAC **1**

Polymer	[η] $mL \cdot g^{-1}$	M_n a) 10^3 g mol^{-1}	M_n b) 10^3 $g \cdot mol^{-1}$	M_w b) 10^3 $g \cdot mol^{-1}$	M_w c) 10^3 $g \cdot mol^{-1}$
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 d)			

a) determined by membrane osmometry

b) determined by size exclusion chromatography

c) determined by light scattering spectroscopy

d) determined by viscosimetry

All chemicals were of the highest purity grade commercially available and were used without further purification. Solutions were prepared with doubly distilled water.

NaCl was employed as the supporting electrolyte. The bulk pH was adjusted using either hydrochloric acid or sodium hydroxide. The pH was measured using a Metrohm pH Meter, Model 691, equipped with a Metrohm pH Electrode, No. 6.0239.100.

Procedures

Surface charge - pH curves of silica in doubly distilled water were determined at room temperature (23 ± 2 °C) using an automatic titration setup of Metrohm. For the measurements 50 mL of a 10 g/L silica suspension, prepared as described above, were purged with nitrogen for at least 30 min. The silica suspension was titrated between pH 3 and pH 10 using 0,01 M NaOH or 0,01 M HCl. Blank titrations in the absence of silica were performed additionally. The blanks were subtracted from titration data in the presence of silica in order to calculate the surface charge density.

Adsorption isotherms were measured at room temperature (23 ± 2 °C) using the depletion method. 1 mL of the silica-suspension was added to 9 mL of a polyelectrolyte solution of certain concentration at different pH and ionic strength and shaken by hand. After 12 hours silica was separated from the solution at 2500 rpm in a Heraeus Labofuge A. The concentration of the supernatand polyelectrolyte was determined by polyelectrolyte titration with the potassium salt of polyvinylsulphate using toluidine blue as indicator (Ref. 9, 10). The titration could be accomplished at a salt concentration smaller than 0,05 mol/L. At higher ionic strength the supernatant solution had to be dialyzed before measuring in order to reduce the salt concentration.

The hydrodynamic layer thicknesses and the state of flocculation of the silica suspensions were determined by measuring the diffusion coefficients of uncovered and covered particles by photon correlation spectroscopy (PCS) using an argon ion laser of Spectraphysics and an autocorrelator (system 4700) of Malvern Instruments. The scattering angle for the PCS measurements was usually 90°.

The layer thicknesses were measured at 25 °C, 1 h after the addition of 1 mL of a silica dispersion to 1 mL of a mixture of polyelectrolyte and salt. The resulting concentration of silica was 0,05 g/L. The hydrodynamic layer thicknesses were obtained by applying the Einstein-Stokes equation (Eq. 1) to the diffusion coefficients of the pure and modified particles and subtracting the radii from each other.

$$a = \frac{kT}{6\pi\eta D} \qquad (1)$$

where a is the radius of the particles, k the Boltzmann constant, T the temperature in K, η the dynamic viscosity of the suspension and D the diffusion coefficient of the particles.

To investigate the flocculation of the particles a continuous measurement of the diffusion coefficient was started straight after mixing the silica suspension with the polyelectrolyte solution at a certain pH and ionic strength. The resulting silica concentration was 0,05 g/L. Because of the small particle concentration it could be assumed that the adsorption process was much faster than the aggregation. Adsorption was finished before the particles began to flocculate. Therefore no difference in the results was observed by changing the sequence of adding the substances.

The diffusion coefficients 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 microelectrophoretic mobilities of the silica particles were measured 15 min after addition of the silica suspension to a solution of the polyelectrolyte as described for the measurements of the adsorption isotherms using a Zetamaster (Malvern Instruments). The zeta potentials (ζ) were calculated from the measured electrophoretic mobilities (μ_e) of the particles with Eq. 2, according to Henry (Ref. 11):

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

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

For f(κa) we used Oshimas (Ref. 12) approximation (Eq. 3), which agrees within 1 % with the exact values over the entire range of κa provided ζ is not too high.

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

RESULTS AND DISKUSSION

All adsorption isotherms of PDADMAC onto precipitated silica are of the high affinity character (see Fig. 1). This entails that the adsorbed amounts of PDADMAC below the maximum are in equilibrium with undetectably low bulk concentrations, i.e., in the adsorption isotherm these points coincide with the ordinate axis. The steep increase of the isotherms is caused by great electrostatic and chemical attraction between the polycations and the oppositly charged silica particles.

At low ionic strength the adsorption of the polyelectrolyte onto the oppositely charged surface is dominated by the electrostatic attraction. In solution the macroions assume a voluminous elongated conformation because of the mutual electrostatic repulsion of the charged chain segments. This also leads to a flat conformation of the polymer at the solid interface. The polyvalent ions have to assume the role of the counterions and are kept in the double layer near the surface. So at low ionic strength the adsorbed amount of saturation on the substrate is dominantly determined by charge compensation (Ref. 13).

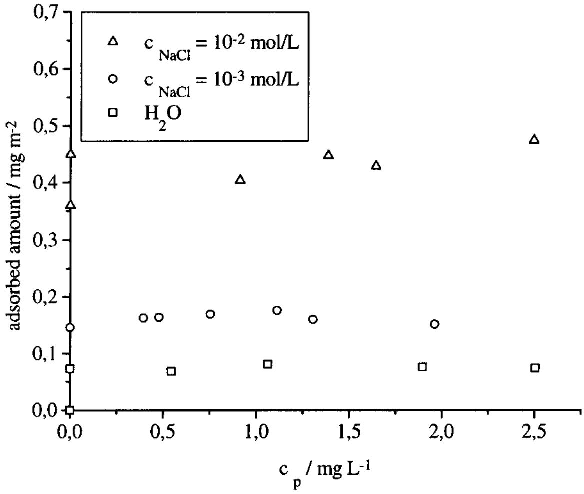


Fig. 1. Adsorption isotherms of PDADMAC 30.000 on silica at pH 5,8 for various salt concentrations

Several authors (Ref. 9, 10, 14) claim that the surface charge density could be determined by adsorbing strong polyelectrolytes. They calculate the surface charge from the amount of adsorbed polyelectrolyte charge assuming charge neutralization. We have recognized that this does not work in the case of silica.

In Fig. 2 we compare potentiometric data with adsorption isotherms as a function of pH. Two ordinates are plotted so that the data are demonstrated as adsorbed amounts in mg/m^2 or as surface charge densities in C/m^2. Because of the dissoziation of the SiOH-groups of silica the surface charge density increases with pH. The charge density measured by potentiometric titration is smaller than that obtained by polyelectrolyte adsorption until a pH value of about 9. The charges at the bare silica surface have larger distances in comparison to the charges of the polycation. Therefore we postulate that during the adsorption process of the polyelectrolytes further dissoziation of the SiOH-groups occurs to compensate the charges of the adsorbed polyelectrolytes in order to minimize the free energy of the system. The adsorption of PDADMAC also takes place at pH 2 - 4, where the bare silica particles are uncharged as obtained from potentiometric titration data. Because of this result we assume that the driving force for polyelectrolyte adsorption is not only the surface charge compensation but also additional chemical interactions between the silica substrate and the polyelectrolyte. This idea is supported by results of Goloub et. al (Ref. 15), who obtained an increase of the surface charge density of Aerosil by surfactant adsorption at low salt concentration. They suppose that the charge adjustment is strongly influenced by the presence of the hydrocarbon tails of the surfactant molecules. At pH values higher than 9 the charge density measured by potentiometric titration doesn't reveal the real surface situation because of the dissociation of SiOH-groups inside the porous surface (Ref. 16). At this pH the zetapotential doesn't increase any more.

In Fig. 2 we can also see that the adsorption is independent of the molar mass of the PDADMAC indicating a flat conformation as expected.

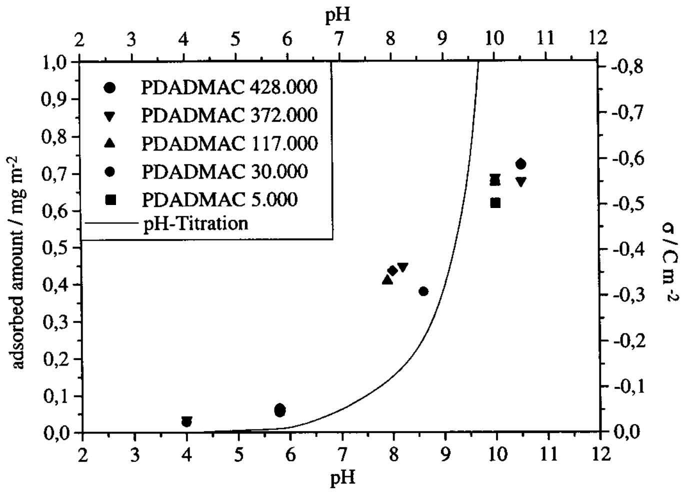


Fig. 2. Adsorbed amounts of PDADMAC of different molar mass (points) and surface charge density obtained by polyelectrolyte adsorption (points) and potentiometric titration (curve) as a function of the pH of the solution without the addition of NaCl

In Fig. 3 the zetapotential of silica at pH 5,8 without any additional salt ions is plotted as a function of the concentration of PDADMAC 5.000 and 428.000. The concentrations are related to concentrations corresponding to the adsorbed amounts in the plateau ($c_{saturation}$). No difference between the two polymers is observed. The zetapotential of the bare silica particles is about -70 mV. With increasing adsorption of PDADMAC the negative value of the zetapotential decreases. At about 80 % of saturation we observe an electrokinetic charge reversal. At the adsorption plateau, $c/c_{saturation} = 1$, the zetapotential is positiv and does not increase further.

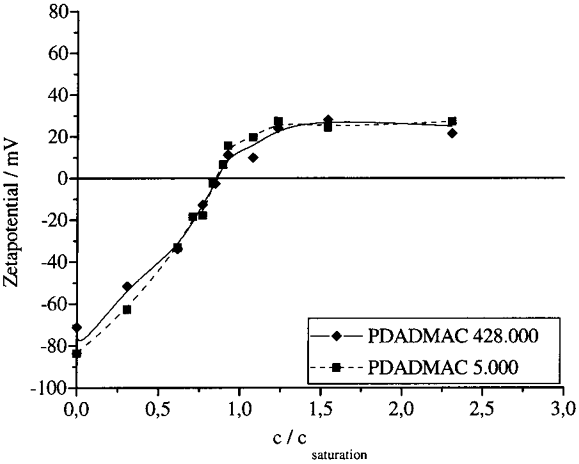


Fig. 3. Zetapotential of silica as a function of the concentration of PDADMAC of different molar mass at pH 5,8 without any added salt

In Fig. 4 the diffusion coefficents of the silica particels at pH 5,8 without any additional salt ions are plotted as a function of the concentration of added PDADMAC 428.000 and 5.000 again normalized to $c_{saturation}$. At low concentrations of PDADMAC the suspension is stable. At about 50 % of saturation for PDADMAC 428.000 and 80 % for PDADMAC 5.000 flocculation occurs. At this concentration the zetapotential, which indicates the repulsion between the particles, is reduced. The suspension is restabilized at concentrations higher than $c_{saturation}$ because of the positive potential between the particles.

With PDADMAC 428.000 and PDADMAC 272.000 (not shown) flocculation starts already at about 50 - 60 % of saturation. This may be due to a mosaic-like charge compensation between two covered particles (Ref. 17). In case of the low molar mass PDADMAC 5.000 the double layer behaves as if it is smeared out. Flocculation starts at higher coverage because of small electrokinetic repulsion due to charge compensation.

The same general features are observed for the flocculation behaviour of PDADMAC at pH 10,5.

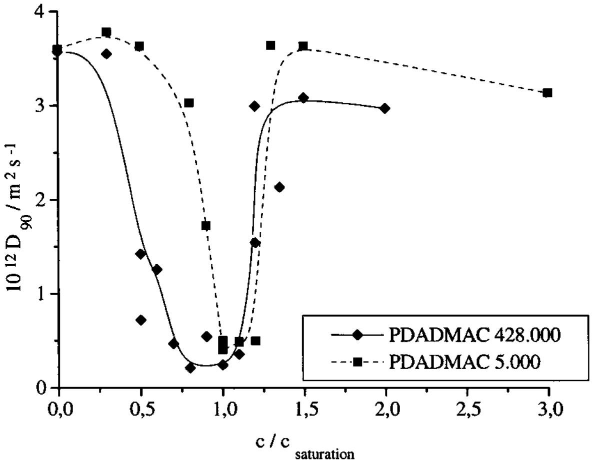


Fig. 4. Diffusion coefficient of silica as a function of the concentration of PDADMAC of different molar mass at pH 5,8 without any added salt

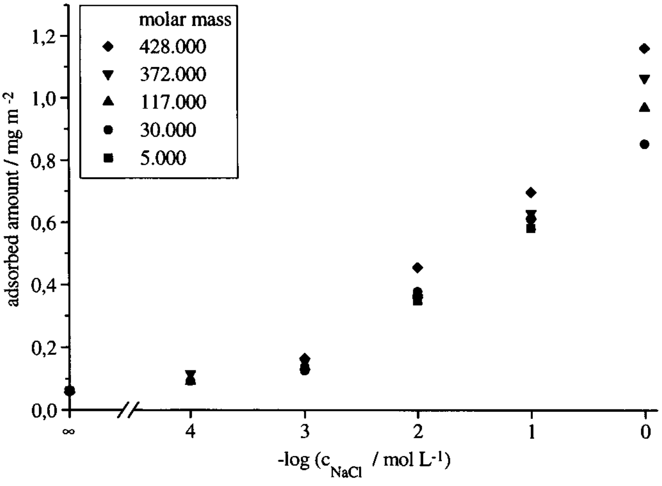


Fig. 5. Adsorbed amounts of PDADMAC of different molar mass as a function of the salt concentration at pH 5,8

In Fig. 5 the data for PDADMAC adsorption at pH 5,8 as a function of the ionic strength are presented. At low salt concentrations the polymer molecules assume a flat conformation at the surface because of the mutual repulsion of the segment charges. The adsorbed amounts are dominated by electrostatic interactions between the polyelectrolytes and the surface. As a consequence molar mass effects are nearly absent. With increasing salt concentration the electrostatic contributions are screened. Loops and tails are formed leading to an increase of the adsorbed amount. The adsorption becomes influenced by the chemical interaction between the surface groups and the adsorbing polymer segments in contrast to pure electrosorption, where the adsorbed amount should decrease with increasing ionic strength (Ref. 18). At very high ionic strength beginning with 0,1 M the adsorbed amounts increase with molar mass due to the formation of longer tails by the high molar mass macromolecules.

An experimental evidence for this explanation is given in Fig. 6 where the hydrodynamic layer thicknesses in the plateau of the isotherms are drawn as a function of salt concentration. With increasing ionic strength the hydrodynamic layer thicknesses for all investigated polymers increase because of the screening of the polyelectrolyte segment charges by the NaCl ions. At high salt concentration the hydrodynamic thicknesses of the adsorbed layer rise with the molar mass of the macroion because the longer polymer molecules form more extended tails than shorter ones.

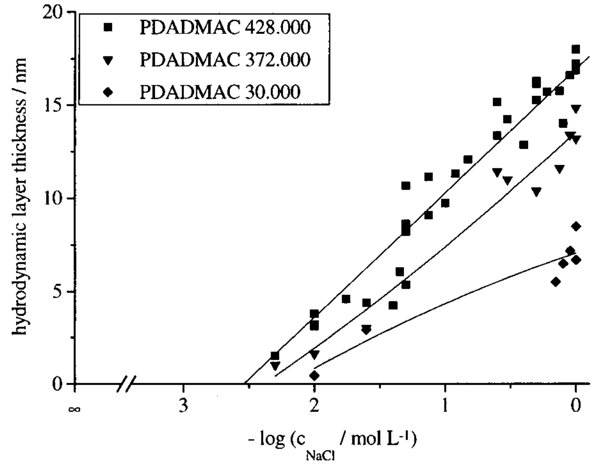


Fig. 6. Hydrodynamic layer thicknesses of some PDADMAC as a function of salt concentration at pH 5,8

The adsorbed amount has large influence on the zetapotential and on the flocculation behaviour of the particles.

Fig. 7 shows the zetapotentials of silica as a function of the added concentration of PDADMAC 428.000 for various salt concentrations at pH 5,8. With increasing salt concentration the value of the negative zetapotential of the bare silica particles decreases because of the screening of the surface charge by salt ions. A decrease is also observed with increasing adsorption of PDADMAC. At about 80 % of the plateau value in H_2O, 30 % in 10^{-3} M NaCl and 5 % in 0,1 M NaCl we observe an electrokinetic charge reversal. The plateau amounts of the corresponding systems are indicated on the abscissa. At the adsorption plateau the zetapotential is positive and doesn't increase further.

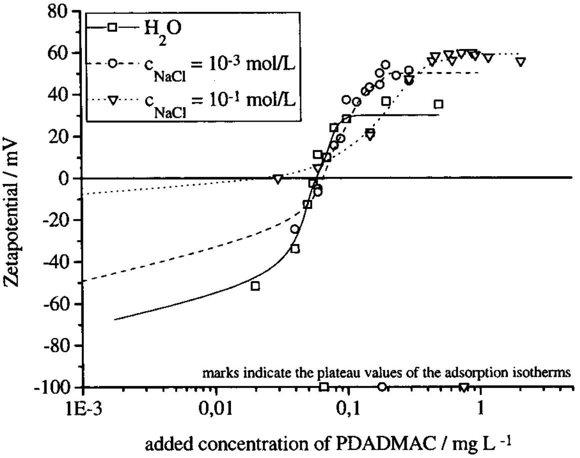


Fig. 7. Zeta potential of silica as a function of the concentration of PDADMAC 428.000 for some salt concentrations at pH 5,8

In Fig. 8 some flocculation data of silica as a function of the added concentration of PDADMAC 428.000 for various salt concentrations at pH 5,8 are presented. At each investigated salt concentration flocculation occurs when the zeta potential of the particles is reduced to about -20 mV. Then the electrostatic repulsion of the silica particles is to small to prevent approach and aggregation. The surface charges of the particles may be screened by salt ions as well as by the adsorbed polycations. In the absence of polyelectrolyte the bare silica particles coagulate at a salt concentration $c_{NaCl} \geq 0,1$ M.

With increasing adsorption of PDADMAC the zetapotential becomes positive, but the suspensions are not restabilized until the surface is saturated. This behaviour may be due to some kind of bridge formation of PDADMAC molecules between two particles, supported by the screening of the segment charges by the salt ions and the resulting reduced rigidity of the polycations. At saturation the suspension is stabilized sterically because of the osmotic segment repulsion of the screened polyelectrolytes.

With the exception of PDADMAC 5.000 the other investigated PDADMAC show the same behaviour concerning zeta potential and flocculation of silica.

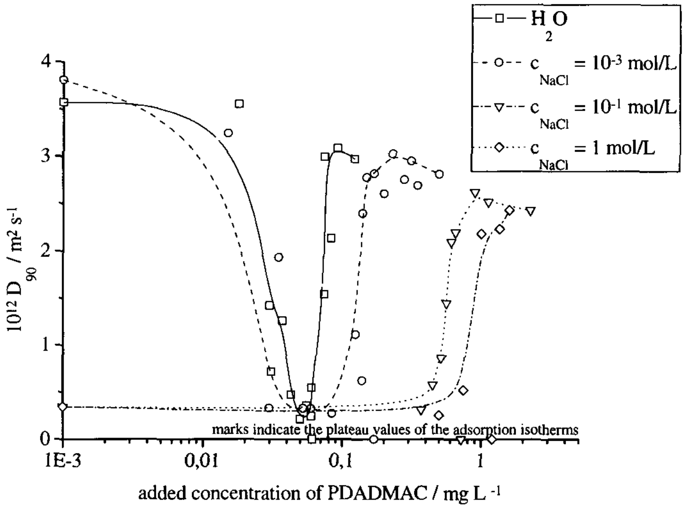


Fig. 8. Diffusion coefficient of silica as a function of the concentration of PDADMAC 428.000 for various salt concentrations at pH 5,8

The influence of the adsorption of PDADMAC 5.000 on the zeta potential and on the diffusion coefficients of silica is shown in Fig. 9 and Fig. 10 for various salt concentrations at pH 5,8. There is no difference between the plots of zeta potential against PDADMAC concentration for PDADMAC 428.000 (Fig. 7) and 5.000 (Fig. 9). Even the flocculation behaviour at $c_{NaCl} \leq 0{,}1$ M is the same (Fig. 8 and Fig. 10). But at 1 M NaCl PDADMAC 5.000 doesn't restabilize silica at any polyelectrolyte concentration. This is refered to the small hydrodynamic layer thickness (see Fig. 6) of PDADMAC 5.000 at high salt concentration in comparison to the larger macromolecules. PDADMAC 5.000 can not stabilize the suspension sterically at high ionic strength.

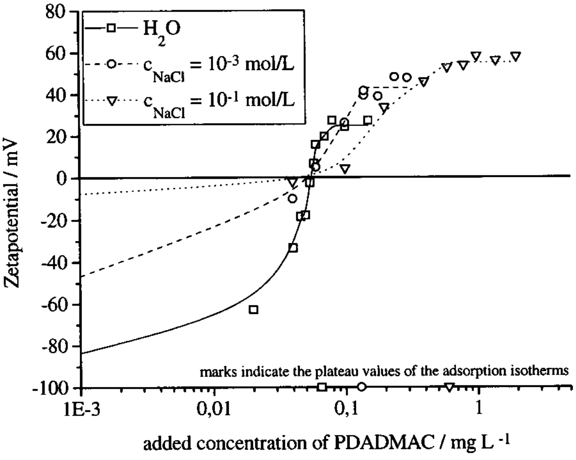


Fig. 9. Zeta potential of silica as a function of the concentration of PDADMAC 5.000 for some salt concentrations at pH 5,8

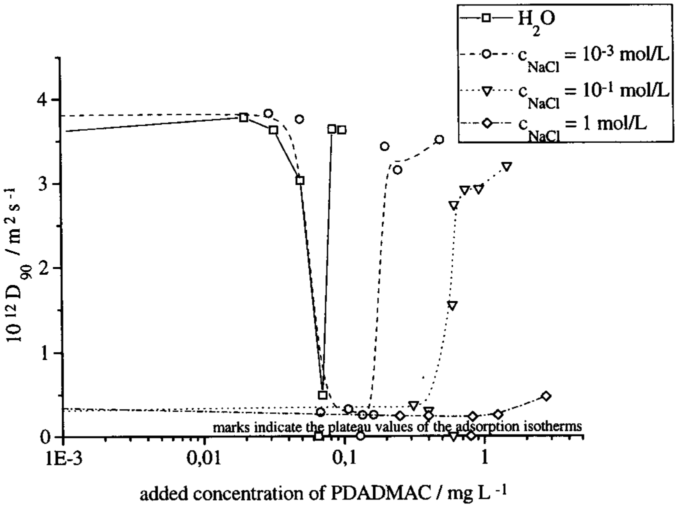


Fig. 10. Diffusion coefficient of silica as a function of the concentration of PDADMAC 5.000 for some salt concentrations at pH 5,8

Adsorption experiments of PDADMAC on silica as a function of ionic strength are also carried out at different pH values (see Fig. 11).

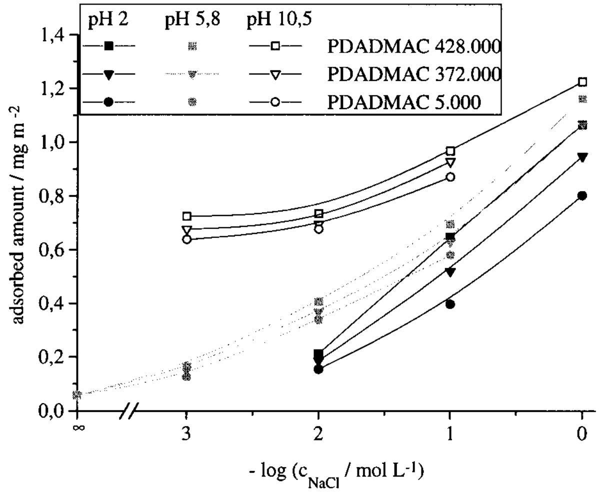


Fig. 11. Adsorbed amounts of various PDADMAC as a function of the salt concentration at pH 2, pH 5,8 and pH 10,5

As shown in Fig. 2 at low ionic strength the adsorbed amounts of PDADMAC increase with pH. Rising salt concentration leads to an increasing adsorption at any pH because of the formation of loops and tails. At pH 2 the steepest increase is observed. Because of the low surface charge at pH 2 the polyelectrolyte is not bounded as strongly as at high surface charge at pH 10,5. So the adsorbed macroions can easier form loops and tails at pH 2 than at pH 10,5. At low pH the smaller number of binding surface sites also leads to a larger increase of the adsorbed amount with molar mass, occuring already in 0,1 M NaCl solution.

The electrokinetics and the flocculation behaviour are almost the same at any pH value with the exception of high ionic strength. At pH 2 PDADMAC of all molar masses restabilize silica at high coverage, also PDADMAC 5.000. This may be due to the favoured formation of longer loops and tails. In contrast, even PDADMAC 372.000 cannot restabilize the suspension in 1 M NaCl at pH 10,5. Only the highest molar mass polyelectrolyte PDADMAC 428.000 can form tails which are long enough to stabilize the suspended particles of high surface charge density at pH 10,5 sterically.

CONCLUSIONS

We have shown that the adsorption of PDADMAC depends on ionic strength, pH, charge density of the substrate and on the molar mass of the cationic polyelectrolyte.

The adsorbed amount is of significant influence on the zetapotential of the particles. If the zetapotential is reduced by screening the surface charge either by salt ions or by adsorbed polyelectrolytes the colloidal particles aggregate. At very low ionic strength the suspensions are restabilized by the adsorption of polyelectrolyte if the zetapotential becomes highly positive according to the electrokinetic charge overcompensation. At medium and high ionic strength the particles are stabilized sterically by osmotic repulsion of the adsorbed polymers. This is only possible if the hydrodynamic layer thickness is large enough. For low molar mass macroions and for polyelectrolyte concentrations smaller than the concentrations corresponding to the adsorbed amounts in the plateau the particles flocculate despite of a high zetapotential. We refer this to the formation of some polymer bridges between the particles supported by the presence of salt ions.

ACKNOWLEDGEMENTS

The authors are indebted to the Arbeitsgemeinschaft Industrieller Fördervereinigungen e.V. (AIF) and D. Bauer thanks the Stiftung Stipendien-Fonds des Verbandes der chemischen Industrie e.V. for financial support.

Especially we are grateful to Dr. Werner Jaeger at the Fraunhofer Institut für Angewandte Polymerforschung, Teltow for the preparation and characterization of the polyelectrolytes.

REFERENCES

1 „Stabilization of Colloidal Dispersions by Polymeradsorption“ (T. Sato, R. Ruch, Eds.), Marcel Dekker, New York 1980

2 J. Laskowski, in Surf. Colloid Sci. **12,** 315 (1982) (E. Matijevic, Ed.), Plenum Press, New York

3 M.A. Cohen Stuart, *J. Phy. France* **49,** 1001 (1988)

4 F. Onabe, *J. App. Polym. Sci.* **22,** 3495 (1978)

5 S. Bárány, A.A. Baran, I. Solomentseva, L. Velichanskaya, in „Macroion Characterization“ (K.S. Schmitz, Ed.), American Chemical Society, Washington, DC 1994

6 S. Bárány, A.A. Baran, D. Gregory, *Colloid Journal* **58,** 9 (1996)

7 D.H. Napper, *J. Colloid Interface Sci.* **58,** 390 (1977)

8 W. Stöber, A. Fink, E. Bohn, *J. Colloid Interface Sci.* **26,** 62 (1968)

9 H. Terayama, *J. Polymer Sci.* **8,** 243 (1952)

10 D. Horn, *Progr. Colloid & Polym. Sci.* **65,** 251 (1978)

11 D.C. Henry, *Proc. Roy. Soc. Ser. A* **133,** 106 (1931)

12 H. Oshima, *J. Colloid Interface Sci.* **168,** 269 (1994)

13 M.A. Cohen Stuart, G.J. Fleer, J. Lyklema, W. Norde, J.M.H.M. Scheutjens, *Adv. Colloid Interface Sci.* **34,** 477 (1991)

14 J. Kötz, K.-J. Linow, B. Phillip, L.P. Hu, O. Vogel, *Polymer* **27,** 1574 (1986)

15 T.P. Goloub, L.K. Loopal, B.H. Bijsterbosch, *Langmuir* **12,** 3188 (1996)

16 J. Lyklema, *J. Electroanal. Chem.* **18,** 341 (1968)

17 J. Lyklema, G.J. Fleer, *Colloids Surfaces* **25,** 357 (1987)

18 T.K. Wang, R. Audebert, *J. Colloid Interface Sci.* **121,** 32 (1987)