

Surface Modification by Polyelectrolyte Complexes: Influence of Modification Procedure, Polyelectrolyte Components, and Substrates

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ABSTRACT: The complex formation between oppositely charged polyelectrolytes (PEL) and their interaction with negatively charged silicate powders have been investigated. The PEL studied were poly(ethyleneimine)s, poly(diallyldimethylammonium chloride), and copolymers of maleic acid and propylene or styrene. PEL complexes (PEC) are formed by a combination of aqueous PEL solutions containing definite amounts of charges (n_- , polyanion; n_+ , polycation). The point of zero charge of the PEC depended on the selection of different PEL. Changing the molar ratio n_-/n_+ permitted the preparation of nonstoichiometric PEC (nPEC). Preformed cationic nPEC were used to modify the silicate powders (variation A). The nPEC were able to generate a strongly cationic surface charge in most cases. It is concluded that the preformed PEC adsorbs roughly with the same stoichiometry on the surface as in solution. Changes of the mechanism and a strong enhancement of the attainable cationic surface charge density could be observed by a two-step modification procedure (variation B). The influence of the surface charge density of the untreated substrates on the extent of surface modification for both variations is also described. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 41–50, 1997

Key words: adsorption; interface; polyelectrolyte; polyelectrolyte complex; substrate

INTRODUCTION

Complex formation between anionic and cationic polyelectrolytes (PEL) has been known for a long time. The driving force in this kind of complexation is mainly the interaction between the oppositely charged macromolecules, but hydrophobic interaction, van der Waals forces, and hydrogen bonding can also play a role in complex stabilization. The stoichiometry, that is, the molar ratio of anionic to cationic groups of these compounds, is important for describing these PEL complexes (PEC). One can find 1 : 1 stoichiometric polysalts, but recent publications have given more attention

to the deviation from this 1 : 1 stoichiometry,^{1–8} which has been stressed for the first time in the work of Tsuchida.⁹ The group of Kabanov developed novel concepts for synthesizing nonstoichiometric PEC (nPEC)^{10,11} by using component PEL differing strongly in the molecular weight. Kabanov et al. characterized PEC with hydrophobic and hydrophilic parts. The charges of the hydrophilic segments should be able to interact with ionic groups on surfaces to modify the properties (surface charge, wettability, hydrophobicity) and the colloid chemical behavior (zeta potential) of the substrates.

The properties of the PEL and of the model substrates determine the results of surface modification. The stoichiometry of the formed PEC is mainly determined by the nature, the density, and distribution of the ionic groups in the poly-

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mers, and by the reaction conditions. Obviously, the charge, the surface charge density, and the porosity of the substrates have an effect on the stability and the extent of surface modification.

This work is directed toward two goals, first, to reach a steady charge modification of the substrate particles by PEC and, second, to understand the mechanism of PEC deposition. Therefore, we examined the influence of modification procedures of different PEL components and substrates. The importance of the surface charge density of the substrates is also discussed. From this general perspective, structure–property relationships of PEC surface modification may be deduced.

EXPERIMENTAL

Methods

PEL Titration

The charge quantification of the stock PEL solutions, of the colloid PEC, and of the silicate samples was carried out by means of PEL titration with an oppositely charged polyion, having a neutralizing effect on the charge (Particle Charge Detector, PCD 02; MÜTEK GmbH, Herrsching, Germany). This method of characterization allowed the quantitative determination of the content of the PEL in solution as well as the detection of the changes in the specific surface charge of the modified particle. Further information of the setup is given elsewhere.⁵ The surface charge density of the substrates was calculated in the following manner:

$$\begin{aligned} & \text{surface charge density in mC m}^{-2} \\ &= \frac{\text{specific surface charge in mC g}^{-1}}{\text{specific surface area in m}^2 \text{ g}^{-1}} \quad (1) \end{aligned}$$

PEL titration was carried out in Millipore water (Millipore GmbH, Eschborn, Germany) pH 7.

Electrophoretic Measurements

The electrophoretic mobility of the prepared colloid PEC and of the bare and modified silicate samples was measured with a commercial Zeta-MasterS microelectrophoresis apparatus (Malvern Instruments Limited, Malvern, U.K.). The electrophoretic measurements were made in 10^{-3}

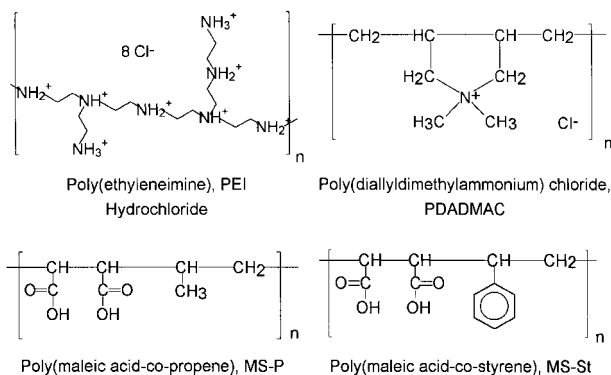


Figure 1 Polycations and polyanions.

mol L⁻¹ potassium chloride at 22°C and at a pH of about 7.

Materials

The cationic PEL were poly(diallyldimethylammonium) chloride (PDADMAC; $M_w \approx 78,000$), provided by the Institute of Chemical Technology (Berlin, Germany), and poly(ethyleneimine)s (PEI) Polymin P and Polymin G 100¹²). The PEI were BASF products and had a molecular weight of $\approx 500,000$ for Polymin P and $\approx 4,000$ for Polymin G 100. All cationic samples were branched polyions (Fig. 1). PDADMAC, because of the quaternary ammonium group, is a strong polycation, that is, the degree of dissociation of the ionic groups is nearly independent over a wide pH range.

The PEI are weak polycations, and the protonation of the primary, secondary, and tertiary amine groups, in the ratio of approximately 1 : 2 : 1, strongly changes with pH. An increase in pH decreases the amount of polycationic charges on the polymer. The anionic PEL used were poly(maleic acid-co-propylene) (MS-P; $M_w \approx 23,000$) and poly(maleic acid-co-styrene) (MS-St; $M_w \approx 58,000$). They were obtained from Leuna AG (Germany). A water-soluble product of the polyanion was reached by the hydrolysis of maleic anhydride copolymer with sodium hydroxide. The degree of dissociation of the carboxylic group is pH dependent, and the copolymers of the maleic acid have to be assumed to be weak PEL.

Stock PEL solutions (10^{-2} mol L⁻¹) were prepared by dissolving the powdered polyanions or by dilution of the highly concentrated polycations with Millipore water. For adjusting the pH of all stock polymer solutions to pH = 7, 0.1 mol L⁻¹ HCl for the polycations and 0.1 mol L⁻¹ NaOH for

Table I Characteristics of the Bare Fine Particles Sikron and Silicic Acid

Characteristic	Sikron	Silicic Acid
Specific surface area ^a (m ² g ⁻¹)	5	16.3
Specific surface charge ^b (mC g ⁻¹)	-170	-241
Surface charge density (mC m ⁻²)	-34	-14.8
Zeta potential ^b (mV)	-52	-49

^a BET measurement.^b 10⁻³ mol L⁻¹ KCl, pH 7.

MS-P and MS-St were used. Further electrolytes were not added to all solutions. By PEL titration the amount of cationic (n_+) or anionic (n_-) charges in the stock solutions was measured and used to calculate the stoichiometric ratio n_-/n_+ of the PEC.

The silicate substrates were Cristobalit fine quartz powder SIKRON SF 6000 (Quarzwirke GmbH Frechen, Germany) and silicic acid (Merck Darmstadt, Germany). The characteristics of the fine particles are listed in Table I. As indicated by BET (Brunauer, Emmett, Teller) measurements (N₂ adsorption), the silicic acid and the Sikron are nonporous.

The ratio of the surface charge density for both substrates is Sikron : silicic acid = 2.3 : 1. The measured zeta potentials of both unmodified silicate substrates are very negative and differ only slightly. Water used for the preparation of the solutions was deionized by a Milli-Q reagent-grade water system (Millipore GmbH, Eschborn, Germany).

Procedures: Preparation of PEC

PEC were prepared by the combination of aqueous PEL solutions containing definite amounts of charges (n_- = polyanion, n_+ = polycation). A constant amount of polycationic charges ($n_+ = 0.24$ mmol) was diluted in 50 mL of Millipore water at pH = 7. The desired amount of polyanion solution (n_- = variable) in 50 mL of Millipore water (pH = 7) was slowly added to the continuously stirred polycation solution (Figure 2). n_-/n_+ is the calculated ratio of anionic to cationic charges and a measure of the complex stoichiometry. Changing the molar ratio n_-/n_+ permitted us to prepare nPEC having differences in the residual amount of charge and the zeta potential. The nonstoichiometric,

stable, and colloiddally dispersed PEC prepared as above was used for the following modification procedure.

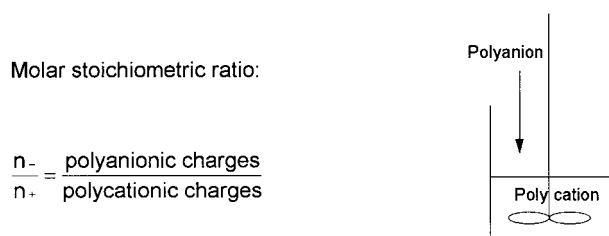
Modification Procedures

Variation A

Colloiddally stable nPEC, which mainly carry excess cationic charges, were used to interact with negatively charged silicate powder and to generate a strongly cationic surface charge. Fixed amounts of the previously prepared nPEC solutions (50 mL of nPEC solution was given to 0.5 g of Sikron and 250 mL of nPEC solution was given to 0.5 g of silicic acid) were contacted with the substrates (Figure 3). PEC was added in excess so that after adsorption, it could be detected in the supernatant. The mixture of the nPEC and the substrate was stirred for 10 min. The modified silicate powders and the solution were separated by centrifugation. All modified substrates were washed with Millipore water and dried in air at room temperature. The surface-modified samples were investigated by measuring the depletion of nPEC and by detecting the specific surface charge and the zeta potential of the modified particles.

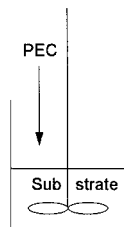
Variation B

A fixed amount of polycation solution was contacted with the substrates. After an adsorption time of 10 min, the polyanion solution was slowly added to the polycation-substrate dispersion. After another 10 min, the substrate was separated from the supernatant and treated as mentioned before. All conditions in relation to the added amounts of PEL and to the differences in the added amount between both substrates were kept constant, as described in Variation A and PEC preparation.

**Figure 2** Preparation of PEC.

Substrate modification
with previously prepared
PEC:

Variation A



Substrate modification
with preadsorbed
polycation:

Variation B

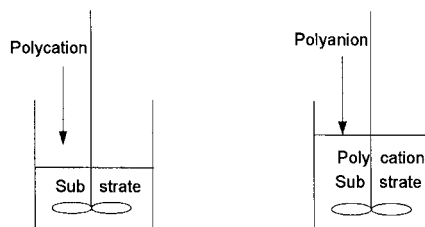


Figure 3 Modification procedures, variations A and B.

RESULTS AND DISCUSSION

PEC Formation

The results of electrophoretic measurements and PEL titration of the PEC of PDADMAC, Polymin P, and Polymin G 100 with MS-St are illustrated in Figure 4. The points of zero charge show a significant dependence on the stoichiometric ratio of anionic to cationic groups. The molar ratio n_-/n_+ of the noncharged complex dispersion is shifted from 0.85 for MS-St/PDADMAC to 0.6 for MS-St/Polymin P. The isoelectric point of the complex MS-St/PDADMAC is situated at the molar ratio $n_-/n_+ = 0.85$. We believe that the flexibility of the PDADMAC chain and the position of the pendant-

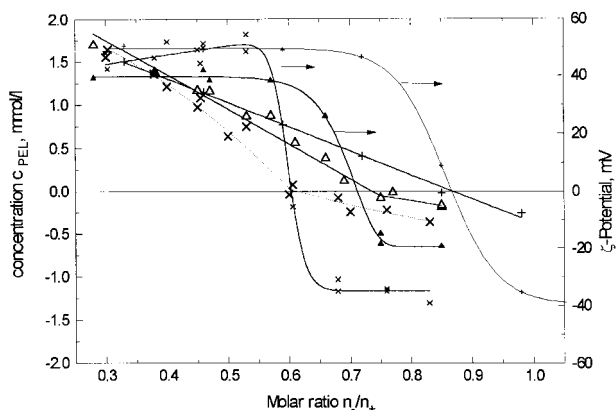


Figure 4 Dependence of zeta potential and net content of PEL on the molar ratio n_-/n_+ for the PEC systems of: MS-St/Polymin P ($x \cdots x$), MS-St/Polymin G 100 ($\Delta - - \Delta$), and MS-St/PDADMAC ($+ - - +$).

type charges in the “side chain” lead to good arrangement of the opposite charge centers. Consequently, a noncharged complex closer to the molar ratio $n_-/n_+ = 1$ was found.

The highly branched PEI differed in size and can be assumed to be rigid particles¹³ with an approximately spherical shape.¹⁴ If the PEI adsorb on the surface, they roughly maintain the size and shape that they had in solution. The different isoelectric points of the PEC of MS-St/Polymin G 100 at $n_-/n_+ = 0.75$ and of MS-St/Polymin P at $n_-/n_+ = 0.6$ could be explained in the context of the difference between the size and the steric hindrance of rearrangement processes during complex formation. Since the polyanion solution is slowly added to the PEI solution, in the initial stage, several polycations are bound to one polyanion molecule. For Polymin G 100, the progressive addition of polyanion leads to some free rearrangement processes because of the small size of Polymin G 100. Polymin P is more voluminous and more hindered during complex formation. It reacts with the polyanion, but the forming PEC is less flexible for rearrangements and further polyanions are preferentially bound on the surface. The PEC particles become uncharged (zeta potential 0), even though cationic charges had to be in the inner parts of the PEC.

However, the stiffness of the PEI particles and the backbone-type charge centers of the PEI in comparison to the pendant-type charge centers of PDADMAC seem to be responsible for the different isoelectric points of the PEC made from PDADMAC and PEI. Table II, shows the isoelec-

Table II Isoelectric Points of PEC of Different PEL Components

PEC	Isoelectric Point of PEC at Molar Ratio n_-/n_+
MS-St/Polymin P	0.60
MS-P/Polymin P	0.60
MS-St/PDADMAC	0.85
MS-P/PDADMAC	0.85
MS-St/Polymin G 100	0.70
MS-P/Polymin G 100	0.85

tric points of all PEL combinations. No changes in the isoelectric points of the systems with PDADMAC and Polymin P were found, although the polyanion was varied and it can be concluded that these polycations have a dominant influence on the stoichiometry of the PEC. A shift of the isoelectric point of the PEC with Polymin G 100 from 0.75 to 0.85 is observed when MS-St is substituted by MS-P. It might be reasonable to assume that the large phenyl group in the copolymer decreases the mobility of the PEC during formation more strongly than the small methyl group in MS-P. These data indicate that the isoelectric points of the PEC are dependent on the selection of the PEL and that steric differences are responsible for the conformation of the PEC and differences in electrokinetic behavior.

The stability of the colloidal dispersions of cationic PEC ($n_-/n_+ = 0.46$) was investigated within 48 h. All PEC systems were found to be stable. No changes were detected in the results of PEL titration, zeta potential, and particle size. However, in the system of MS-St/Polymin G 100, a slight decrease of the particle diameter and an increase of the zeta potential were measured. Coagulation and settlement of PEC could not be observed.

Adsorption of Preformed PEC: Variation A

Influence of Different PEL Components

The dependence of zeta potential and surface charge density of modified Sikron powder on the molar ratio n_-/n_+ and on the PEC components is presented in Figure 5. The zeta potential curves show that the unmodified negative Sikron (-52 mV) was recharged by the deposition of the non-stoichiometric cationic PEC. High surface charge densities in the magnitude of $+40$ – $+60$ mC/m²

could be reached by the PEC of PEI. It is important to stress here that PDADMAC only in the PEC of PDADMAC/MS-St is able to recharge the substrate and to produce cationic surface charge densities. In the PDADMAC adsorption experiment,⁵ the polycation was unable to introduce a positive surface charge density. It can be assumed that the flexibility of the PDADMAC was restricted by the interaction of MS-St. This might also be responsible for the different shape of the surface charge density curves of MS-St/PDADMAC and of MS-St/Polymin P.

However, in all cases, the zeta potential and the surface charge density of the modified powders become 0 when the isoelectric point of the respective PEC systems is reached. At higher n_-/n_+ , negative zeta potentials and negative surface charge densities of the modified Sikron were found.

The surface charge density and zeta potential of PEC-modified Sikron powder and the zeta potential of the PEC of MS-St/Polymin P are compared in Figure 6. The shape of the zeta potential curves of the PEC is very similar to that of the modified Sikron. From that, it can be concluded,

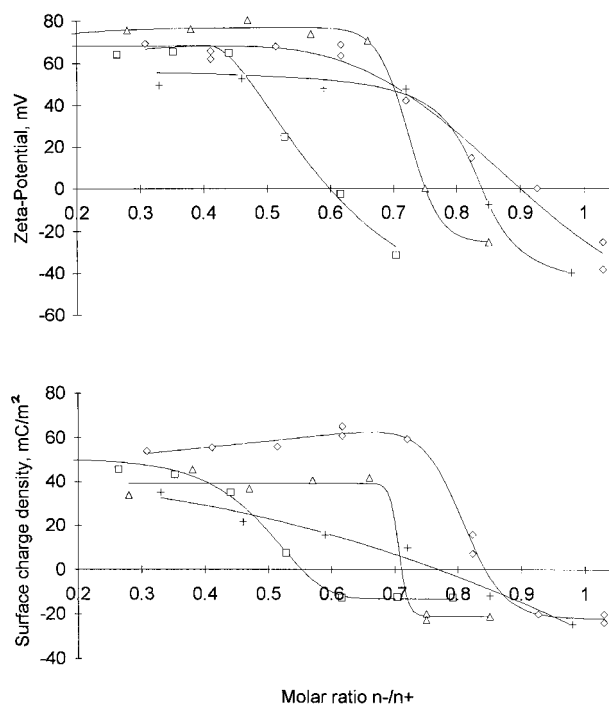


Figure 5 Dependence of zeta potential and surface charge density of modified Sikron on the molar ratio n_-/n_+ and on the PEC components, variation A: (Δ) MS-St/Polymin G 100, ($+$) MS-St/PDADMAC, (\square) MS-P/Polymin P, (\diamond) MS-P/Polymin G 100.

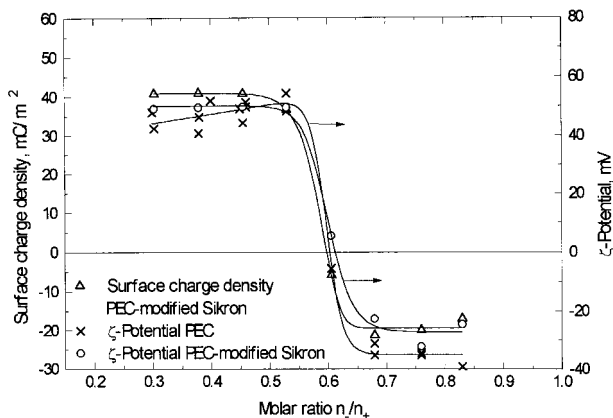


Figure 6 Comparison of surface charge density and zeta potential of modified Sikron powder with the zeta potential of PEC, MS-St/Polymin P system, variation A.

that the preformed PEC adsorbs from solution nearly stoichiometrically unchanged. The composition of the PEC during deposition remains constant, and the properties of the closed polymer layer completely mask the properties of the untreated substrate. The same behavior of complexes of Polymin SN and lignin sulfonate adsorbed on sulfite fibers was found by Ödberg and Ström.¹⁵

Influence of Different Substrates

In Figure 7, the attainable cationic surface charge densities on Sikron and on silicic acid are compared. Obviously, PEC modification of Sikron generated higher surface charge densities, as in the case of the modification of silicic acid. The difference in the magnitude is roughly 2 : 1 and is con-

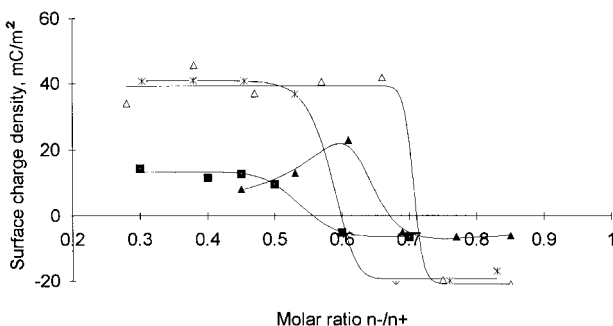


Figure 7 Comparison between the reachable cationic surface charge density on Sikron (open symbols) and silicic acid (black symbols), variation A: (* and ■) MS-St/Polymin P, (△ and ▲) MS-St/Polymin G 100.

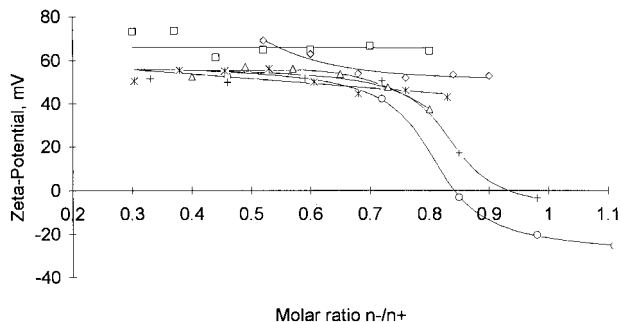


Figure 8 Dependence of the zeta potential of the modified Sikron on the molar ratio n_-/n_+ of the PEC, variation B: (*) MS-St/Polymin P, (△) MS-St/Polymin G 100, (□) MS-P/Polymin P, (◇) MS-P/Polymin G 100, (+) MS-St/PDADMAC, (○) MS-P/PDADMAC.

sistent with the surface charge densities of the untreated substrates. The above relation on the surface charge density of the untreated substrates confirms that the number of “anchoring points” on the surface is responsible for the order of surface modification. On the other hand, only by the application of PEC were we able to introduce cationic surface charges in the case of Polymin P and to increase the surface charge density of the modified silicic acid.⁵ For Polymin G 100 adsorption, a surface charge density of the modified silicic acid of $+4.7 \text{ mC m}^{-2}$ could be reached, whereas for PEC of MS-St and Polymin G 100, the surface charge density rose to about $+20 \text{ mC m}^{-2}$.⁵

Modification with Preadsorbed Polycation: Variation B

Influence of Different PEL Components

The dependence of the zeta potential and surface charge density of the modified Sikron on the molar ratio n_-/n_+ of the PEC due to modification by variation B is presented in Figures 8 and 9. Obviously, the zeta potential curves show significant differences between the PEC systems of PDADMAC and PEI. The zeta potential curves of Sikron modified with PEC of PEI are positive over the entire range, and it can be assumed that probably the surface structure of the PEC layer is changed. The competition of both polyanion and substrate for the PEI is stronger than in the case of PDADMAC. In the systems with PDADMAC, the zeta potential curves of the modified powder after variations A and B have almost the same shape. We believe that in the PDADMAC systems, even if variation B is applied, the complex formation predominates,

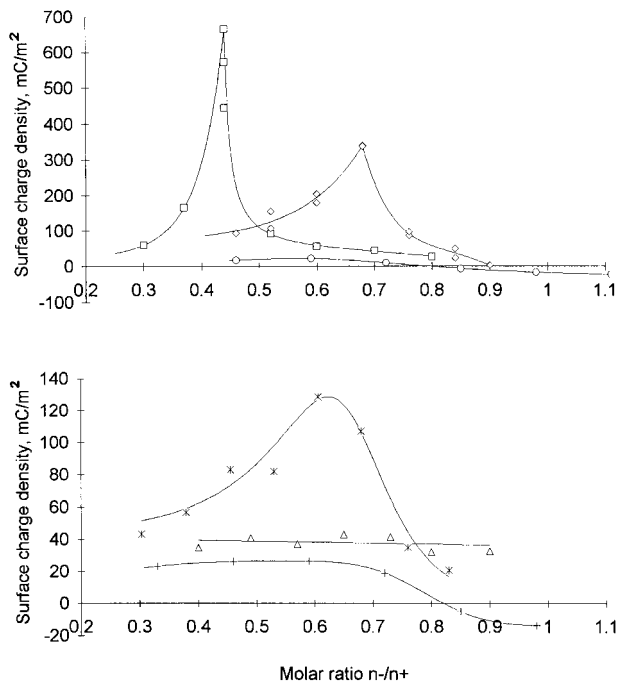


Figure 9 Dependence of the surface charge density of the modified Sikron on the molar ratio n_-/n_+ of the PEC, variation B: (\square) MS-P/Polymin P, (\diamond) MS-P/Polymin G 100, (\circ) MS-P/PDADMAC, ($*$) MS-St/Polymin P, (\triangle) MS-St/Polymin G 100, ($+$) MS-St/PDADMAC.

that is, the PDADMAC has a higher affinity for the polyanion than for the substrate, and that after PEC formation in solution, the PEC adsorbs on the substrate.

A big enhancement of the attainable cationic surface charge density of the modified powders was observed when variation B is applied to the systems of MS-P/Polymin G 100 and MS-P/Polymin P. The surface charge density could reach values up to 13 times higher than that due to the application of variation A, but the three measured surface charge densities of MS-P/Polymin P at the same molar ratio also indicate that the enhancement is subject to high fluctuations. The enhancement of the MS-St/Polymin P system was only three times higher, and in the MS-St/Polymin G 100 system, no reinforcement compared with variation A could be detected. A comparable amplification effect in relation to the co-adsorption of several phenols and surfactants was described by Schwuger et al.^{16,17}

In Figures 10 and 11, the surface charge density and zeta potential of modified Sikron powder and the zeta potential of PEC of the MS-P/

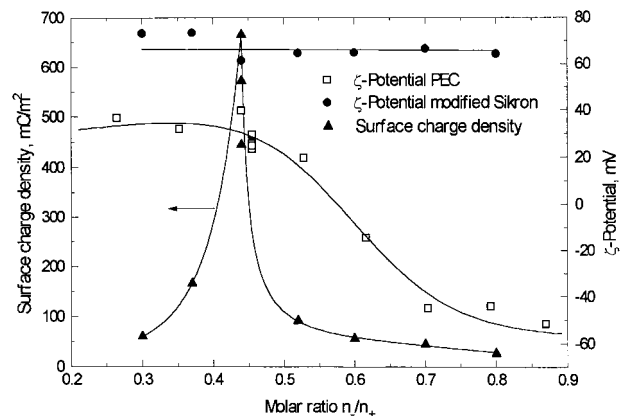


Figure 10 Comparison of surface charge density and zeta potential of modified Sikron powder with the zeta potential of PEC, MS-P/Polymin P system, variation B.

Polymin P and MS-St/PDADMAC systems are compared. The MS-P/Polymin P system in Figure 10 illustrates that the shapes of the zeta potential curves of the PEC and of the modified Sikron are different. Accordingly, we cannot assume a relatively unchanged adsorption of preformed PEC from solution, as mentioned for variation A. The negatively charged surface effectively competes with the polyanion for the polycation; this causes a changed deposition mechanism of the PEL or PEC on the surface, and a difference in the conformation of the PEL in the modification layer can be considered.

As a result of these processes in some cases, we can establish that

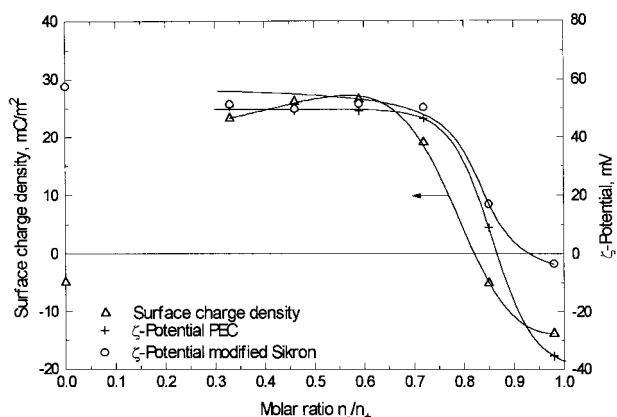


Figure 11 Comparison of the surface charge density and the zeta potential of modified Sikron (variation B) and the zeta potential of the PEC (MS-St/PDADMAC system).

- an enhancement effect in relation to the surface charge density of the modified substrates was found
- exclusively positive zeta potentials and surface charges of the modified substrates were observed, even at molar ratios n_-/n_+ , where negatively charged PEC were found and where negative surface charge densities of the substrate modified by variation A were registered.

From this, it can be assumed that the amplification effect of the surface charge density has to be connected with the formation of a surface layer, which predominantly should contain polycation or nonstoichiometric cationic PEC in the most outer surface regions.

The comparison of Figures 10 and 11 emphasizes the difference between the PEC systems with PEI and PDADMAC. The similar shapes of the zeta potential and the surface charge density curves in Figure 11 let us conclude that the relatively unchanged preformed PEC adsorbs on the substrate, even though variation B is used. However, slightly higher positive surface charge densities close to the isoelectric point were found.

Influence of Different Substrates

The dependence of the zeta potential and of the surface charge density of modified silicic acid on the molar ratio n_-/n_+ of certain PEC systems with PEI (variation B) is presented in Figure 12. The zeta potentials were always positive, but they tend toward less positive values in the direction of molar ratios $n_-/n_+ = 1$. Comparison of the zeta potential curves in Figure 12 with those in Figures 5 and 8 shows that an intermediate position between variations A and B for the PEI systems on silicic acid can be assumed.

Increased values of the surface charge density can be observed, but compared with variation A, the values are only three times higher. As in Figure 9, the systems of MS-P/Polymin P and MS-P/Polymin G 100 are most enhanced; the enhancement factor of MS-St/Polymin P is only 2. In the PEC system of MS-St/Polymin G 100, no reinforcement could be detected. From that, it can be concluded that the enhancement and the attainable surface charge density of the modified powders are affected by the surface charge density of the untreated substrate. The higher the surface charge density of the solid surface, the higher the amplification of the cationic surface charge.

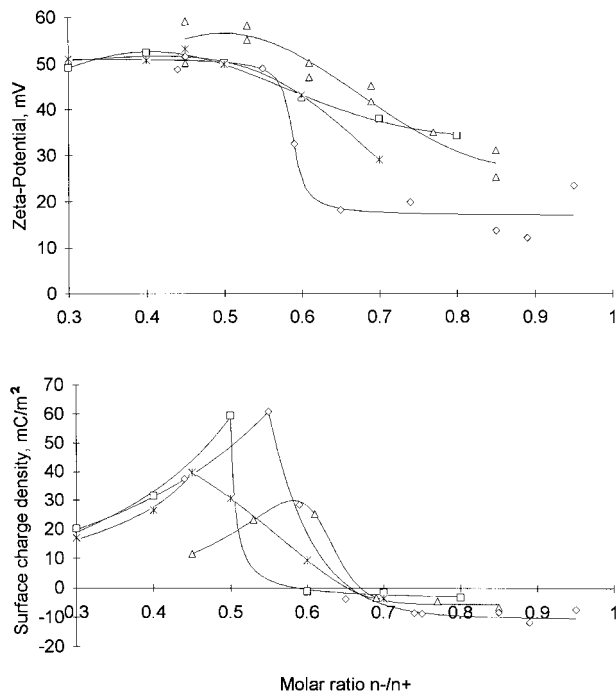


Figure 12 Dependence of zeta potential and surface charge density of modified silicic acid on the molar ratio n_-/n_+ of the PEC, variation B: (*) MS-St/Polymin P, (Δ) MS-St/Polymin G 100, (\square) MS-P/Polymin P, (\diamond) MS-P/Polymin G 100.

CONCLUSIONS

The ability of PEC to modify the surface of negatively charged inorganic substrate materials has been investigated. The influence of the modification procedure, of the PEL components, and of the substrates was of particular interest.

The point of zero charge of the PEC depends on the selection of certain PEL. The MS-P/PDADMAC and MS-St/PDADMAC PEC systems exhibited coinciding isoelectric points near stoichiometric ratio ($n_-/n_+ = 1$), which indicates that PDADMAC is flexible in the PEC and the dominant component.

The increased steric hindrance of rearrangements during PEC formation might be responsible for bigger deviations from the 1 : 1 stoichiometry of the PEC systems with PEI. Polymin P absolutely dominates the PEC stoichiometry, but in the PEC systems with Polymin G 100, a structural effect of different polyanions is also observed.

The nPEC carrying cationic excess charges are able to modify the surface properties of silicate powders (variation A). In contrast to the adsorption of polycations, strongly positive zeta poten-

tials and cationic surface charge densities could be generated by nonstoichiometric cationic PEC. It is important to note that, due to the complex formation between PDADMAC and MS-St, PDADMAC is able to produce a cationic modified substrate.

The results also permit us to conclude that the preformed PEC adsorb from solution roughly stoichiometrically unchanged. The composition of the PEC during deposition keeps constant, and the properties of the closed polymer layer completely mask the properties of the untreated substrate.

Significant differences of the zeta potential and the surface charge density curves were found between variations A and B (a two-step procedure), as well as between the PEC systems of PDADMAC and PEI. The behavior of the PEC systems with PDADMAC is almost independent of the modification procedure. PDADMAC prefers complexation with the polyanion, and after PEC formation, the complex adsorbs on the substrate.

In contrast to PDADMAC systems, a highly increased cationic surface charge density and entirely positive zeta potential of the modified powders are observed when variation B is used for the MS-P/Polymin G 100 and MS-P/Polymin P systems. The surface charge density could reach values up to 13 times higher than that due to variation A. In these PEI systems, the negatively charged surface effectively competes with the polyanion for the polycation and this causes a change in the deposition mechanism of the PEL or PEC on the surface. Differences in the surface structure of the PEL, that is, a predominant installation of polycation or nonstoichiometric cationic PEC in the outer parts of the surface modification layer, have to be assumed.

However, the variety of investigated systems permits us to describe conditions which may lead to an enhancement of the surface charge density of the modified substrates:

- It is necessary that, over the entire cationic range including the isoelectric point, stable nPEC can be prepared. Otherwise, a competition between the structure responsible for the enhancement and the PEC precipitation has to be expected.
- The maximum of the enhancement was always observed in the cationic range, immediately before reaching the isoelectric point of the nPEC.
- The enhancement also depends on the iso-

electric point of the nPEC in solution. The enhancement increases with increasing shift of the isoelectric point of the PEC from the molar ratio $n_-/n_+ = 1$.

- The reinforcement is stronger on substrates with high negative surface charge densities than on substrates with low negative surface charge densities.
- The amplification was only found by the application of variation B.

The surface charge density of the untreated substrates also affects the reachable cationic surface charge density of the modified powders. Variation A can generate high surface charge densities on Sikron as well as on silicic acid. The difference in the attainable surface charge is roughly 2 : 1 and corresponds to the surface charge densities of the untreated substrates. This indicates that the number of "anchoring points" on the surface is responsible for the degree of surface modification.

It could also be pointed out that the surface charge density of the untreated substrates affects the enhancement found in variation B. The higher the surface charge density of the substrate, the higher the amplification of the attainable cationic surface charge.

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