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ORIGINAL CONTRIBUTION

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# Preparation and characterization of different polyelectrolyte complexes and their application as flocculants

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**Abstract** Polyelectrolyte complexes (PEC) from poly(diallyl-dimethyl-ammoniumchloride) PDADMAC and two different polyanions, formed in aqueous solution, were characterized by different methods (zeta-potential, net content, turbidity) and applied as flocculants.

The flocculation of clay was investigated by sedimentation measurement as well as by a dynamic method, using a Fibre Optical Flocculation Sensor. The results of both methods showed that the most important advantages of PEC were the high velocity of sedimentation and a very broad range of the optimum flocculation concentration. In spite of the differences in the complex-forming behavior of the two polyanions used, no significant differences between complexes of the same composition but different polyanions are obtained. In contrast, the ratio of anionic to cationic charges is of great importance for the mechanism of flocculation.

**Key words** Polyelectrolytes – pre-formed polyelectrolyte complexes – flocculation – sedimentation – mechanism

## Introduction

Up to now, salts or polyelectrolytes with opposite charge are applied for flocculating solid materials like clay, silica, or cellulose. Polymers produce larger and better settling flocs than do simple coagulating electrolytes.

In some cases, different combinations of two components were used, especially for flocculation in the paper industry [1, 2], but also other fields like flocculation of harbour sediments, waste water or sugar beet washings were mentioned [3–5]. These so-called dual systems normally comprise a polycation of relatively low molecular weight and either cationic or anionic polyacrylamide ($M_w$ 5–10 × $10^6$). They need better control in terms of optimum polymer balance, and time and position of addition to the furnish.

Our previous work was focused on the detailed investigation of flocculation with two oppositely charged polymers, which were added step by step, first the polycation, followed by the polyanion [6, 7]. As an advantage it was shown that the efficiency of flocculation is higher compared to conventional flocculants. But the data obtained so far appear to suggest that the dual systems are very sensitive. The composition of the two-component polymer system influenced the effectiveness of flocculation in a large extent. Further, a polymer (polyanion) with very high molecular weight will be unsuitable because it can be no longer dispersed in the medium.

Another topic of our previous work was the formation and characterization of polyelectrolyte complexes and their use for surface modification of solid materials. It was found out that polyelectrolyte complexes with certain properties can be prepared in a simple procedure [8, 9].

In this work the suitability of pre-formed polyelectrolyte complexes (PEC) for flocculation was investigated to overcome the problems with the application of dual

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systems. Although some work has been done on this field, the following questions were not answered in detail up to now.

Are pre-formed polyelectrolyte complexes useful as flocculants? Is there any influence of the polymers used on the properties of the PEC formed? What are the advantages and disadvantages of flocculation with PEC? Is there any special action when PEC are used as flocculants?

## Experimental

### Polymers

To study the flocculation with pre-formed polyelectrolyte complexes, a series of different PEC was made from the polycation poly(diallyldimethylammoniumchloride) (PDADMAC) $M_w = 35\,000$, Katpol Chemie Bitterfeld, Germany, in combination with two different polyanions: Poly(maleic acid-co-α-methylstyrene) (P-MS-α-MeSty) $M_w = 30\,000$, Leuna GmbH, Germany and Poly(vinylsulfate)-K salt (KPVS) $M_w = 245\,000$, Serva, Germany.

The quantity of polycation was kept constant (0.005 mol/l). The charge of the two polyanionic solutions was determined by polyelectrolyte titration. Two different amounts of these polyanionic solutions were added for changing the ratio of anionic to cationic charges $n^-/n^+$ of the complex ($n^-/n^+$ of complexes prepared is 0.2 and 0.6 respectively). For preparation of the pre-formed complexes, 50 ml of a polycationic solution (0.01 mol/l) was stirred slowly. A certain amount of the polyanion in water (total: 50 ml) was added dropwise by a metering pump. Each complex was prepared separately without further addition of salt and was characterized by polyelectrolyte titration (PCD 02, Mütek, Germany), electrokinetic measurements (Zeta master 3, Malvern Instruments Limited, Malvern, UK), and turbidimetry (Luminescence LS 50, Perkin-Elmer).

### Substrate

For the experiments we used suspensions of clay FKS 84 (Amberger Kaolinwerke, Germany). The clay particles (size: 12 $\mu$m, determined by sedimentation analysis) have a BET-surface of 13 $m^2/g$.

### Methods

#### *Adsorption of PDADMAC on clay*

Adsorption isotherms were determined by measuring the concentration of residual polymer above the clay suspension (10 g/l) after 15 min with stirring at pH of about 5.6.

### Flocculation behavior

Flocculation was investigated by simple sedimentation measurement as well as by a Fibre Optical Flocculation Sensor (FOFS) made by BASF [10]. It enables a rapid *in situ* measurement of the so-called $F$-value, which is based on the degree of flocculation as a function of auxiliary dose. The concentration of the suspension in this case is 2 g/l.

The performance of polyelectrolyte complexes was assessed by flocculation experiments in terms of supernatant quality, volume of the sedimented material, $F$-value, and settling rate of the flocs. All experiments were carried out without further addition of salt.

For sedimentation experiments we used a simple apparatus. Six 50 ml jars can be applied simultaneously with controlled agitation. Different volumes of the pre-formed PEC-dispersion were added to the clay suspension. A concentration of 25 g/l of clay was found to be the most advantageous to follow the sedimentation process. After turning the device for 20 times, the process was stopped. When the flocculation occurred, a clear separation was noticed between the upper part of the jar and the lower part occupied by the flocs. The speed of settling was measured over 1 h. After this time, the height of the flocculated volume and the turbidity of the supernatant were measured.

## Results and discussion

The characterization of PEC is presented in Fig. 1. As a result it was demonstrated that the preparation of stable polyelectrolyte complex dispersions with cationic surface charge is possible. The dispersions contain relatively large (the size in the range of about a few hundred nm) charged particles. The composition of complexes is influenced by different factors, e.g. the nature of the two polymers and their concentration.

As detected also for complexes with different polycations (studied by polyelectrolyte titration and zeta-potential measurement), it was observed that the two different polyanions used differ in their complex-forming behavior [11]. Complexes with zero charge are formed for the strong polycation (PDADMAC) and the strong polyanion (KPVS) if $n^-/n^+ = 1$, according to the theory. In contrast, complexes made from PDADMAC in combination with the weak polyanion (P-MS-α-MeSty) are neutral if $n^-/n^+$ smaller than 1. Such deviations from a 1:1

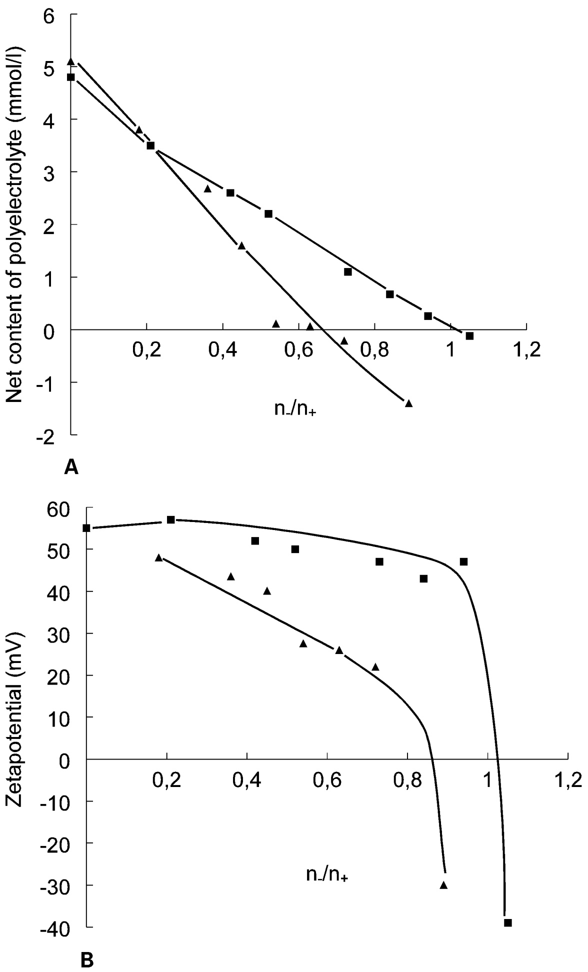


**Fig. 1** Properties of pre-formed PEC, made from 0.005 mmol/l PDADMAC and different polyanions; dependence of the net content of polyelectrolyte (A) and zetapotential (B) on the ratio $n^-/n^+$: (▲) PDADMAC/MeSty; (■) PDADMAC/KPVS

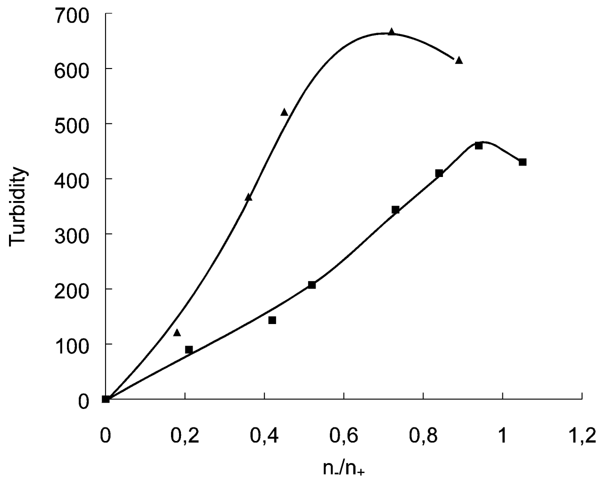


**Fig. 2** Properties of the pre-formed PEC dependence of the turbidity on the ratio $n^-/n^+$ (symbols as in Fig. 1)

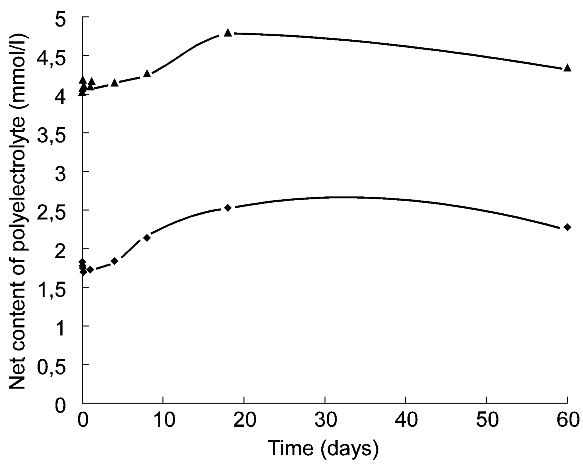


**Fig. 3** Stability of the pre-formed PEC (PDADMAC/MeSty) with different composition in depedence on time: (▲) PDADMAC/MeSty, $n^-/n^+ = 0.2$; (♦) PDADMAC/MeSty, $n^-/n^+ = 0.6$

stoichiometry with regard to ionic groups are observed rather frequently. The reasons were discussed by Philipp [12] or by Buchhammer [13].

The deviation from a 1:1 stoichiometry for one of the two polyanion–polycation systems leads to the consequence that the two PEC with the same $n^-/n^+$ can differ in their cationic charge. This result is confirmed by polyelectrolyte titration as well as by zeta potential measurements (Fig. 1A, B).

The turbidity of complexes increases with increasing $n^-/n^+$ and reaches a maximum at a certain composition. Then the turbidity decreases because of the precipitation of complex particles (Fig. 2). The so called "turbidimetric end point" is in accordance with the end point, determined by polyelectrolyte titration or zeta-potential measurement.

An important factor for the suitability of the complexes as flocculating agent is their stability. By means of polyelectrolyte titration it was demonstrated that the net content of polyelectrolyte of the PEC is quite stable over a period of more than two month. The reasons for changes, noticed at the beginning of this time, have to find out yet (Fig. 3).

The adsorption of polymer onto dispersed particles is of prime importance for the discussion of the mechanism of flocculation. Figure 4 shows the adsorption of the pure polycation on clay in salt-free solution.

For describing the flocculation of clay, we will apply the model of Levine and Friesen [14]. They described

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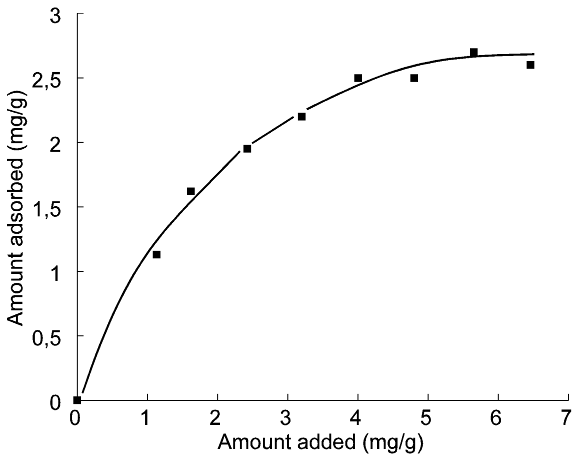



**Fig. 4** Adsorption of PDADMAC on clay

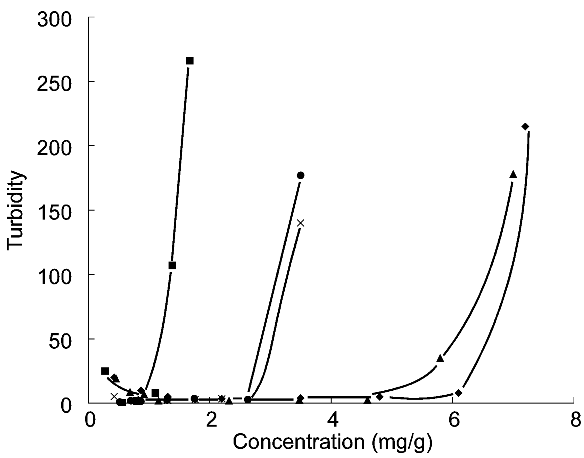



**Fig. 5** Flocculation of clay with PDADMAC or pre-formed PEC – the turbidity of the suspensions as a function of polymer concentration: (■) PDADMAC; (×) PDADMAC/MeSty, $n^-/n^+ = 0.2$; (●) PDADMAC/KPVS, $n^-/n^+ = 0.2$; (♦) PDADMAC/MeSty, $n^-/n^+ = 0.6$; (▲) PDADMAC/KPVS, $n^-/n^+ = 0.6$

a model with three regions of polymer concentration: a stable region at very low concentrations of flocculant, a flocculation region, and a region of restabilization at high concentration. Within the boundaries of the flocculation region, which is demarcated by the critical flocculation concentration (CFC) and the restabilization concentration (RSC), the optimum flocculation concentration (OFC) lies.

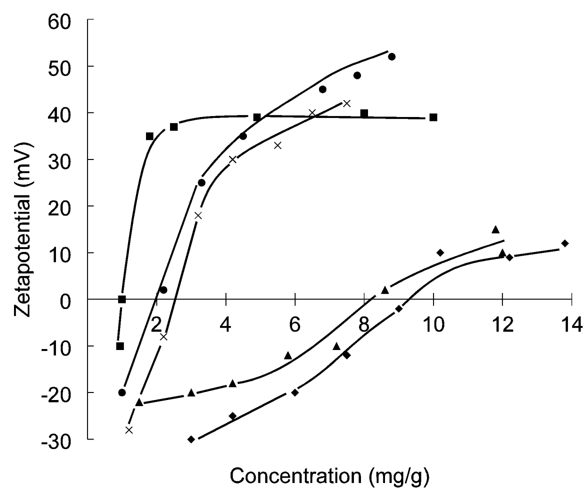
If clay is flocculated by the pure polycation, turbidity decreases from about 300 (unflocculated dispersion) to a value, less than 10. The OFC is about 0.9 mg/g. At concentrations higher than this value, redispersion is obtained (Fig. 5).

The PECs with higher surface charge ($n^-/n^+ = 0.2$) are similar to the pure polycation but they carry only 80% of their charge. The OFC-value increases and the region becomes broader, if they are used as flocculants. In general, there are no significant differences between complexes with the same molar ratio but different polyanions. Further, it is of great importance that reflocculation is not noticed in a wide range of concentration for flocculation with PECs.

Figure 6 shows the zeta potential (electrokinetic measurement) of flocculated particles. For the polycation, a coincidence was found between the dose which corresponds to the optimum of flocculation and the zeta potential of zero. This is a good indication that flocculation is due to simple charge neutralization. Although the range of optimum flocculation is very broad for PEC, a steady increase of the zeta potential with increasing amount of complex was noticed too. Neutral particles were obtained at about 2 mg/g PEC ($n^-/n^+ = 0.2$). For the PEC with $n^-/n^+ = 0.6$ about 9 mg/g are necessary for neutralization. This is more than necessary for optimum flocculation. These results suggest that the mechanism of flocculation has been changed with increasing $n^-/n^+$. The complex particles become larger and more instable.

Figure 7A demonstrates the sedimentation behavior over 1 h. Particles flocculated by the pure polycation have a higher volume compared with complex-flocculated particles, especially in the first time. In Fig. 7B the velocity of sedimentation, calculated from the sedimentation curves is shown. As a reason it is postulated that complex particles are larger than the pure polycation (some hundreds of nm for both PEC) and can form flocs having a very high velocity of sedimentation.

**Fig. 6** Flocculation of clay with PDADMAC or pre-formed PEC – zetapotential of flocculated particles as a function of polymer concentration (symbols as in Fig. 5)



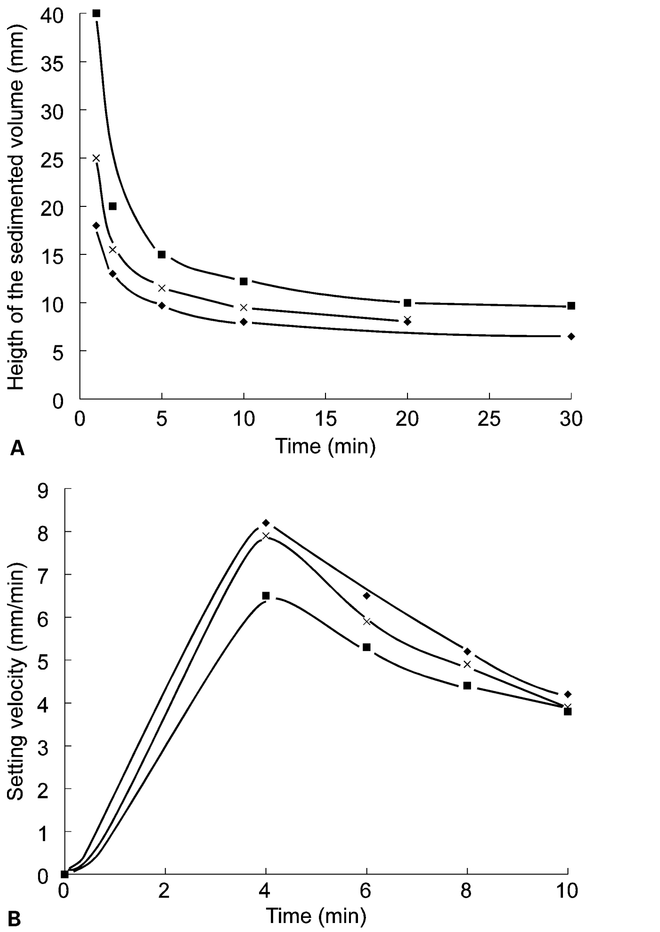



**Fig. 7** Sedimentation of clay particles, flocculated with PDADMAC or PEC; (A) height of the sedimented particles in dependence on time. (B) Settling velocity as a function of time (symbols as in Fig. 5)

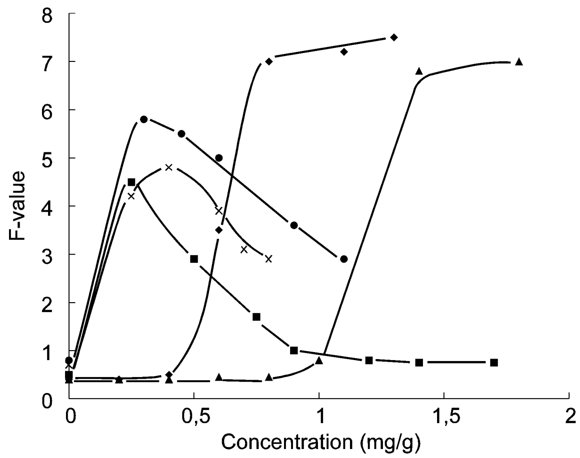



**Fig. 8** Flocculation of clay suspension (2 g/l) with FOFS – $F$-value in dependence on the concentration of PDADMAC or pre-formed PEC of different composition (symbols as in Fig. 5)

Figure 8 shows the $F$-values obtained by dynamic flocculation experiments with Fibre Optical Flocculation Sensor. According to the other methods, the polycation and complexes with high surface charge are similar, but complexes with high content of polyanion ($n^-/n^+ = 0.6$) seem to have a different flocculation behavior. At relatively high polymer concentrations they produce very large flocs. Up to now it is not clear, if the differences between the PEC, governed by the two different polyanions, are significant.

If the cationic charges of complexes would be responsible for flocculation, the PDADMAC/KPVS-complexes would have higher $F$-values than the PDADMAC/MeSty-complexes at the same concentration. But our data seem to imply that another type of flocculation is working. Complexes grow with increasing $n^-/n^+$ and become unstable. In order to further elucidate the details, investigations are in progress.

The results of experiments, established with the model suspension (clay FKS 84 in water) were confirmed by investigation of a real system from Kaolinwerke Caminau, Germany. The stock suspension (80 g/l) was diluted to 16 g/l (pH, 5.2). The most important findings on the special action of polyelectrolyte complexes were justified by these measurements. Compared with the industrial used high molar mass polyacrylamide derivatives (anionic or cationic), PEC with high content of polyanion are similar in relation to the $F$-values (size of flocs) but not as good as the PEC in relation to clarification.

## Conclusions

Pre-formed polyelectrolyte complexes are able to flocculate suspensions of finely dispersed inorganic particles. A reflocculation is not noticed in a wide range of concentration. These findings were confirmed by different methods, by sedimentation measurement as well as by dynamic measurement with FOFS.

The OFC of the PEC is in the same order of magnitude as for the pure polycation. In contrast to other workers, [15] or [16], which use two-component systems for flocculation of inorganic particles too, we got a very good clarification also for the pure (commercial) polycation PDADMAC. Advantages of the PEC used here are their high velocity of sedimentation and the broader OFC-region. But excellent properties seem to be generated by complexes which are almost neutral ($n^-/n^+ = 0.6$ for PEC with P-MS-$\alpha$-MeSty). Although only a small cationic charge is detectable, a strong flocculation (e.g. very large flocs, high velocity of sedimentation and good clarification) is obtained. The flocculation behavior like the

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increase of $F$-value in dependence on the polymer concentration, obtained by flocculation sensor, is different from other systems in this case. The mechanism of flocculation seems to be changed.

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