Properties of Polyelectrolyte-Modified Clays: Influence of the Particle Concentration on the Degree of Modification*

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ABSTRACT: Adsorption of polycation as well as the modification with oppositely charged polyelectrolytes is a useful tool for surface modification. As shown previously, a strong enhancement of the attainable specific cationic surface charge was observed, e.g., with poly(diallyl-dimethylammonium chloride) (PDADMAC) as the polycation and poly(maleic acid-*co*-α-methylstyrene) (P(MS-α-MeSty) as the polyanion, at a ratio of anionic to cationic charges of $n-/n+ = 0.6 \ldots 0.7$. However, because the surface charge seemed to be strongly affected by the conditions of modification, the influence of particle concentration was investigated in detail. One gram of clay was suspended in different volumes of water so that the particle concentration was varied from 1 to 100 g/L. These suspensions were treated under the same conditions. For characterizing the surface charge of clay polyelectrolyte titration, dye adsorption, or microelectrophoresis was used. The comparison between the results of polyelectrolyte titration and the carbon content in the residual solution allowed prediction of the existence of a polyelectrolyte complex and calculation of the stoichiometry. It was found for a constant concentration of PDADMAC per 1 g of clay that the surface charge of modified clays changed from negative (1 g/L) to strong positive, depending on the particle concentration. The cause was assumed to be the differences in the probability of interaction of particles, combined with the changes in the stoichiometry of the polyelectrolyte complex built in the solution, whereas the effect of other factors (conductivity, time of adsorption) was rather low. A strong cationic surface modification was obtained for medium and high particle concentrations only. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 16–25, 2000

Key words: adsorption, modification, polycation, polyanion, surface charge

As shown previously[1] the interaction between two oppositely charged polyelectrolytes in the presence of solid surfaces can be used for strong surface modification. This is an interesting new and simple way for preparing materials with definite properties as a support for the attachment of enzymes or drugs. The reason for the formation of such high surface charges (higher than those reached by adsorption of the polycation) is as-

sumed to be the reaction between the polycation and the polyanion under formation of a polyelectrolyte complex, with polycation in excess, which is adsorbed on the cellulose surface by electrostatic interaction. The modification effect depends to a large extent on the conditions of reaction, such as the molar ratio of anionic to cationic charges, $n-/n+$, the properties of the polyelectrolytes used, the concentration of polycation, the method of modification (premixed complexes or step by step modification), or the surface properties of the untreated substrates, as investigated in detail.[2–7]

Table I   Comparison between Different Experiments

	Laboratory Experiments	Large Scale Experiments
Total amount of clay (g)	1	1000
Concentration of dispersion (g/L)	10	100
Concentration of polycation (mol/L)	0.01	0.1
Volume of the polycation (L)	0.03	3.0
Volume (total) (L)	0.1	10.0
Millimoles polycation/1 g clay	0.3	0.3
Attainable surface charge (C/g)	0.25	3.0

A strong enhancement of the attainable specific cationic surface charge (compared with adsorption) was observed, e.g., with poly(diallyldimethylammonium chloride) (PDADMAC) as the polycation and poly(maleic acid-*co*-α-methylstyrene) (P(MS-α-MeSty)) as the polyanion at a ratio of anionic to cationic charges of $n-/n+$ $= 0.6 \ldots 0.7$. At first the solution of polycation was added to the suspension, followed by the polyanion. Under these conditions (concentration of polycation = 0.3 mmol/1 g of solid material), the surfaces became positively charged, but the attainable cationic surface charge seemed to be influenced to a large extent by the conditions of modification, mainly by the concentration of the particle dispersion to be modified (at constant amount of polycation per 1 g clay). To modify big amounts of clay in large-scale experiments, it was necessary to increase the particle concentration and the concentration of polymer solution as well. Surface charges 10 times higher than those in the laboratory experiments were found at particle concentrations of 100 g/L (Table I). Because it was not clear why such differences with respect to surface charge occurred and what were the reasons for this behavior, a detailed investigation was performed. None of the previous studies have been concerned with this problem.

We know that predominantly three processes are of great importance for modification: the adsorption of polycation on the substrate, the complexation between the (nonadsorbed) polycation and the polyanion in solution, and the "precipitation" of this complex on the surface. These processes were influenced by factors such as pH, concentration of polyelectrolyte solutions, and ionic strength.

The aim of our research was to investigate these processes in detail, with respect to the influence of particle concentration, if possible under uniform conditions. Many investigations are necessary to identify the general tendencies.

Although the adsorption of polyelectrolytes on clay—the first step of our modification procedure—has been the subject of a number of studies, the description of several problems is obviously incomplete. Such systems are very complicated. In order to obtain a reasonable understanding of systems that are used in practice it is, therefore, necessary to choose model systems that are simple but not oversimplified and reasonably closely related to the application in mind. Thus, the influence of salt on the adsorption of polyacrylate and carboxymethylcellulose[8] or the adsorption and flocculation in dependence on the molecular weight[9] or charge density of polycations[10] were investigated. It was found for different types of cationic polyacrylamides that the clay also exhibits a negative "excess" charge after adsorption. These experiments were done with particle concentrations of 4 g/L. Only a few works deal with the influence of particle concentration on adsorption or on flocculation. For latex and silica, it was found[11] that the efficiency of flocculation increased with particle concentration (at the optimum flocculation concentration.) Under certain conditions flocculation could not be observed for dilute suspensions.

We also investigated the influence of particle concentration on adsorption and modification, with respect to the properties of the modified clay. Therefore, in all of the experiments we treated 1 g of clay but in different volumes (1 L–10 mL). Thus, the concentration of the dispersions was varied from 1 to 100 g/L. To get the same total concentration of polycation in all experiments (0.3 mmol/g), it was necessary to change the concentration of initial polymer solutions (0.001–0.1 mol/L).

In a previous work we detected the strong influence of the concentration of polycation on the surface modification effect by use of polycation in combination with polyanion. The creation of high surface charge was obtained only when the con-

centration of polycation was high enough that adsorption on the surface occurred as well as the complexation in solution.[1] In these experiments the total quantity of polycation (mg/g) was varied, but the initial polymer concentration was kept constant (0.01 mol/L).

In the present work we have to distinguish between the influences of particle concentration and the concentration of polymers. Therefore, both the adsorption and modification experiments were made at constant particle concentration and in dependence on it, to point out the differences between these two treatments and the influence on the properties of modified material. For this purpose another significant parameter $(n-/n+)$ was kept constant: For modification experiments a desired amount of polyanion was added slowly so that the ratio of anionic to cationic charges always had the optimum value of $n-/n+$ = 0.6 . . . 0.7, which is necessary to get a strong surface modification. Because the processes also are very sensitive to mixing and stirring, these conditions were kept constant. The influences of hydrodynamic conditions on the reaction will be investigated in a further work.

EXPERIMENTAL

Procedure

First we studied the adsorption of PDADMAC. After homogenizing the suspensions with different concentrations of clay in deionized water from a Millipore Q system (1 h under stirring), the polycation (the required amount, diluted in water) was added. After a certain adsorption time, the material was separated by filtration. Residual PDADMAC was determined by polyelectrolyte titration (particle charge detector PCD 02, Mütek GmbH, Germany) and by using an organic carbon analyzer (TOC 5000, Shimadzu, Japan). For modification experiments the polycation was added first, followed by the polyanion, which was added continuously by a metering pump (900 mL/h). The surface charge of clay (after washing with 50 mL of water and drying in air) was characterized by polyelectrolyte titration, zeta-potential, or by adsorption of the anionic dye bromocresol green (BCG).

Materials and Methods

The cationic polymer PDADMAC was obtained from Katpol Chemie Bitterfeld (Germany) as a 20°% aqueous solution. The molecular weight (M_w) was 35,000 g/mol, according to the manufacturer. The anionic polyelectrolyte used in this study was poly(maleic acid styrene) (P(MS-Sty)) with a weight average molecular weight M_w of about 300,000 g/mol, provided by Leuna GmbH, Germany.

The initial polymer solutions were prepared with deionized water (Millipore Q). They were gently stirred for 20 h and characterized with polyelectrolyte titration before use.

The clay (FKS 84, Amberger Kaolinwerke, Germany) had a BET-surface of 13 m^2/g and a particle size x_{50} of 12 μm. The surface exhibits a negative charge (0.8 C/g). In most of the experiments, the clay was used without purification, to simulate the conditions in large-scale experiments. For investigating the influence of conductivity, the clay was purified by washing with deionized water for 3 days, until the conductivity of a 100-g/L suspension ranged between 5 and 10 μS/cm.

To characterize the cationic surface charge of the modified substrates, the adsorption of the anionic dye BCG, obtained by Fluka (Switzerland) was measured. A solution (40 mg/L, pH 6.6) was brought into contact with the material and shaken at room temperature. The residual concentration after separation was determined by a UV VIS spectrometer (Lambda 2, Perkin-Elmer), and the sorption capacity was calculated.

The particle charge detector PCD 02 (Mütek) in combination with a Mettler Titrator DL 21 also was used for the characterization of particles by polyelectrolyte titration, as follows: 0.1 g of clay was suspended in 10 mL of KCl (10^{-3} mol/L) and treated in an ultrasonic bath for 2 min. The consumption of cationic (or anionic) titer for neutralizing 1 g of the particle dispersion is characteristic for the surface charge obtained.

The microelectrophoretic mobilities of the particles were measured in KCl (10^{-3} mol/L) at 22°C using a Zetamaster (Malvern Instruments). The suspension had been treated in an ultrasonic bath for 1 min just before the measurements were started. The zeta potentials (ζ) are calculated from the measured electrophoretic mobilities (μ_e) of the particles with the Henry equation, eq. (1):

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

$$\text{with } f(\kappa a) = 1 + \frac{1}{2}$$

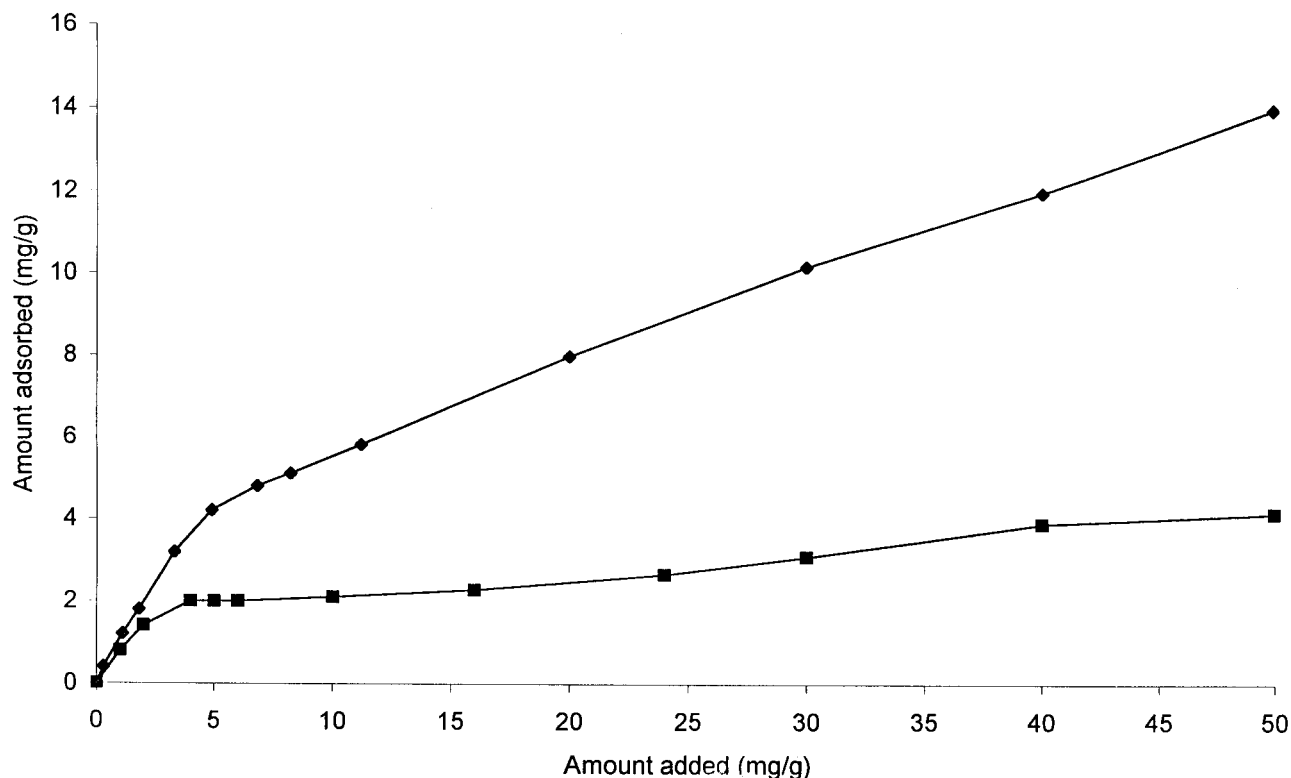$$\times \left(1 + \frac{2{,}5(1 + 2\exp(-\kappa a))}{\kappa a}\right)^{-3} \quad (1)$$

Figure 1 Adsorption of PDADMAC on clay FKS 84 at different particle concentrations. ♦, 100 g/L; ■, 10 g/L.

where ε is the dielectric constant, ε_0 is the dielectric permittivity of vacuum, κ is the Debye-Hückel screening parameter, and a is the radius of the particles. The size of particles was measured by HELOS particle size analysis (Sympatec GmbH, Germany).

Results and Discussion

Adsorption.

The adsorption isotherms were of the high-affinity type, as usual for polyelectrolytes on oppositely charged particles. They differed, however, for different particle concentrations (Fig. 1). Investigating the adsorption process in detail with a constant amount of polycation per 1 g of clay, as described above, we were able to confirm (Fig. 2) that the particle concentration influences the amount of PDADMAC adsorbed and, as a result, the surface charge of particles. Both methods for characterizing the residual polymer solution (polyelectrolyte titration and organic carbon analysis) agreed very well. The amounts adsorbed are rather low for low particle concentration (5–10% of the amount added) but increased significantly

for higher concentrations of clay. Therefore, large differences of attainable surface charge (reaching from positive to negative values) were obtained.
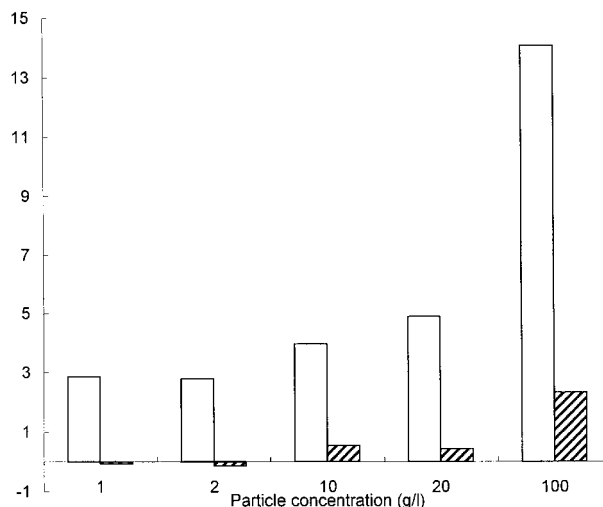

Figure 2 Adsorption of PDADMAC (0.3 mmol/g) on clay FKS 84. Amount of PDADMAC adsorbed and surface charge of clay in dependence on particle concentration. □, amount adsorbed (mg/g); ▨, surface charge (C/g).
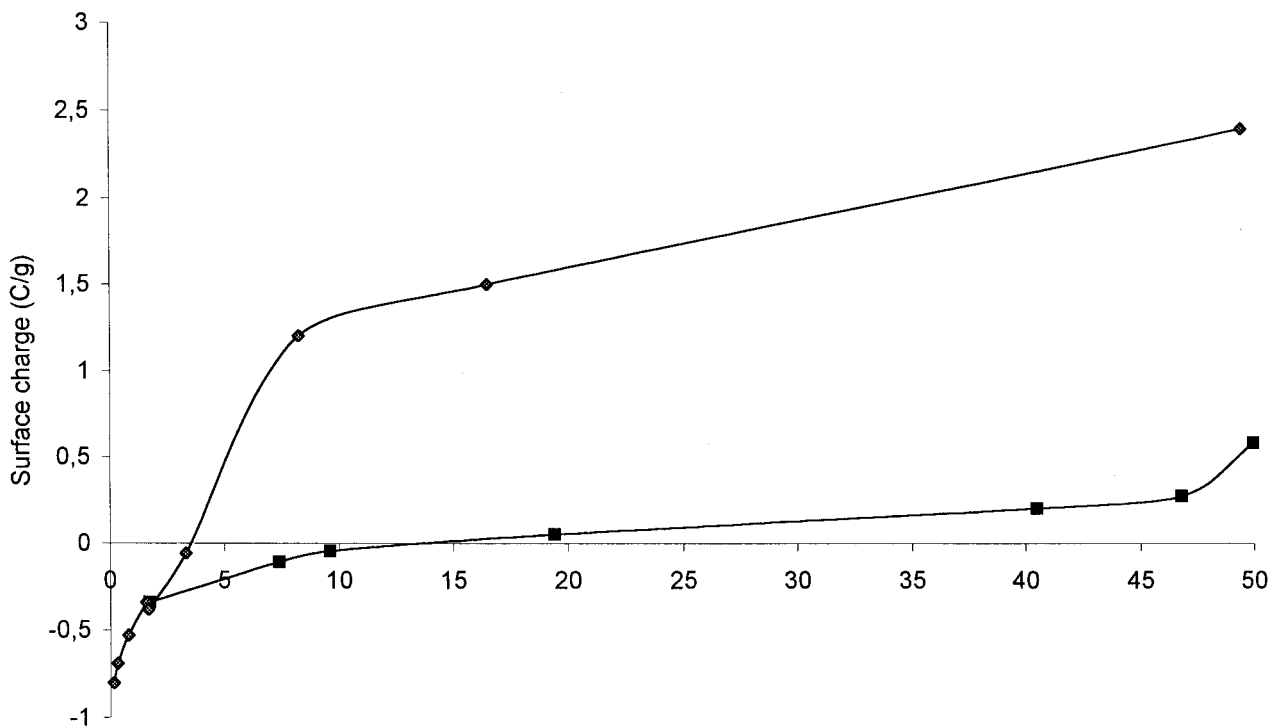
Figure 3 Adsorption of PDADMAC on clay FKS 84. Surface charge of particles in dependence on the amount added. ♦, 100 g/L; ■,10 g/L.

It was demonstrated that for charge reversal a certain amount of PDADMAC must be added to the material. According to theory,[11] such highly charged polycations adopt a very flat conformation because of their affinity for the particle surface. Below saturation, the particle surface has a mosaic pattern of positively and negatively charged regions. Negative surface charge of particles was found for suspensions with low particle concentration (1 or 2 g/L) and for relatively high amounts of PDADMAC. That means that the charge carried by the adsorbed cationic polymer is not sufficient to reduce the negative charge on the clay particles to any significant extent. The application of the same quantity of PDADMAC leads to positively charged surfaces in case of higher particle concentrations (Fig. 3). The surface charge strongly increases with the amount of PDADMAC adsorbed.

Further, we were able to demonstrate that a variation of the initial polymer concentration (as done in the experiments of Fig. 2) at constant particle concentration has no influence on the amount adsorbed and on surface charge. The result agreed with Figure 2. Surface charges also were found to be negative for particle concentrations lower than 10 g/L.

Because it is well known[12] that the time needed to reach equilibrium can be very long, especially for low concentrations of clay (without salt), we also examined the influence of the adsorption time. As demonstrated in Figure 4, the amount adsorbed was also low for 1 g/L of clay, even for a relatively long time of adsorption. The amount adsorbed increases with time, but the influence of particle concentration is much higher (Fig. 5).
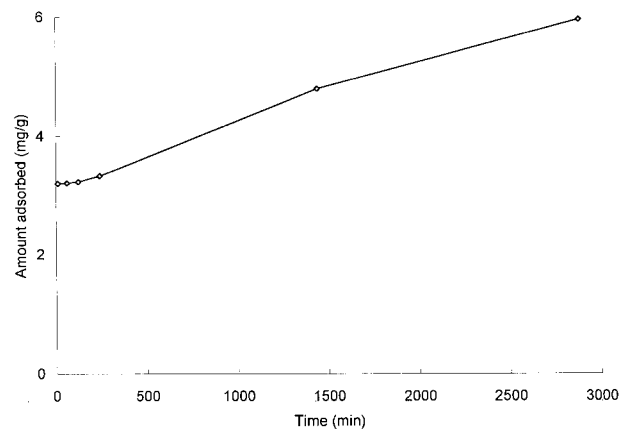

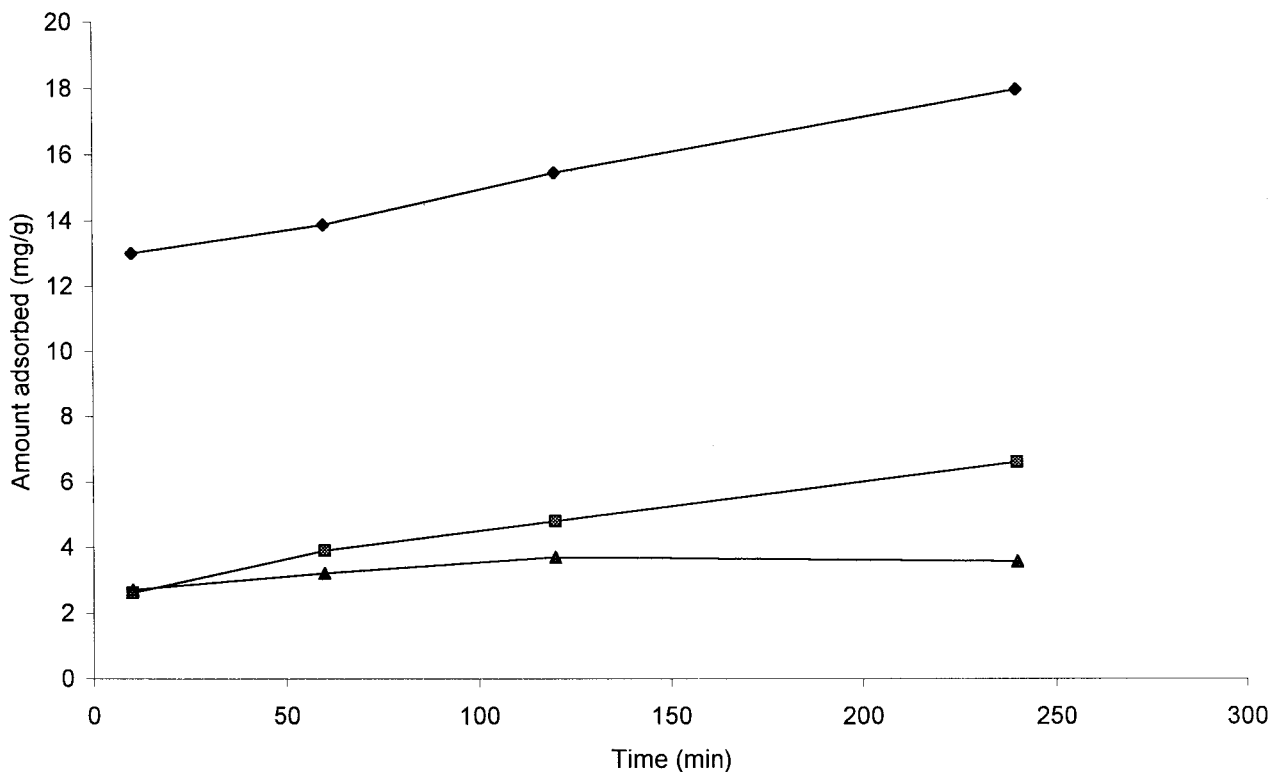**Figure 4** Adsorption of PDADMAC on clay (1 g/L). Amount adsorbed in dependence on time.

Figure 5 Adsorption of PDADMAC on clay. Amount adsorbed in dependence on time. ◆, 100 g/L; ■, 10 g/L; ▲, 1 g/L).

But why does the particle concentration influence the adsorption so strongly? The variation could not be attributed to the concentration of polycation nor to the time of adsorption. Other factors that could have an influence were the hydrodynamic parameters (bag mixing) or the conductivity of the unpurified clay, used in these experiments. To decide if the latter is of crucial importance (changes in the conductivity from 10 μS/cm for 1 g/L up to 480 μS/cm for 100 g/L), we also performed the adsorption experiments with purified clay.

It was shown that the amount adsorbed decreased when purified clay was applied (Table II), especially for high particle concentrations. This is in accordance with the theory[13] that the adsorption of polyelectrolytes is influenced, to a large extent, by the salt content. As a result of reduced adsorption the surface charge of the purified clay is lower. So we found particles with a very low

Table II   PDADMAC: Adsorption on Clay

Particle Concentration (g/L)	Clay	Conductivity (μS/cm)	Amount Adsorbed (mg/g)	Surface Charge (C/g)
1	Purified	5–10	2.6	−0.32
10	Purified	5–10	3.8	+0.08
100	Purified	5–10	8.3	+2.1
1	Natural	10	2.86	−0.05
10	Natural	70	4.9	+0.43
100	Natural	480	14.1	+2.3

Time of adsorption: 1 h.

positive charge (nearly neutral) at particle concentrations of 10 g/L; however, as in the experiments with nonpurified clay, the influence of particle concentration is of crucial importance. We calculated that the probability of interaction between particles and polymers increases significantly with increasing volume fraction of particles. The distance between two clay particles is about 10 μm for concentrated dispersions (100 g/L) but about 100 μm for diluted dispersions (1 g/L). Therefore, the distance between two particles is equal to the "length" of 200 molecules of PDADMAC in the first case, but 2000 molecules in the second. So one can understand that the higher probability of interaction leads to higher surface charge.

As another example, the conductivity of the 1 g/L dispersion was raised by adding an "extract" of the 100 g/L dispersion (from 10 to 440 μS/cm.). In this case the amount adsorbed slightly increased because of the influence of ionic strength, and the surface charge of particles became positive (0.8 C/g). We can, however, consider that the surface charge obtained in this way is not as high as for the high particle concentration. Thus, we demonstrated again that the most important influence seems to be the probability of interaction between polycations in solution and particles during the adsorption time.

Modification Experiments

Additional polyanion (polyelectrolyte complex modification) strongly increases the quantity of PDADMAC bound to the substrate. Only small amounts of polycation were found in the residual solution, compared with the pure adsorption. A considerable increase of surface charge (compared with adsorption) was observed (Fig. 6). At a certain concentration (2 g/L under these conditions), we get positively charged surfaces with modification, whereas the adsorption leads to negative net charge. Strong surface modification is combined with aggregation of the particles. For higher particle concentration a strong flocculation was observed.

In accordance with adsorption, the modification effect was shown to be independent from the initial concentration of polymer solutions used at constant particle concentration. The results of polyelectrolyte titration for characterizing the surface charge were confirmed by the adsorption of an anionic dye or by zeta potential (see Properties of the Charged [Modified] Particles).
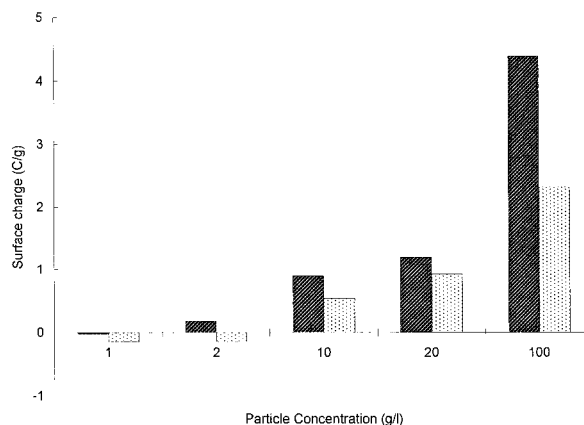

Figure 6 Surface charge of treated clays (adsorption [▦] compared with modification [■]) in dependence on particle concentration; (0.3 mmol PDADMAC/1 g clay).

To find out why modification at high particle concentrations is more effective in the creation of surface charges, we analyzed the residual polymer solutions for adsorption and modification experiments as well. By comparing the two methods (organic carbon analysis and polyelectrolyte titration), we were able to distinguish between polyelectrolytes and uncharged complexes. Whereas in the case of adsorption the two methods agree very well (which means that the quantity of nonadsorbed polycation, detected by polyelectrolyte titration, agrees with organic carbon measurement), we find less polycation by titration but a higher carbon content in the case of modification with polycation and polyanion. That means that not only polycation is in the residual solution but also a considerable amount of (uncharged) polyelectrolyte complex, which can not be detected by titration. By calculating the differences between the amount of polymer added (polycation and polyanion) and the composition of the residual solution, we found that the complex formed has a ratio of n−/n+ = 1 in the case of experiments with low particle concentration (1 g/L). However, n−/n+ is <1 (0.8) at higher concentrations, and thus it seems that this fact is one of the reasons for the differences in surface charge.

For a similar system (strong polycation PDADMAC in combination with poly-(maleic acid co-α-methylstyrene) investigating the "pure" polyelectrolyte complex, we showed previously that neutral complexes were formed for n−/n+ < 1.[2,14] That means that the charge of the complex detected by zeta potential or polyelectrolyte titration is zero, though it contains more polycation
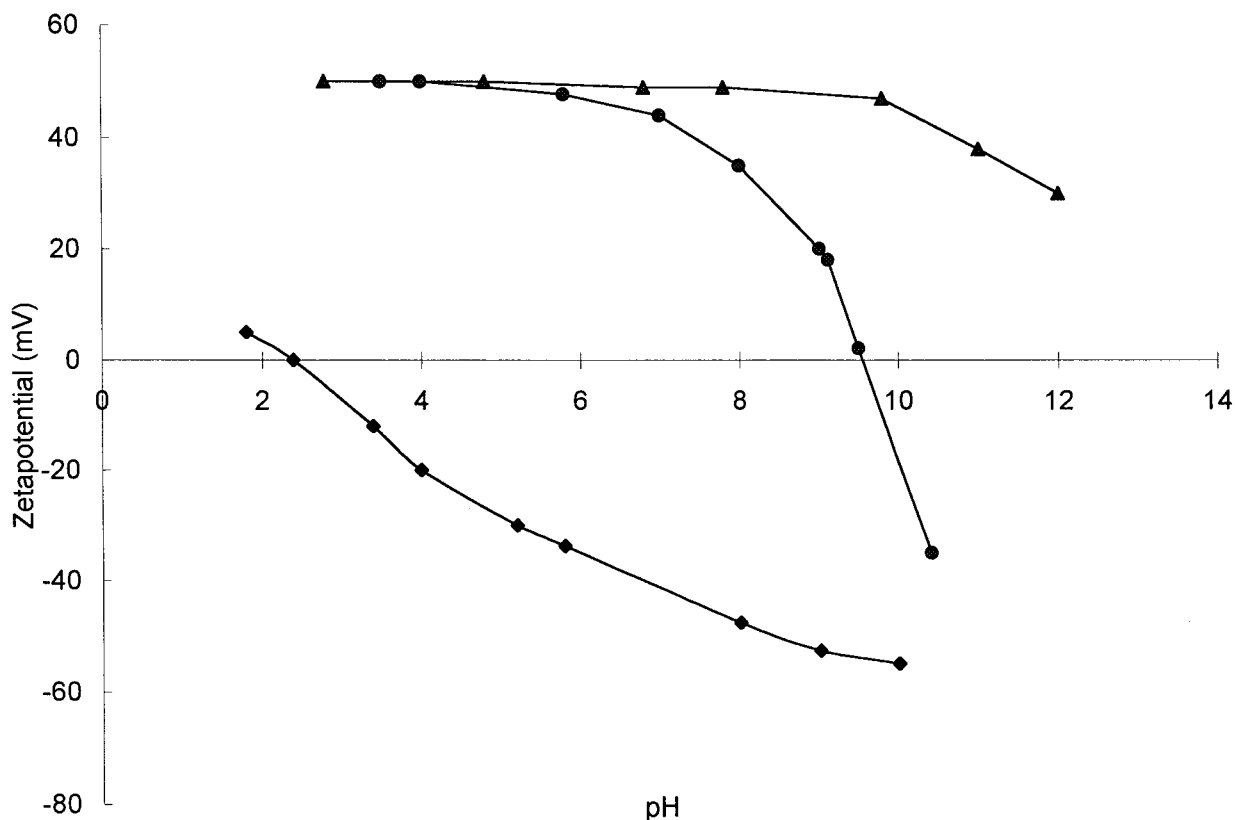
Figure 7   Zeta potential of unmodified or modified clay particles in dependence on pH (0.3 mmol/g PDADMAC/1 g clay). ◆, unmodified; ●, after adsorption; ▲, after modification.

than polyanion. Such complexes tend to agglomerate to large aggregates[15] and, as a result, to precipitate in the presence of a substrate.[16] For modification, this leads to an enrichment of polycation on the surface, which was found for higher particle concentrations (which were treated with polymer solutions of higher concentration).

Such deviations from a 1 : 1 stoichiometry with regard to ionic groups are observed rather frequently.[17] Size and shape (conformation) of the two oppositely charged polymers were assumed to be a cause of this behavior. In our case, it also seems that the different concentrations of polyelectrolytes used in the experiments are responsible for the deviations. In the present work for dispersions with low particle content (1 g/L), the polymers were applied as 0.001 molar solutions. The interaction between the polymer molecules is rather low and not disturbed and "ideal" 1 : 1 complexes can be formed. In contrast to this, the initial concentration of polycation was 100 times higher for large-scale experiments (particle concentration of 100 g/L). We found by comparing the

results of polyelectrolyte titration and TOC measurement that the isoelectric point of the formed complex was shifted to n−/n+ = 0.8 in this case.

For the formation of "pure" polyelctrolyte complexes (without substrate), it was shown that an increase in polymer concentration also leads to a significant increase of particle mass and radius, especially in salt-free solutions.[17]

We think that these various effects (changes in the stoichiometry of polyelectrolyte complex at the isoelectric point and increase of complex radius and mass) together with the higher probability of interaction in concentrated dispersion are responsible for such a high degree of modification.

This supposition has to be verified by analyzing the complex formation in dependence on the concentration of the two polyelectrolytes in solution. It seems to be very complicated because a lot of factors can influence the complexation, such as changes in the viscosity. Usually, for basic research in the field of polyelectrolyte complexes, the polymer solutions were highly diluted. But in technical application of polymer solutions, the

1. Preadsorption of Polycation

clay particles
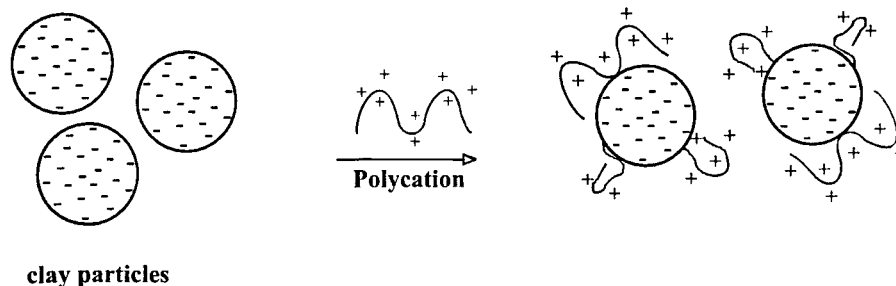
2. Addition of Polyanions

n- / n+ = 0.6...0.7

PEL-surface complex

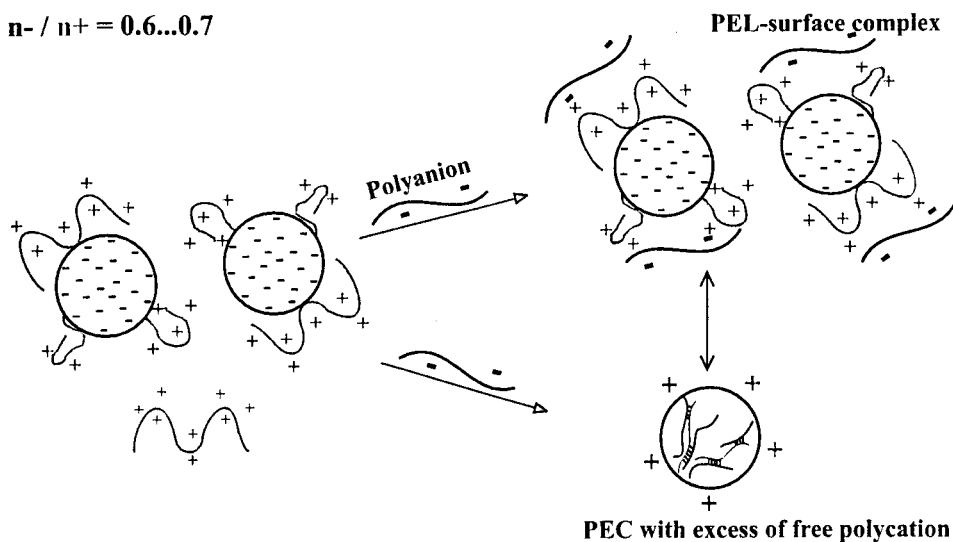**Polyanion**

PEC with excess of free polycation

Figure 8   Proposed mechanism of adsorption and modification.

semi-dilute region is of interest, which is defined by the condition of the complete volume occupation by the polyions.

Properties of the Charged (Modified) Particles

As pointed out previously, the properties of modified materials strictly differ. The surface charge can vary from negative to positive, depending on particle concentration. The results described above were confirmed by zeta potential measurement and adsorption of an anionic dye.

The zeta potential, which is dependent on pH, shows a characteristic behavior for the modified particles. As shown in Figure 7, the isoelectric point of the negatively charged clay is shifted to positive values due to adsorption, but up to very high pH values due to modification with polycation and polyanion. An isoelectric point of about 10 can be determined for different substrates

fully covered with PDADMAC,[18] whereas a shift of the isoelectric point up to such a high pH as observed for clay dispersions (100 g/L), modified with polycation and polyanion, was not found for other substrates.

This special behavior also was confirmed by BCG adsorption experiments. The binding capacity for an anionic dye (as a model) increases with increasing (positive) surface charge, and therefore it depends on the particle concentration during the adsorption/modification. In addition, the dye adsorption process is influenced by the structure of modified material (particle size, aggregates) and accessibility. Drying the clay after modification leads to a very slow adsorption process (changes of the residual color in the time up to 60 days). In contrast to the theory,[19] the particles were hydrophobic, despite the high cationic charge and the high zeta potential, respectively. The adsorption process was faster (with the same

capacity), with wet material applied directly after the modification.

The amount of BCG adsorbed increases with increasing particle concentration, up to about 7 μmol/g. However, when comparing the amount of BCG bound per molecule of PDADMAC adsorbed, the ratio is about 0.2 for a high degree of modification, but increases for particles with better accessibility for the model dye.

Because size and structure of the modified materials were found to be so important for their binding capacity, the particle size was measured, depending on the particle concentration. The x_{50} value grows from 12 μm (unmodified clay) up to about 20 μm (10 g/L) and >30 μm (100 g/L) when measured directly after modification (without drying). Particles aggregate, especially when the modification is carried out in concentrated dispersions. More than 90% of the particles have a size up to about 110 μm in this case. The reaction is very intense because of the good contact between clay and the two polymers. We found that the agglomeration is partly reversible in the wet state. Because the agglomerates were very impenetrable after drying in air, ultrasonic treatment (2 min) was used for preparation before characterization.

CONCLUSIONS

The results confirm our opinion that the formation of positively charged surfaces is influenced by the adsorption of polycation on clay as well as the formation of a nonstoichiometric polyelectrolyte complex, with polycation in excess, and reversible interaction, with polyanion in the surrounding solution. This scheme of modification is shown in Figure 8.

Our data indicate that these processes are changed at relatively low concentrations of clay dispersions because of the reduced probability of interaction between particles and polymers. The amount of PDADMAC adsorbed decreases, and therefore the clay particles are not positively (or only weakly positive) charged. Further, the formation of PEC in solution is influenced by the state of polymers in solution. Changing from diluted to semi-diluted solutions as necessary in technical application seems to change the properties of polyelectrolytes and polyelectrolyte complexes in large extent. The formation of nonstoi-

chiometric complexes necessary for strong surface modification was not found for diluted polymer solutions. In contrast, the increase of polymer concentration leads to the formation of larger particles that tend to agglomerate and to precipitate on the clay particles, which are tightly packed. Therefore, substrates with very high surface charge were obtained. If concentration of the system becomes too low, the effect of strong surface modification will disappear.

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