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Polyelectrolyte Complexes in Flocculation Applications

Gudrun Petzold and Simona Schwarz

Abstract This review concentrates on the interactions between oppositely charged polyelectrolytes and on the formation of complexes, which can be used for different applications such as paper retention or water treatment. Three different possibilities for the appearance of polyelectrolyte complexes (PECs) in flocculation applications are described. Starting with the "classical" dual system (step-by-step addition of polycation and polyanion to a negatively charged suspension of fibers or particles), the interaction between a "soluble polyanion" (such as anionic trash) with polycation is described as well as the formation of well-defined pre-mixed PECs and their application as flocculants.

The influence of several parameters related to the characteristics of the solid materials (e.g., charge, particle size), the polyelectrolyte (e.g., type of charge, charge density, molar mass, hydrophobicity) and the flocculation regime (e.g., order of addition, pH, ionic strength) are discussed.

Research in this area shows great potential. Over the past 30 years, dual systems have been applied mainly in the paper industry. The application of PECs, described as particle-forming flocculants, provides new possibilities in solid–liquid separation processes. For an effective system, the application parameters have to be optimized (e.g. polymer type, concentration, charge, molecular weight). Therefore, direct and efficient methods for the characterization of the flocculation behavior (sedimentation velocity, packing density of the sludge, particle size distribution) are necessary and will be described.

Finally, the most advanced applications for PECs are discussed.

Keywords Dual system · Flocculation · Polyanion · Polycation · Polyelectrolyte complex · Pre-mixed complexes

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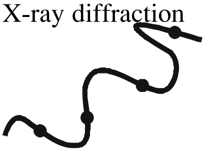
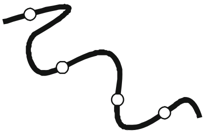
Contents

Abbreviations and Symbols

AFM	Atomic force microscopy
CD	Charge density
CMC	Carboxymethylcellulose
cmc	Critical micelle concentration
CNT	Carbon nanotubes
CPR	Carboxylated phenolic resin
DCS	Dissolved colloidal substances
DLS	Dynamic light scattering
DMAPAA	*N*,*N*-Dimethylaminopropylacrylamide
DSC	Differential scanning calorimetry
FTIR	Fourier transform infrared spectroscopy
GPE	Short-chained guest PEL
HA	Humic acid
HCS	Highly cationic starches
HMW	High molecular weight
HPE	Long-chained host PEL
LCST	Lower critical solution temperature
LMW	Low molecular weight

MMW	Medium molecular weight
NaPA	Poly(sodium acrylate)
NaPAMPS	Poly(sodium 2-acrylamido-2-methylpropanesulfonate)
NaPSS	Poly(styrene-*p*-sodium sulfonate-sodium salt)
NIPEC	Nonstoichiometric interpolyelectrolyte complex dispersion
NPEC	Nonstoichiometric polyelectrolyte complex
OM-PEI	Oligo-maltose-modified PEI
P(MSP)	Poly(maleic acid-*co*-propylene)
P(MS-α-MeSty)	Poly(maleic acid-*co*-α-methylstyrene)
PA	Polyanion
PAA	Poly(acrylamide)
PAC	Poly(acrylic acid)
PAE	Polyamideamine epichlorohydrine condensate
PAMPS	Poly(sodium 2-acrylamido-2-methylpropanesulfonate)
PC	Polycation
PC/D/PA	Polycation/dye/polyanion complexes
PCA5	Polycations containing *N*,*N*-dimethyl-2-hydroxypropylene ammonium chloride
PCA5D1	Polycations containing *N*,*N*-dimethyl-2-hydroxypropylene ammonium chloride with different hydrophobic units
PDADMAC	Poly(*N*,*N*-diallyl-*N*,*N*-dimethyl-ammonium chloride)
PEC	Polyelectrolyte complex
PEI	Poly(ethyleneimine)
PEL	Polyelectrolytes
PEO	Poly(ethylene oxide)
PI	Polydispersity index
PMADAMBQ	Copolymer of *N*-methacryloyloxyethyl–*N*-benzyl-*N*,*N*-dimethyl-ammonium chloride
PNIAA	Poly(isopropylacrylamide-*co*-acrylic acid)
PNIPAAM	Poly(*N*-isopropylacrylamide)
PNVCL	Poly(*N*-vinylcaprolactam)
PPEI	Phosphonomethylated derivative of PEI
PR2540	Poly(acrylamide-*co*-sodium acrylate)
PSC	Polyelectrolyte–surfactant complex
PSS	Poly(styrene sulfonate)
PTMMAC	Poly[*NNN*-trimethyl-*N*-(2-methacryloxyethyl) ammonium chloride]
PVA	Poly(vinyl alcohol)
Quartolan	Dodecyl-amidoethyl-dimethylbencyl-ammonium chloride
SDS	Sodium dodecylsulfate
siRNA	Small interfering RNA
TC	Trash content
TOC	Total organic carbon content
XPS	X-ray photoelectron spectroscopy

XRD	X-ray diffraction
Polycation	
Polyanion	
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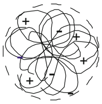
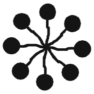
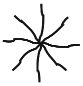
Polyelectrolyte complex	
Micelle	
Negatively charged waste	
Surfactant	
Star-like polymer	

1 Introduction

Solid–liquid separations are an important part of many industrial processes such as papermaking, water treatment, or mineral processing.

For the separation of particles or unwanted components from a dispersion, it is necessary to add flocculants. Salts, such as ferrous (III) or aluminum salts, which were used as flocculants in the past, have many drawbacks such as high demand for salt, the formation of small, unstable flocs, and a large volume of sludge. Therefore, they were replaced by water-soluble polymers (or were used in combination with them). Small polymer concentrations can produce large aggregates that can be separated easily. Numerous flocculating agents with different chemical properties are commercially available. Their flocculation mechanism as well as the results of the separation process are influenced by the properties of the polymers, such as their charge and molecular weight, and of the dispersed material. Nearly every solid–liquid system is different from every other. Therefore, there is no general rule on how to treat them. In different fields of application, the solid–liquid systems can be extremely different. So, the particle size can range from a few nanometers up to micrometers, or the solid content from parts per million up to 20%. The removal of solids of nanometer-size range from the dispersion is a crucial stage in many environmental technologies. Such colloidal particles are too small to be effectively separated by filtration, flotation, or sedimentation. Therefore, the most effective way to remove them is to cause the particles to flocculate so that larger units are formed.

As already mentioned, an effective separation can be realized by using only one polymer (monoflocculation). But, because water is becoming an increasingly scarce and limiting resource, the demand for treatment technologies has grown and, in recent years, there has been considerable interest in cases where more than one polymer is used. Such combinations of polymers can have significant benefits over the use of single polymers. Moreover, we will show that some of the new challenges in the industry can only be solved by using new types of flocculants.

We will discuss the possible interactions of such polymer mixtures from polycations (PC) and polyanions (PA), which can form polyelectrolyte complexes (PECs) or can be applied as “dual systems”.

There are some different possibilities for the appearance of PECs in flocculation applications. The most important options are presented in Fig. 1.

The first option is the application of two-component flocculants of opposite charge, which are added step by step (Fig. 1, top). During the flocculation process an interaction can occur between the two flocculants PA and PC, resulting in the formation of PECs, as well as between the polymer (mostly PC) and the suspension (inorganic particles or fibers). A summary of former results and recent developments will be presented in Sect. 2.

The complex formation between a (mostly negative) charged suspension and PC (Fig. 1, center) will be described in Sect. 3. The “basic” type of flocculation, i.e., the interaction between a negatively charged particle suspension and PC has often been studied and is not the topic of this review. But, instead of a particle suspension, the PC

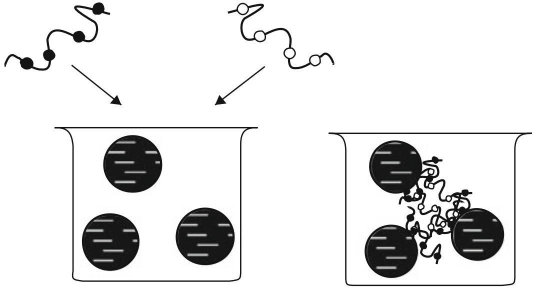
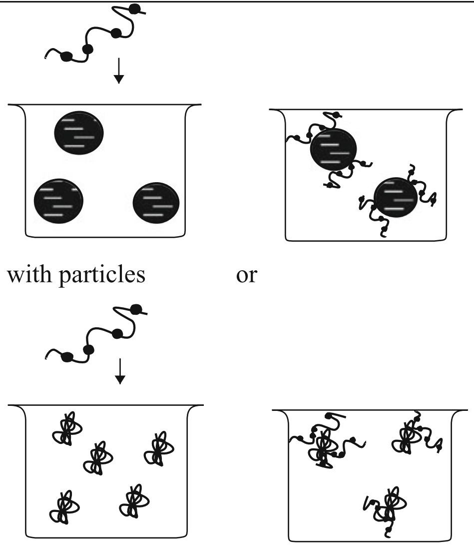
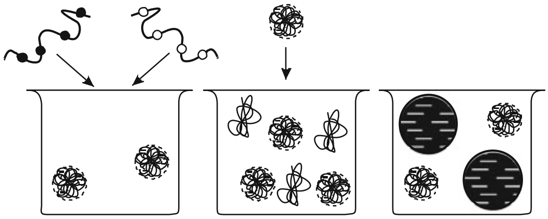
2 **Dual system** **(Step by step addition)** Interactions between two flocculants (dual system) in presence of solid materials (such as fibers or fillers)	
3 **"Direct" Interaction between the flocculant (polycation) and an anionically charged suspension**	 with particles or with charged "waste" like humic acid or stickies
4 **Pre-mixed complexes as flocculants**	 with anionic trash with anionic particles

Fig. 1 Different types of polyelectrolyte complexes (PECs) in flocculation applications

can interact also with colloidal detrimental substances such as stickies (Fig. 1, center). Relatively few systematic investigations of such interactions have been reported.

The third possibility is the formation and application of pre-mixed PECs in a first step, which can then be applied as flocculants (Fig. 1, bottom).This will be described in Sect. 4.

The use of polymer combinations for the improvement of flocculation efficiency is not new and was described earlier [1–24]. Two or even more components, added in sequence as flocculant systems, produce synergistic effects on the flocculation. Many different systems have been applied in the paper industry, and also in other fields like peat dewatering [1], flocculation of harbor sediments [2], wastewater [3], or sugar beet washings [4].

But, in the meantime, the importance of flocculation applications has been growing because of increasing requirements in several fields, such as for:

The paper industry:

- Excellent dewatering combined with good retention
- Reduction of high anionic trash content in combination with the reduction of water use in paperprocessing (due to the closure of circuits)

In other fields, flocculation is used in the following processes:

- Separation of ultrafine- or nanoparticles
- Separation of uncharged and/or colored materials
- Purification of fruit and vegetable wash water
- Reduction of the moisture content in separated sludge
- Sorption of low concentrated organic molecules from water, such as enzymes or hazardous materials
- Removal of humic acid from drinking water
- Preparation of carrier materials with great potential in health care and environmental sciences
- Splitting of emulsions and the removal of oil from oily sludge

The next three sections show that some of the problems that flocculation is required to deal with can only be solved with new types of flocculants like polymer combinations or aggregates.

2 Dual Systems (Step-by-Step Addition)

Flocculants are usually applied to accelerate separation processes, such as the drainage process during paper making, and to increase the retention of the finely dispersed material in the paper. Flocculation is one of the most important factors and influences both the machine runability and paper quality. Many chemical and physical factors influence flocculation in a complex way.

Usually, cationic polymers of high molar mass are used for flocculating the anionically charged suspension. However, the improved effect of dual systems is also appreciated. The application of two or even more components, added in sequence as flocculant systems, produces synergistic effects on the flocculation. Many different systems have been applied, especially in the paper industry.

The so-called dual system was first described in literature in the 1970s and consists of two oppositely charged polymers. It can produce distinct improvements in retention and dewatering [5, 6]. From the 1980s until now, much work has been done to improve our knowledge about such systems. This has been especially true in research areas like paper forming and floc shear stability. A special type of dual system, the so-called microparticle containing system, has been developed. In this system, the addition of a cationic polymer is followed by the addition of an anionic submicron particle suspension. Examples of this type of retention aid system are cationic starch used in conjunction with anionic colloidal silica or anionic colloidal alumina hydroxide and cationic copolymers of acrylamide used together with sodium montmorrilonite. Several systems of this type are commercially available. They are said to be very efficient flocculants, which give smaller flocs at an equal degree of flocculation compared to single-component systems.

Very good reviews, which include a survey of some aggregation mechanisms and comparisons between different dual systems, are available [7–12].

This chapter focuses on polymer–polymer systems, mainly in the paper industry. But, current approaches used in other fields of flocculation will also be mentioned.

2.1 Interaction with Cellulose (Paper Industry)

An example of an early and very detailed investigation of such a dual system is the work of Moore [13], in which different types of cationic polymers were combined with hydrolyzed polyacrylamides at various alumina concentrations. In contrast to other workers, Moore studied the charge relationship of the various charged species. He discovered that a combination of cationic and anionic polymers can give very high levels of retention with high shear resistance only in the case of a proper balance of charges and concentrations.

Müller and Beck [14] have investigated cationic polyethylene imine (PEI) or polyamidoamine in combination with an anionic polyacrylamide. They explained that under conditions of optimum performance, two mechanisms are operating: charge patch formation and bridging. The relatively short-chain PC produces a very fine flocculation of the particles via a charge patch destabilization mechanism. If a long-chain polyacrylamide (PAA) is then added to the stock, the negatively charged chains "get a good grip" on the positive patches of the primary floc and bring further linkages by forming bridges. Other aspects of the floc formation mechanism were studied by Petäjä [15], including the influence of the type and amount of PC, the time delay between cationic and anionic addition, and the degree of turbulence. It was shown that the agitation level and control of floc formation after cation addition are very important for good sheet formation.

In Table 1, a wide variety of examples of polymer–polymer systems from the literature are listed. The most commonly used systems are those in which the PC is added prior to a high molar mass PA. It was confirmed by different authors that the

Table 1 Examples of different types of polymer–polymer dual-systems

Type of polycation (PC)	Type of polyanion (PA)	Remarks/reference
PEI or PAAm; LMW; 0.2–0.3 wt%	PAA; HMW; 0.02–0.04 wt%	Optimum ratio is necessary; for waste paper [14]
PEI or other PC; LMW up to HMW	"PA"	Dual systems are not the solution to all retention problems [15]
PDADMAC of MMW, high charge density or dimethyl-amino-epichloro-hydrin resin of LMW; 0.07 wt%	PAA, HMW; medium charge density; 0–0.12 wt%	Three different dual systems are compared [16]; cationic polymer should be added before the anionic
LMW polymers, e.g., polyamines (highly cationic)	PAA	Dual systems need better control in terms of optimum polymer ratio [17]
Polyacrylamide copolymer	PAA (medium or HMW)	The cationic charge density of the polymer affected initial flocculation as well as reflocculation; fiber fines and filler responded differently on flocculation [18]
Starch 2 wt%	PAA; 0–0.08 wt%	Classical dual systems are both less reversible and show a lower dewatering compared with microparticle systems [19]
PDADMAC; MMW	PAA; HMW; low or medium charge density	The necessary amount of PC depends on the charge of the suspension [20, 21]
Cationically modified PVA	PAA-derived PA; HMW; low charge density	Improvement in the flocculation of fine clay particles [22]
PC with low charge density of 6 mol%	PA with high charge density of 35 mol%	Optimum at a 1:1 mass ratio, corresponding to about sixfold excess of negative over positive charges in the adsorbed layer [23]
PAA-derived PC with charge density 50%	Three different synthetic PAA-based PA	It is necessary to consider the overall system of sedimentation and filtration of the sludge; PC followed by PA is more effective than PA followed by PC [2]
Cationic starch (degree of substitution > 0.5)	Synthetic PAs	The results of [24] are comparable to those in [2]

The quantity of polymers used is mostly given in weight percent

order of addition is essential for efficacy. Drainage and retention are significantly increased if the PC is added before adding the PA, a treatment usually superior to the addition of a single PC. However, the dose rates of such systems are said to be often higher than those for single polymers [9]. It may be that the optimum polymer balance was not reached in these cases.

Table 1 demonstrates the large differences in the composition of dual systems. The quantity of polymers is mostly given in weight percent (wt%) without consideration of the charge content of the systems to be flocculated.

In contrast to microparticle-containing systems, which were widely used in the paper industry, the “classical” dual retention aid systems (polymer–polymer) are said to give high retention combined with a poor dewatering [19]. But, some researchers were able to show that an optimized polymer–polymer system has many advantages, such as good dewatering, superior retention, and shear-resistant flocs.

These effects are obtained by a combination of charge patch formation and bridging. The behavior especially depends on the concentration of PC (according to the anionic character of the suspension) and the molar ratio of anionic and cationic charges.

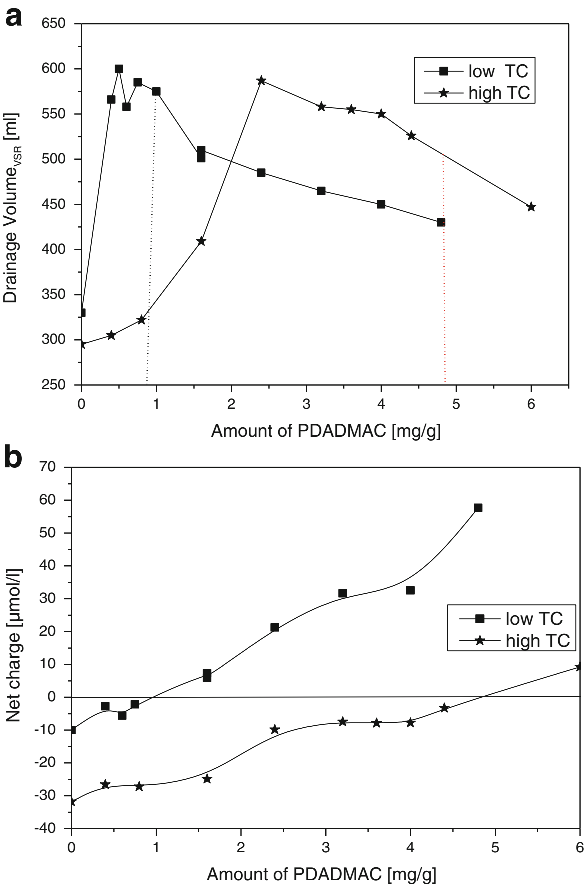
We have studied the mechanism of such polymer–polymer interactions as well as the interaction between polymers and fibers or particles [20]. After investigating the reaction between the strong PC poly(diallyl-dimethyl-ammonium chloride) (PDADMAC) and two cellulosic model suspensions with low or high anionic trash content, the influence of added PA on flocculation and dewatering was studied [20, 21]. As shown in Fig. 2a, for both suspensions, the drainage volume increased with increasing polymer (PC) concentration in the suspension up to a maximum. The charge of the suspension is slightly negative at this point, as shown in Fig. 2b. However, at higher polymer dosage the efficiency of flocculation decreases. Something like a plateau can be found; however, at the polymer dosage where the system is neutral, the volume V_{SR} strongly decreases. The polymer amount that is necessary for optimum flocculation depends on the charge of the suspension to be flocculated. For instance, the optimum polymer concentration (cationic demand) significantly increases with increasing trash content, but the drainage behavior (maximum of the drainage volume) was similar in both cases (Fig. 2a). The amount of PC necessary for optimum flocculation is of great importance for the optimization of the whole dual system and, as a rule, it should be determined first.

It was also found that the molar mass of the added PA has large influence on flocculation and dewatering. The higher the molar mass, the better the efficiency in flocculation. In contrast to this observation, the charge density of the PAs should not be very high. Most excellent results were obtained with PAA having a low (less than about 30%) anionic charge. The difference between a step-by-step addition of polymers to cellulosic suspension and the addition of pre-mixed complexes [25] will be discussed in Sect. 4.

2.2 Interaction with Humic Acid

The influence of charge and molar mass on the flocculation mechanism was also confirmed by results obtained for water treatment, where the influence of humic acid on the flocculation of clay was investigated [26]. The separation of clay particles was influenced by the presence of humic compounds, which act like an additional PA in the clay dispersion. Owing to their adsorption on clay and the higher anionic charge

Fig. 2 Drainage behavior of cellulosic model suspensions with low or high anionic trash content (TC) in the presence of PDADMAC. (**a**) Drainage volume V_{SR} in dependence on the amount of PDADMAC; the *dotted lines* exhibit the point of zero charge in the suspension. (**b**) Net charge of the residual solution/mixture in dependence on the amount of added PDADMAC



of the system to be flocculated, the optimum PC concentration is higher compared with clay in water. PCs with high charge density are efficient at removing humic acid owing to complex formation and precipitation. It was shown that the complexes formed by the highly charged PDADMAC and the weak PA humic acid are also able to collect fine particles. Most effective removal of humic acid was obtained by a combination of the highly charged PC and small amounts of a high molar mass PA (dual system). In this case, a broad flocculation window (Fig. 3) was obtained because of the bridging mechanism, as well as larger flocs than obtained with monoflocculation [26].

2.3 *Removal of Minerals or Heavy Metals*

Dual systems were also used for the flocculation of mineral suspensions [27, 28] or for the precipitation of heavy metals such as Cu^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+}, and Pb^{2+} [29, 30]. Glover [27] investigated the effect of a dual system on the compressive yield stress and

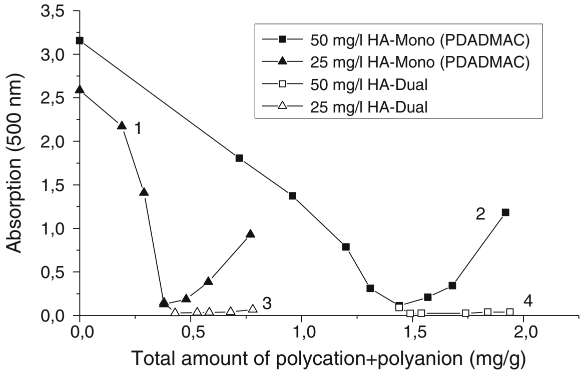


Fig. 3 Monoflocculation (*curves 1* and *2*) compared with dual flocculation (*curves 3* and *4*) of clay (10 g/L) in solutions of humic acid (HA) in water (25 or 50 mg/L) showing dependence of the absorption of the supernatant on the total amount of polymer used. PDADMAC was used for monoflocculation; PDADMAC + HMW PA were used as dual system. Figure adapted from [26]

hindered settling function of positively charged alumina suspensions, as measured by a filtration technique.

The removal of various heavy metal ions such as Cu^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+}, and Pb^{2+} from aqueous solutions was conducted [29]. Heavy metal binding with a phosphonomethylated derivative of PEI (PPEI) was initially allowed to occur and then, upon equilibration, PEI was added to initiate precipitation of the PEC together with the heavy metal ion. The PPEI–PEI system was found effective for heavy metal scavenging purposes, even in the presence of high concentrations of non-transition metal ions like Na^+. The PPEI–PEI PEC was found to be more effective than traditional precipitation methods; however, the result was not obtained by the application of premixed complexes, but by a step-by-step addition of PPEI and PEI (similar to other dual systems described here).

Gohlke described the separation of heavy metal ions with a PEC comprising a polycation and a polyphosphone compound [30].

Another field of an advanced separation is the flocculation and efficient dewatering of ultrfine coal (>150 μm) with a polymer blend (unmodified and sonicated flocculant) as dual system [31]. The authors proved that ultrasonic conditioning may be an effective alternative for a dual system in which two different flocculants are used.

2.4 *Dual Systems Using "New Polymers"*

In contrast to studies where most advantageous results were obtained by an optimization of the polymer amount and properties (molar mass, charge density) [20, 21], other groups have been trying to improve the results by the application of "new" polyelectrolytes. Water-soluble starch derivatives with a high degree of substitution up to 1 (containing quaternary ammonium groups) were used in combination with a high molar mass PAA for the flocculation of harbor sediment suspensions [32].

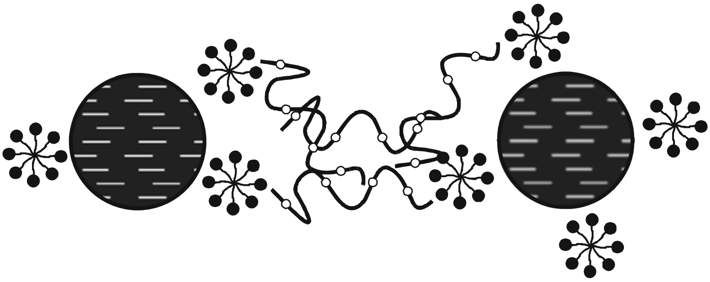


Fig. 4 Clay flocculation induced by dual-polymer system based on Star-P(MeDMA) polymers. Adapted from [33]

Li et al. [33] investigated the application of cationic star polymer with 21 arms as part of a novel component in a dual-component flocculation system for fine clay particles. Several cationic star polymers with different hydrodynamic sizes were applied as both single- and dual-component flocculation systems. The results indicated that the dual-component systems were superior to the single-component systems. In combination with a PAA-based anionic polymer (Percol 173) with high molar mass, very effective flocculation was achieved using the star polymer. Electrostatic interactions between the clay and Star-P(meDMA) polymers, as well as those between the Star-P-pretreated clay and anionic polymer, were studied via the determination of adsorption isotherms. It was concluded that the star polymers played an important role in inducing highly effective bridging flocculation (Fig. 4). Moreover, the reported system also removed soluble aromatic compounds simultaneously with the flocculation.

A new type of dual system was also described by Sang [22]. In conjunction with an anionic PAA-based polymer with high molar mass and low charge density, cationic modified PVA induced effective flocculation of fine clay particles.

As mentioned above, two-component flocculants often present advantages over a single-component flocculant, such as better control of flocculation kinetics and improved floc strength. Most dual-component flocculants consist of two polyelectrolytes, two polymers, or a polyelectrolyte and a nanocolloid. Usually, one of the components adsorbs on the surface of the particles to be flocculated and the second component bridges these polymer-coated particles. Therefore, this combination of "patching" and "bridging" is believed to be responsible for excellent results, as described for instance for retention systems (Fig. 5) [10].

2.5 Dewatering and Sludge Conditioning

Sludge conditioning by single and dual polymers has been investigated [34, 35]. Capillary suction time (CST) or specific resistance to filtration (SRF) were used to assess sludge dewaterability. Experimental results showed that sludge conditioned with dual polymers showed a better dewaterability, with less chance of overdosing

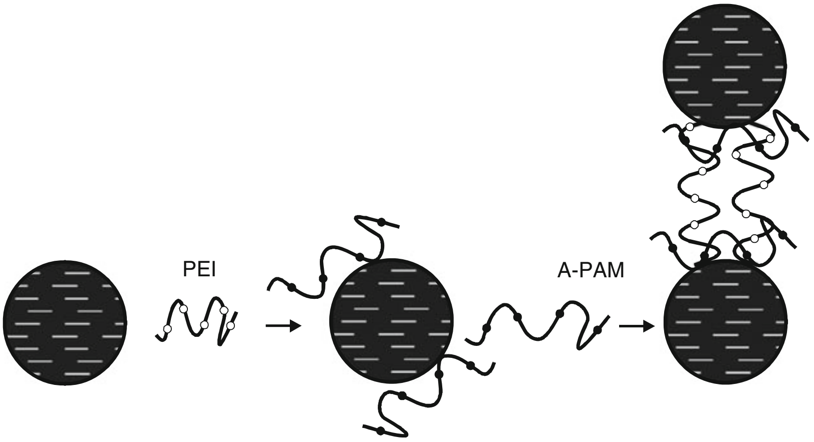


Fig. 5 Combinations of polyelectrolytes with different charge. Primary flocs are formed with the help of patching, after which primary flocs are linked together by bridging. *PEI* poly(ethyleneimine), *A-PAM* anionic polyacrylamide copolymer. Adapted from [10]

compared with sludge conditioned using a single polymer. In addition, sludge conditioned with dual polyelectrolytes (PEL) performed better in fine particle capture and in the formation of larger aggregates, which resulted in a better dewaterability and less chance of overdosing [34, 35].

The formation and breakage of flocs using dual systems was also investigated by Yukselen and Gregory. In the case of cationic–anionic polymers, the re-growth of flocs was fully reversible and the breakage factors were smallest, indicating highest floc strength. In contrast, flocs formed using nonionic polymer together with anionic or cationic polymer did not produce strong flocs [36].

Wang et al. [37] investigated the dual conditioning of activated sludge utilizing a polyampholyte in combination with ferric chloride or cationic PEL. The investigations indicated that dual conditioning of sludge exhibited better dewaterability at lower doses compared with single conditioning. The advantages of PDADMAC over ferric chloride as applied in dual systems were also discussed [38].

As shown for clay [39], the sediment height and therefore the density of the sediment can be measured quantitatively using the separation analyzer LUMiFuge. The results obtained agreed very well with other methods like the JAR-Test, which is not so convenient.

One example of a very special dual-component polymeric flocculant is poly (ethylene oxide) (PEO) and carboxylated phenolic resin (CPR), usually referred to as a cofactor. It has been shown that this dual flocculant can induce a richness of flocculation behavior depending on the concentration of the two components [40, 41]. Flocculation, deflocculation, and reflocculation of cellulose particles were studied for various CPR:PEO ratios. It was found that reflocculation is a strong function of this ratio. For low ratios, no reflocculation occurs after a few cycles, whereas for high ratios very limited flocculation and reflocculation occurs.

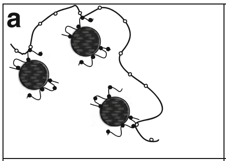
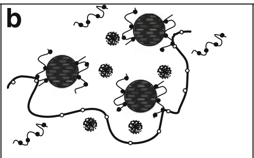
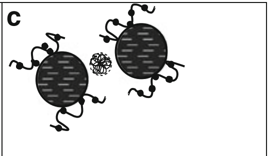
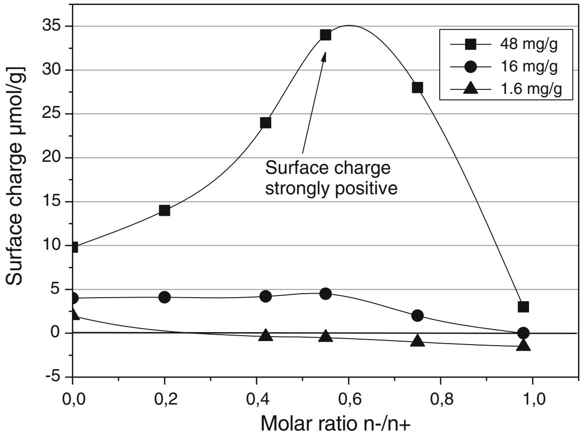
		
low amount of polycation	higher amount of PC (than in 6a), formation of PEC as an additional flocculant	dosage of PC and PA at the same time

Fig. 6 Different types of interaction between PC and PA in the presence of particles, depending on the amount of PC and the order of addition: (**a**) low amount of polycation, (**b**) higher amount of PC (than in **a**), formation of PEC as an additional flocculant, (**c**) dosage of PC and PA at the same time

Fig. 7 Surface charge of sulfite cellulose, modified with PDADMAC/P(MS-α-MeSty) in dependence on the molar ratio of PA and PC at different dosage levels of the PC



2.6 *Surface Modification*

We have described how a step-by-step addition of oppositely charged PEL can improve the quality of flocculation. A possible flocculation mechanism is described (Fig. 5) and is also shown for comparison in Fig. 6a. However, an increase in the PC amount can also lead to the formation of PEC in solution (Fig. 6b), which can be used as an additional flocculant. In the case that the PC and PA are added at the same time, the complex formation is favored (Fig. 6c).

The situation shown in Fig. 6b can also be applied for a strong surface modification of particles or fibers [42–45]. As demonstrated [43], in the presence of cellulose the complex formation between the two PEL is favored in the solution, and this complex itself is adsorbed on the surface by electrostatic interactions, which also causes flocculation. Under the condition that a large quantity of PC is still in solution when the PA is added dropwise, it is possible that the incorporation of the PC into the expanded complex takes place. As shown in Fig. 7, the surface charge of flocculated cellulose increases and has a maximum at a molar ratio of negative to positive charges ($n-/n+$) of about 0.55–0.6.

Clay particles whose surfaces have been modified by the PC PDADMAC and the sodium salt of the weak PA poly(maleic acid-*co*-α-methylstyrene), P(MS-α-MeSty), were used as sorbents for removal of surfactants from aqueous solutions [46].

2.7 Dual Systems with Thermosensitive Polymers

A novel strategy for faster and better flocculation in solid–liquid separation processes has been reported. The natural polyelectrolyte chitosan was used in combination with a biocompatible thermosensitive polymer [poly(*N*-vinylcaprolactam); PNVCL]. The flocculation of silica dispersions (Aerosil OX50) was evaluated using laser diffraction and turbidimetry studies. The sedimentation velocity, which was determined with an analytical centrifuge, was doubled by addition of PNVCL. Furthermore, at 45°C the density of the sediment was 33% higher than when chitosan was used. This results from the temperature-sensitive behavior of PNVCL, which phase-separates expelling water at temperatures higher than its lower critical solution temperature (LCST; 32–34°C). By using this strategy, the sediment is more compact, contains less water, and contains a very small amount of biodegradable chitosan and biocompatible PNVCL.

The flocculation of clay using mixtures of chitosan and a thermosensitive polymer was investigated as a function of the polymer concentrations and the temperature at different pH values [47].

The compaction of TiO_2 suspensions [48] as well as the dewatering of inorganic drinking water treatment sludge using dual ionic thermosensitive polymers was described by Sakhohara [48, 49]. By using both cationic and anionic modified PNIPAAm, the anionic thermosensitive polymer poly(NIPAM-*co*-AAC) in combination with cationic poly(NIPAM-*co*-AAC), the dewatering rate was remarkably increased at relatively low temperatures. This increase was attributed to the formation of a polymer complex that decreased the LCST of the polymer molecules adsorbed on the sludge.

3 “Direct” Interaction Between the Flocculant (PC) and an Anionically Charged Suspension

In contrast to the situation shown in Fig. 1 and described in Sect. 2, where different interactions between two oppositely charged PEL on one side and the solid material (fibers or particles) on the other side can occur, in this section we describe the “direct” interaction between a flocculant (PC) and a charged suspension, which acts like a PA. But, as shown in Fig. 1, the suspension can contain particles as well as “soluble” anionically charged material.

Those interactions are very important in the paper industry [50, 51] because the effectiveness of cationic polymers as retention and drainage aids in the manufacture of paper is strongly affected and sometimes even limited by anionic macromolecules, which dissolve in the white water. Such polymers are, for example, lignin or carbohydrates from wood. Therefore, the application-relevant effect of pine xylan on the use of PEI, and acrylamide copolymer as retention and drainage aid, for an unbleached sulfite pulp was investigated [50]. The formation of PECs between pine xylan and three cationic polymers has been studied as a function of pH and ionic strength [51]. Complex formation was found to be nonstoichiometric and both soluble and insoluble complexes are formed, with maximum precipitation occurring when the complexes are neutral. A tentative structure of the complexes was suggested.

3.1 Paper Recycling

The problems of complex formation are growing because the increasing use of de-inked pulps, in combination with the closure of paper machine circuits in pulp and paper industry processes, is leading to an accumulation of so-called trash material or tacky substances. The formation of a high amount of these substances affects paper production negatively due to lower retention of the filler or increased deposition on paper machines. These substances are brought into the process through many different sources. The recycling of paper is one of the most important ways of producing paper.

The variety of tacky materials present in papermaking systems have different names: for instance, the accumulated pollutants in the water recycling system are called dissolved and colloidal substances (DCS). The composition of DCS, which mainly come from pulp, filler, recycled water, and the chemicals added during the papermaking process, is very complex.

Pelton [40] describes PEC formation as an important part of paper technology. One example is the strategy for removing the anionic PEL components of the DCS by adding oppositely charged polymers to form PEC. Oppositely charged PEL will form complexes over a broad range of stoichiometric ratios. However, the complexes tend to be water-soluble unless they are nearly stoichiometric because an excess of either positive or negative particle charge will confer water solubility. This behavior is illustrated by the interaction of PDADMAC, a linear cationic PEL, with kraft lignin, which is a branched anionic phenolic polymer resulting from the decomposition of lignin in the kraft pulping process. The formation and the amount of precipitated kraft-lignin–PDADMAC complex were investigated as a function of the mass ratio (kraft lignin/PDADMAC) and the pH [40]. But, kraft lignin is not ideally suited for fundamental studies of PEC formation because lignin is a polydisperse polymer with a complicated structure; hence, most of the basic information about PEC comes from investigations on well-defined synthetic polymers [52] (see Sect. 4).

3.2 Sticky Removal

The appearance of so-called stickies is described for instance by Hubbe [53]. These are most often the result of synthetic polymers used in pressure-sensitive label adhesives. The full characterization of stickies is not easy to assess since there are many different types of stickies that have to be considered [54].

The existence of primary stickies (from raw materials) and secondary stickies, which were built by the interaction in such systems, has been described, together with many different characterization methods(including mechanical methods) for quantifying the efficiency of different fixing agents [55, 56]. In addition, physico-chemical methods such as measuring the cationic demand, the zeta-potential, or the turbidity of wastewater have been applied.

Unfortunately, none of the sticky test methods investigated was found to be universally applicable, i.e., suitable for all types of stickies. Therefore, the most suitable method must be chosen for each particular case and problem area [56].

Previous articles or reviews (such as [53, 57]) have considered the origin, the nature, as well as the removal of DCS.

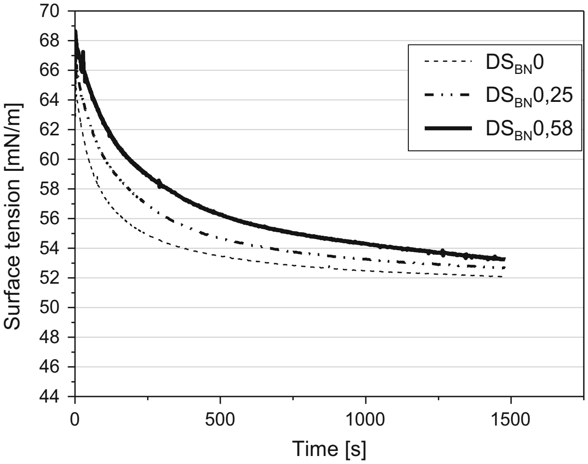
Among the organic polymers used in the paper industry to combat deposit problems are polymers with a huge ranges of molecular mass, charge, and hydrophilic versus sparingly soluble character. The effects of these polymers are greatly dependent on how these materials interact with the suspension or with surfaces [53]. Important classes of polymers are cationic polymers with very high mass, e.g., acrylamide polymers (well known as retention aids) or high charge cationic polymers [58, 59]. Hydrophilic polymers of intermediate mass are applied as well as PEL with partially hydrophobic character or surfactants. The adsorption tendency of PEL onto tacky materials can be increased by derivatization with hydrophobic substituent groups. Various copolymers of cationic, hydrophilic monomers, and hydrophobic monomers have shown promise as detackifying agents for resinous material [60, 61].

According to Meixner et al. [62], tailor-made cationic polymers are very effective for fixing interfering substances because they reduce the tendency of adhesive, hydrophobic substances to agglomerate and slow down the rate at which secondary stickies are formed. Using different types of models (hydrophilic or hydrophobic) and fixing agents, Meixner et al. were able to demonstrate that, for efficient sticky removal, not only is the cationic charge necessary but also the hydrophobicity. Whether (or not) a certain polymer is effective depends on the type of detrimental substances.

3.3 Natural Polymers for Sticky Removal

A few articles describe the application of starch, modified starch, or other carbohydrate polymers as flocculant for sticky removal [63–66]. The role of charge on the destabilization of microstickies was investigated by Huo by comparing the strong PC

Fig. 8 Dynamic surface tension of mixtures between a highly surface-active model suspension and modified starches having the same cationicity, but different degrees of benzylation, DS_{BN}, at a mixing ratio (volume suspension:volume starch) of 10:1; surface tension was measured using a profile analysis tensiometer (t = 1,200 s) [67]



PDADMAC with commercial cationic starch. The agglomeration of microstickies with PDADMAC occurred mainly via a charge neutralization mechanism. In contrast, the agglomeration of microstickies with cationic starch "had a more complicated behavior" [64].

Luo and Wang [65] prepared highly cationic starches (HCS) with different branching degrees and molar mass. The DCS controlling effects were investigated using zeta-potential, cationic demand, drainage speed, and turbidity. The study indicated that the degraded linear HCS had better performance in controlling microstickies than the branched HCS, which had better performance in paper strengthening.

Recently, we have investigated the interaction between tailored cationic starches wearing hydrophobic groups and model extracts of recycled newspaper and sticky material [67–69]. The properties of the prepared extracts differed in turbidity, total organic carbon (TOC), and charge. The surface tension was established as a useful tool for characterizing the surface activity and, therefore, the sticky content of the suspension. The interaction of three modified starches with the same "medium" cationic charge, but different hydrophobicity (degree of substitution by benzyl groups, DS_{BN}) with model suspensions was investigated. The interaction and complex formation was confirmed by complex precipitation, resulting in a decrease in turbidity and TOC, but an increase in surface tension. The most important consequence of this work was the finding that the amount of cationic charge is essential for sticky removal, especially for the reduction of turbidity and TOC, but that sticky removal can be improved by a higher degree of starch hydrophobicity. The highest surface tension of the mixture between the model suspension and different starch types (mentioned above) was obtained with the benzyl starch, having the highest DS_{BN} (Fig. 8).

The surface tension of this mixture between modified starch and the suspension with a very high sticky content can be further increased by the addition of bentonite (Aquamont) [72], so that the resulting supernatant is almost free of surface-active substances (surface tension about 70 mN/m). It is also important that the mixing

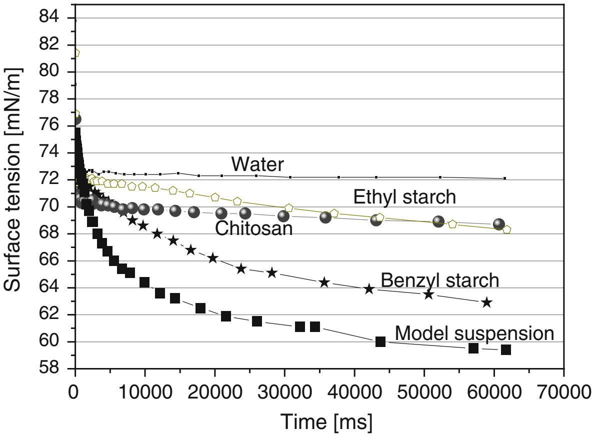


Fig. 9 Dynamic surface tension of mixtures between a highly surface-active model suspension and solutions (1 g/L) of modified natural polymers at the same mixing ratio (volume suspension: volume polymer) of 10:1; dynamic surface tension, was measured by bubble pressure tensiometer ($t = 60$ s)

ratio significantly influences the properties. Despite the fact that the turbidity removal is good in most cases, differences in the surface tension were obtained. The most effective composition (lowest TOC and highest surface tension) was obtained at a mixing ratio were the system is neutral.

Sticky removal with different natural polymers has been compared [69]. Tailored starches, with benzyl as well as with ethyl substituents, from very low to high cationic starch density, were investigated as well as benzylated chitosan.

In contrast to previous results [67, 68], the bubble pressure method, a relative simple and time-saving test method, was used for the dynamic surface tension measurement [69]. For comparison it was shown that the addition of unmodified starch did not have any positive influence on sticky removal: neither for decreasing the turbidity or TOC content, nor for the reduction of surface activity. In contrast, the interaction between the functionalized starches and DCS, and therefore the sticky removal, is significantly influenced by the main properties of the modified starches, i.e., their cationic charge density and their hydrophobicity. As already described, the stickies were removed due to complex formation between the tailored modified starch and the colloidal substances in the suspension having anionic charge. As demonstrated in Fig. 9, the surface tension of a sticky-containing model suspension increases due to the addition of modified natural polymers bearing cationic charge. As already shown [67, 68], the efficiency of sticky removal depends on the charge ratio (anionic:cationic charge), which means that it depends on polymer dosage. Most effective removal was obtained when the mixture between the starch and the SCS was neutral.

Consequently, the results shown in Fig. 9 do not show an optimum because the natural polymers have different cationic charge densities. Whereas the modified starch with low cationic charge (benzyl starch) is more effective at higher polymer dosage, the modified chitosan, having higher cationic charge, has optimum sticky removal at the dosage shown in Fig. 9. The ethyl starch, despite its low cationic charge, is also effective in reducing the surface activity due to its hydrophobicity [69].

4 Pre-mixed PECs as Flocculants

4.1 Complex Formation and Characterization

It is well known that oppositely charged PEL will form complexes over a broad range of stoichiometric ratios.

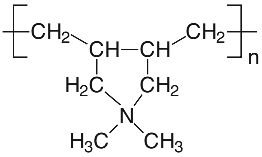
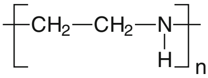
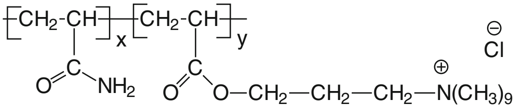
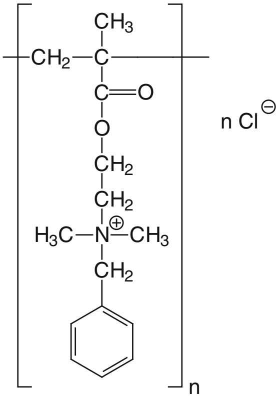
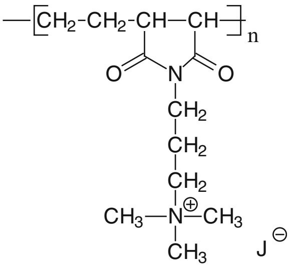
Such interactions were investigated, among others, by Tsuchida [70], Dubin [71], Philipp and Dautzenberg [72, 73], Müller [74–76], Pergushov and Müller [77], Dragan [12], and the group of Kabanov [78, 79]. Some of the most important PEL used for complex formation are summarized in Table 2 and in works by Dragan [12] and Jaeger et al. [80].

Kabanov et al. described the formation of water-soluble nonstoichiometric PECs (NPEC) as a result of the interaction of oppositely charged PEL in nonequivalent ratios. They are obtained by the interaction of polyions with different degree of polymerization, i.e., different molar masses. The polyions are introduced into the reaction in nonequivalent ratios so that a relatively long-chained host PEL (HPE) is incorporated into an NPEC particle in some excess in comparison with the opposite charged relatively short-chained guest PEL (GPE). Such NPEC are water-soluble because of their big differences in molar mass, and their properties can be studied by classical methods. An NPEC can be represented as a peculiar block copolymer with alternating hydrophobic double-strand blocks and hydrophilic single-strand blocks composed of sequences of HPE units incorporated in NPEC in excess (Fig. 10). One of the most important properties of NPEC is their ability to participate in intermacromolecular exchange and substitution reactions in aqueous solutions, as described by Kabanov [77]. These properties can be used to flocculate and separate materials such as dyes.

PEC nanoparticles, prepared by mixing solutions of the commercial low-cost PEL components PEI and PAC, were described by Müller et al. [75]. It was found that the size and internal structure of PEI/PAC particles can be regulated by process, media, and structural parameters. The mixing order, mixing ratio, PEL concentration, pH, and molar mass were found to be especially sensitive parameters for regulating the size (diameter) of spherical PEI/PAC nanoparticles, in the range between 80 and 1,000 nm, in a defined way.

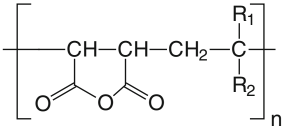
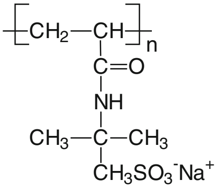
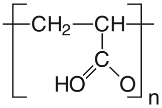
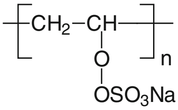
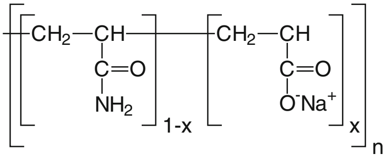
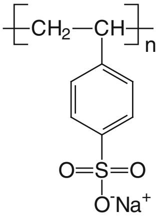
The formation of PECs using structurally uniform and strongly charged cationic and anionic modified alternating maleic anhydride copolymers was described by Mende [81]. The hydrophobicity of the PEL was changed by the comonomers (ethylene, isobutylene, and styrene). Additionally, the $n-/n+$ ratio of the molar charges of the PEL and the procedure of formation were varied. Dynamic light scattering indicates that, besides large PEC particle aggregates, distinct smaller and more compact particles were formed by the copolymers having the highest hydrophobicity (styrene). These findings could be proved by AFM. Measurements of fractal dimension, root mean square roughness, and the surface profiles of the PEC particles adsorbed on mica allow the following conclusions: the higher the hydrophobicity of the polyelectrolytes, the broader the particle size distribution and

Table 2 Structures of some of the most commonly used types of PEL for complex formation

Polycation (PC)	
Name	Structure
PDADMAC: poly(*N*,*N*-diallyl-*N*,*N*-dimethyl-ammonium chloride)	
PEI: poly(ethyleneimine)	
PAA: polyacrylamide (cationic)	
PMADAMBQ: copolymer of *N*-methacryloyloxy-ethyl-*N*-benzyl-*N*,*N*-dimethyl-ammonium chloride	
Poly(ethylene-trimethylammonium-iodidepropylmaleimide)	
Polyanions (PA)	–

(continued)

Table 2 (continued)

Polycation (PC)	
Name	Structure
Maleic anhydride copolymers	
NaPAMPS: poly(sodium 2-acrylamido-2-methylpropanesulfonate)	
PAC: polyacrylic acid	
PVS: poly(vinylsulfonate)	
PAA: polyacrylamide (anionic)	
PSS: poly(styrene sulfonate)	

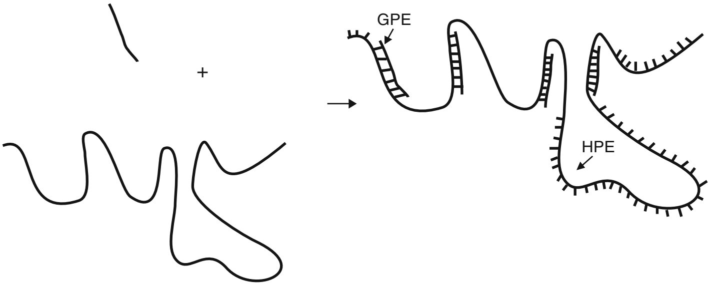


Fig. 10 Fragment of a nonstoichiometric PEC particle having hydrophilic as well as hydrophobic units. *GPE* guest PEL, *HPE* host PEL. Adapted from [82]

the minor the swelling of the PEC particles. Hence, the most compact particles were formed with the very hydrophobic copolymers.

4.2 Influence of Polymer Type on Complex Properties

From basic research on PECs, we can summarize the following important points.

There are many parameters that can influence the formation of PECs:

Charge density of the polyelectrolytes

- Strong polyelectrolytes (the charge does not depend on pH) with high charge density have a rod-like structure; they form complexes with a ladder-like-structure.
- In strong polyelectrolytes with low charge density, the polymer is coiled. In the case of a weak PEL such as PEI, PAC, or chitosan as a natural polymer, the complex formation is influenced by the pH dependence of the polymer charge. In such cases, the complexes are formed between coils of PC and coils of PA.

Molar mass

Complexes made from polyelectrolytes with low and medium molar mass (such as PDADMAC, PSS, PEI, PAC) are studied very often and are used in different fields of application.

Complexes made from PEL with very high molar masses (more than 10^6 g/mol) are used in paper production; such complexes are formed from big polymer coils and therefore such PECs are very large.

Polyelectrolytes with big differences in their molar mass form PECs that are water-soluble.

Substances bearing hydrophobic parts such as PSS, PMBQ, styrene or surfactants and micelles form complexes that are very dense or compact. The stability is often low.

Other parameters that can influence complex formation are the mixing conditions such as mixing speed, order of addition, ionic strength, and pH.

4.3 Application of Pre-mixed Complexes as Flocculants

For a long time, the application of pre-mixed PECs as flocculants seemed to be a field of academic work that had not found a practical application [20]. But, as found earlier [82], such complexes made from oppositely charged polymer solutions have interesting properties and are very effective for the flocculation of finely dispersed inorganic particles. A reflocculation was not noticed in a wide range of concentrations. Investigations on PECs as flocculants for inorganic particles like silica are important for the understanding of flocculation mechanism. But, PECs will never be applied as flocculant for such inorganic particles in practice. Nevertheless, PECs play an important role as flocculants in certain applications for special problems in wastewater treatment, such as low content of solids, soluble detrimental substances, or small amount of dye that can color a big volume of water. Therefore their removal is important.

As one of the first to study this, Somasundaran and coworkers [83] found that combinations of polystyrene sulfonate and cationic polyacrylamide enhanced the flocculation of (positively charged) alumina suspensions. The weight ratio of the two polymers was kept at 1:1 for all experiments. But, pre-mixing of the two polymers did not give as good results as those obtained when the polymers were added step by step [82]. In our opinion, the charge ratio of both PECs is extremely important and influences the flocculation mechanism. Effective flocculation can be found with highly charged complexes as well as with complexes near the 1:1 ratio of charges.

Onabe [84] analyzed the drainage behavior of pulp suspensions with a two-component system, with attention to polyion complex formation. With cationic and anionic polyacrylamides (molecular weights 3,000,000 and 1,000,000 g/mol) added individually, a polyion complex with an irregular three-dimensional structure was precipitated on the fiber surface. This reduced the homogeneity of the paper sheets. In contrast to this, a pre-mixed system of an anionic and cationic polyacrylamide [83] resulted in an improvement in pulp retention and paper quality (paper strength). Because of the very high molar mass and thus the big coil diameter, the formed PECs are very big and are therefore good flocculants.

Wagberg and coworkers [85] described the preparation and characterization of complexes for dry and wet strength improvement of paper. They investigated the structure of complexes formed by two oppositely charged PEL commonly used in the paper industry: polyamideamine epichlorohydrine condensate (PAE) and carboxymethylcellulose (CMC). They found that complexes can have a good resistance to PEC aggregation/dissolution at high salt concentrations and that it was possible to adjust the net charge of the complex particle solutions, making the PEC of great value in papermaking for covering the fibers with a high amount of material in a one-step procedure.

CMC-rich cellulose sheets were prepared by Uematsu [86] with a cationic retention aid. When 5% poly(*NNN*-trimethyl-*N*-(2-methacryloxyethyl) ammonium chloride (PTMMAC) and 5% CMC were added to cellulose slurries, approximately 94% of the polymers were retained in the sheets by formation of a polyion complex.

PEC dispersions have been used as a fixing agent, flocculant, or retention aid to increase the water resistance of paper [87].

Detailed studies of particle (silica) flocculation using pre-mixed complexes were done by Buchhammer [88], Schwarz and Dragan [89], and Mende et al. [90, 91].

The flocculation efficiency of some nonstoichiometric interpolyelectrolyte complex dispersions synthesized by the interaction between poly(sodium 2-acrylamido-2-methylpropanesulfonate) (NaPAMPS) and three strong PCs bearing quaternary ammonium salt centers in the backbone on a stable monodisperse silica dispersion have been tested. The PCs PDADMAC and PCA5 alone showed a very narrow range of flocculation. In the case of the most hydrophobic PC, PCA5D1, the window of optimum flocculation concentration was broader compared with other PCs [88].

Mende investigated the flocculation of silica dispersions in dependence of the properties of nonstoichiometric PECs with different charge excess and hydrophobicity as well as different average hydrodynamic particle size. PDADMAC as PC and different PAs such as poly(styrene-*p*-sodium sulfonate) (NaPSS) and poly(acrylamide-*co*-sodium acrylate), were used so that PECs with different charge excess and hydrophobicity as well as different average hydrodynamic particle size could be prepared. The work was focused especially on the stability of complexes and it was pointed out that a higher tendency to instability results for complexes with PAs that have a Π-system (phenyl-) in the polymer chain [94]. The average hydrodynamic particle size and the polydispersity indices (PI), determined by dynamic light scattering were strongly influenced by the mixing conditions of the PECs and the nature of the used polyelectrolytes. It was found that particles with narrow or monodisperse distribution can be prepared under the condition that the PC is the starting solution, as shown in Fig. 11. Dispersions with PI values between 0.03 and 0.06 are described as monodisperse, whereas a narrow particle size distribution is found at PI values between 0.1 and 0.2. A broad particle size distribution is represented by PI values between 0.25 and 0.5; at PI > 0.5 the result is not analyzable [89].

The reaction process between silica and the used flocculants can be divided into three intervals (destabilization, flocculation optimum, and restabilization) as known for all other polymer flocculants. For an effective flocculation of a charged substrate, both electrostatic as well as hydrophobic interactions play an important role. The interval up to the beginning of the flocculation optimum is mainly influenced by electrostatic interactions (the charge density of the flocculant) but the broadness of the flocculation optimum depends largely on hydrophobic interactions. Hydrophobic interactions also play an important role in the shear stability of the formed flocs.

As shown in Fig. 12, the floc size rapidly increases in dependence of flocculant charge added to the silica dispersions. The size of flocs obtained with complexes is larger than the size of flocs obtained with the pure PC. The monomodal particle size distribution for the silica dispersion ($n = 0$) changes to bimodal or multimodal under the influence of the amount of cationic charge. With increasing amount of cationic charge, the volume proportion of single silica particles decreases and the fraction of bigger aggregates increases (Fig. 12a). The beginning of the flocculation optimum

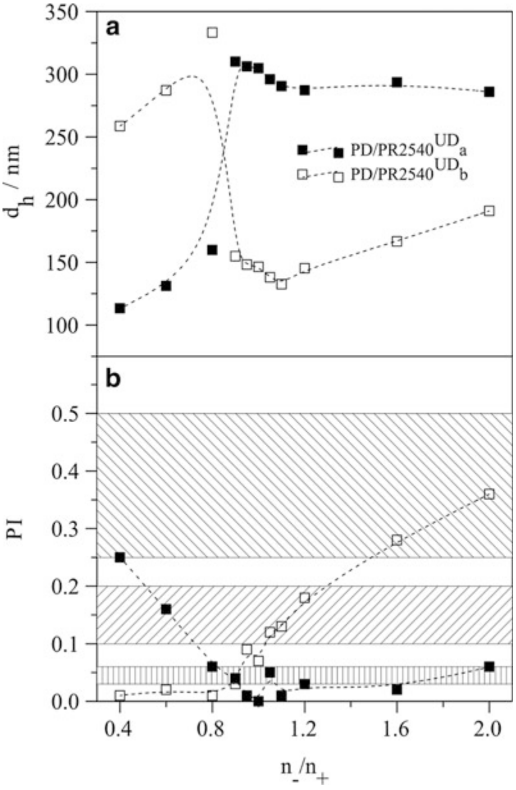


Fig. 11 Average hydrodynamic particle size d_h (*top*) and polydispersity index (PI) (*bottom*) of the studied stable PEC dispersions in dependence on the molar ratio *n*−/*n*+. PDADMAC (PD) as PC is combined with a commercial polyacrylamide copolymer (*PR2540*): (**a**; filled quares): PD is the starting solution, (**b**; empty squares): PR2540 is the starting solution

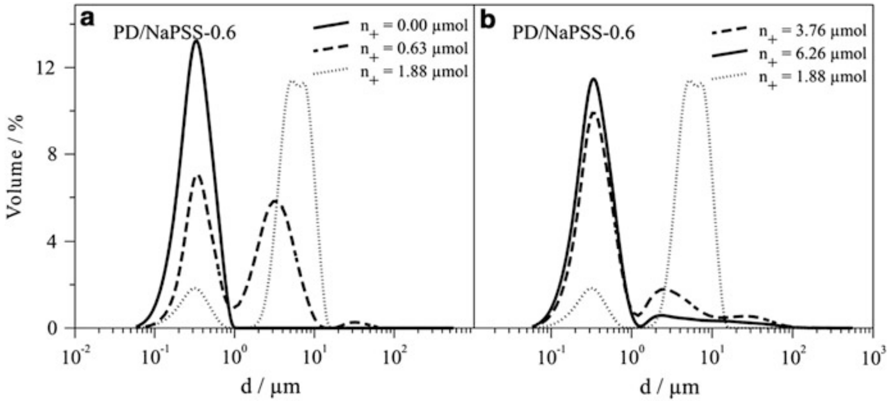


Fig. 12 Particle size (diameter; % volume distribution) of silica dispersions without flocculant (*n*+ = 0.00 μmol) and treated with PD/NaPSS complexes with *n*−/*n*+ ratio of 0.6 in dependence on the flocculant charge (*n*+) added to silica dispersions: (**a**) low cationic charge (0–1.88 μmol/L); (**b**) higher cationic charge (1.88–6.26 μmol/L)

was found at $n+ = 0.63$ μmol, where the peaks of both fractions have nearly the same size. At very high concentrations of cationic charge (Fig. 12b), the particle size distribution becomes smaller again. It was also confirmed by sedimentation analysis that the broadness of the so-called flocculation window (range of optimum flocculant concentration) depends on the hydrophobicity of the flocculant [90].

Nyström et al. [92, 93] correlated the observed flocculation behavior of calcium carbonate, induced by mixtures of cationic starch and anionic poly(sodium acrylate) (NaPA) at various electrolyte concentrations, with the complex properties. A strong correlation exists between the properties of the PEL mixture, primarily the amount of complexes formed, and the flocculation behavior. Several mechanisms are involved in this flocculation process induced by the two polymers. However, interparticle bridging by the PECs and charge neutralization induced by the deposition of the complexes were found to be the main reasons for the enhanced flocculation.

As already mentioned, the removal of different dyes is one of the fields where complexes can successfully be applied [94–97]. The "direct" formation of complexes between a PC and anionic dyes with two, three, or six sulfonic groups was investigated using UV–vis spectrophotometry and viscosimetry. Dragan et al. [12] also reported the formation of complexes having three components. They were formed by the interaction between nonstoichiometric PC/dye complexes with PAs. PCs differed in their content of the *N*,*N*-dimethyl-2-hydroxypropylene ammonium chloride units in the main chain. NaPA, NaPAMPS, and NaPSS were used as PAs. Crystal Ponceau 6R and Ponceau 4R with two or three sulfonic groups were used as anionic dyes. The formation of the three component PC/dye/PA complexes takes place mainly by the electrostatic interaction between the PA and the free positive charges of the PC/dye complex. The stoichiometry and the stability of such complexes depends on the PC structure, the structure and molar mass of PA, the dye structure, and the P:dye molar ratio. A high amount of the dye was excluded from the complex before the end point, when a branched PC was used. The higher the solubility of the dye, the lower the stability of the PC/dye/PA complexes [12].

The mechanism of dye incorporation into triple complexes was also intensively studied by Zemaitaitiene et al. It was shown that cationic polymer tends to react with anionic textile finishing chemicals and auxiliaries such as anionic detergents, forming intermolecular complexes of different stoichiometry. Under controlled conditions, these complexes can incorporate the dye and precipitate. Surprisingly, the disperse dye (which was uncharged) also seemed to be bound by polymer–polymer complexes [98, 99].

Buchhammer et al. [100] investigated the flocculation behavior of two PCs in comparison with pre-mixed PEC nanoparticles. These results show that depolarization of the dye solution can be achieved with the PCs as well as with the complex dispersions, depending on the type and quantity of the flocculant used. However, significant differences with regard to the removing efficiency and the usable range for effective flocculation exist. For both PCs used, which differed markedly in terms of their structure and chain length, a relatively narrow flocculation window was found. It was also interesting that the concentration ratio $c_{\mathrm{dye}}/c_{\mathrm{polymer}}$ is determined essentially from the properties of the PC. The concentration ratio is shifted significantly to lower values with the long chain PMADAMBQ that is sterically stabilized. For application, this means that long chains as well as branched polymers are particularly effective when used as flocculants for depolarization of textile effluents containing, e.g., disperse dyes at low concentration. Further, it was shown that the dye structure had a marked influence. The dye content after separation was at least 15% for the disperse dye Celliton Fast Blue, whereas the degree of dye removal was much better for Cibacet Red [104]. Solid–liquid separation processes in general use highly hydrophilic linear polyelectrolytes with excellent water solubility as processing aids, but not all flocculation processes can be carried out with sufficient efficiency. These disadvantages may be overcome using associating or aggregating cationic polyelectrolytes as flocculants. A significant enhancement of the flocculation properties can be achieved by introduction of hydrophobic functionalities into the PEL backbone [101–103].

4.4 Polymer–Surfactant Complexes

It was also interesting to investigate the application of pre-mixed polymer–surfactant complexes (PSCs). Such mixtures of polymers and surfactants are common in many industrial formulations. The interaction between surfactants and water-soluble polymers provides special effects, e.g. enhancing the surface activity, stabilizing foams and emulsions, etc. It is, therefore, very important to study the interaction between surfactants and water-soluble polymers, especially between components of opposite charge. The first results were described in the literature of the 1970s, and from 1980 until now much work has been done to improve the understanding of such systems [104–107]. Very detailed investigations using different characterization methods such as surface tensiometry, light scattering, neutron scattering, NMR or ESR, and surface rheological methods [108–123] are mentioned. Usually, mixed solutions at fixed PEL and variable surfactant concentrations are investigated and it can be shown that the association between PEL and oppositely charged surfactant starts at very low surfactant concentration (typically one to three orders of magnitude below the cmc of the surfactant). The degree of surface tension lowering depends not only on the type of PEL (on their hydrophobicity, charge density, molar mass), but also on the mixing conditions (order of addition, influence of time) and salt content [124]. In most studies, a fixed polyelectrolyte amount was added to solutions of an oppositely charged surfactant (the “polymer to surfactant regime” [123]). Because the interaction between polymer and surfactant starts at very low surfactant concentration, basic research is often carried out below the cmc, but for industrial applications the interaction with polymers at higher surfactant concentration is also important. However, despite the importance and common use of PSCs there are only very few publications about application-relevant properties. As mentioned above, it is possible to tailor stable, differently charged dispersions made from oppositely charged polyelectrolytes and surfactants that can be used for different applications, such as surface modification of powders, sorption of organic molecules from wastewater, or as flocculants. As an example, complexes with PDADMAC as PC and sodium dodecylsulfate (SDS) as an anionic surfactant are shown in Fig. 13.

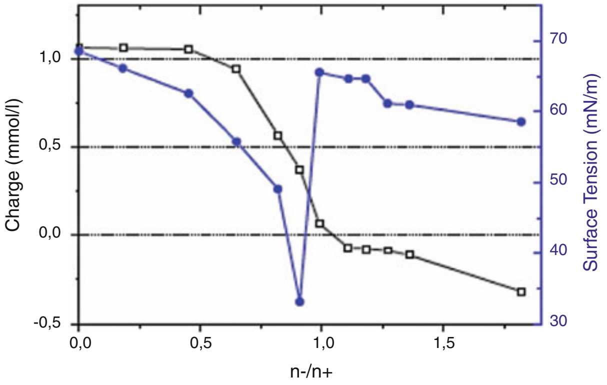


Fig. 13 Charge and surface tension of PSCs made from PDADMAC and SDS in dependence on *n*−/*n*+

Whereas the charge continuously decreases with increasing SDS content, the surface tension has a minimum near the 1:1 charge ratio. Such complexes were used for the separation of silver particles on zeolite. The separation of such fine particles was impossible with commercial flocculants, but successful with PCSs.

The interactions between a technical cationic surfactant (dodecyl-amidoethyl-dimethylbencyl-ammonium chloride) and anionic polyelectrolytes were investigated [123, 125]. The cationic surfactant strongly interacts with different PAs such as copolymers of maleic acid or PSS. This makes it possible to tailor complex dispersions with different properties that are sufficiently stable and can be used for the separation of dyes or dye-containing wastewater. Such nanoparticles are able to bind disperse dyes effectively due to their size (i.e., in the same range as the dye molecules) and their structure. They can bind the individual dye aggregates via hydrophobic as well as electrostatic interaction forces. The more stable dispersion with poly(maleic acid-*co*-propylene), P(MSP), compared with the α-methylstyrene copolymer P(MS-α-MeSty) is favorable for use in different applications. PSCs are very effective flocculants [124]. Whereas not more than 85% of Celliton Fast Blue could be removed with PECs, this value can be increased up to more than 95% by using PSCs. The supernatant is clear and seems to be colorless. Factors affecting the quality of flocculation are the charge and the hydrophobicity of the components and, as a consequence, the particle size. The application of "neutral" complexes results in a broad flocculation window.

The flocculation performance of polyampholytes (terpolymers containing hydrophobically modified cationic, hydrophilic nonionic, and anionic monomer units, always with an excess of cationic charges) was investigated [126]. The results were compared with homopolymers and with those obtained using nonstoichiometric (PSC) dispersions with adjustable surface charge density. The polyampholytes as well as the PSC can successfully remove the dye Celliton Fast Blue (Dispers Blue 3). The efficiency of dye separation is mainly influenced by the charge of polymers or complexes, demonstrating that charge neutralization is one possible flocculation mechanism. However, PSC, which are almost neutral, are also able to remove the dye due to their size and structure. In this case, the degree of dye removal is a little better and the so-called flocculation window is broader, as in the case of charge neutralization.

The removal of dye was also investigated [127]. PECs, described as “new particle forming flocculants”, were used in comparison with PCs to separate dyes from sludge (mixture of organic and inorganic components). The charge of the system to be flocculated was shown to be the most important property for influencing flocculation behavior. Therefore, sludge with strong anionic charge could be separated with commercial PC according to a patch mechanism, whereas for the removal of nearly “uncharged” sludge or dye the complex particles were more effective. The latter can be easily tailored with different properties by the interaction between aqueous solutions of dodecylamidoethyl-dimethylbencyl-ammonium chloride (Quartolan), which carries a positive charge, and a PA such as PSS. In dependence on the mixing ratio $n-/n+$ as well as on the dosage, these complexes can effectively eliminate commercial dyes such as Acid Yellow 3 or Acid Blue 74 due to their hydrophobicity and structure.

PSCs can be also used as flocculants in montmorrilonite dispersions [128]. An anionic surfactant (SDS) was combined with a cationic polymer (PDADMAC). At a 1:1 molar ratio, optimal flocculation was obtained owing to the formation of an insoluble surfactant–polymer complex in the presence of particles. Such interactions may lead to a flocculation mechanism that combines polymer adsorption, charge neutralization, and hydrophobic interactions. Other experiments have shown that a similar flocculation process can be achieved by using a cationic surfactant and anionic polymer [127].

4.5 Removal of Organic Pollutants

Buchhammer [129] described the design of new materials for removing organic pollutants such as *p*-nitrophenol or dyes from wastewater. The sorption of solved organic molecules on previously formed PSCs or PECs (PC/PA) was studied. The scheme of complex formation and possible structures is presented in Fig. 14. The sorption capability of such macromolecular assemblies increases with increasing molar mass and hydrophobicity of the macromolecules used.

The solubilization of hydrophobic molecules such as pyrene (a fluorescence probe), or Nile Red (a solvatochromic probe) in nanoparticles was investigated by Nizri et al. [130]. They studied the morphology of the resulting nanoparticles and their ability to solubilize hydrophobic materials. As shown by AFM and SEM imaging, the particles are spherical, having a diameter of about 20 nm. From pyrene solubilization it appeared that the hydrophobicity of the nanoparticles depends on the ratio between SDS molecules and the charge unit of the polymer and therefore they confirmed the results described by other authors [128].

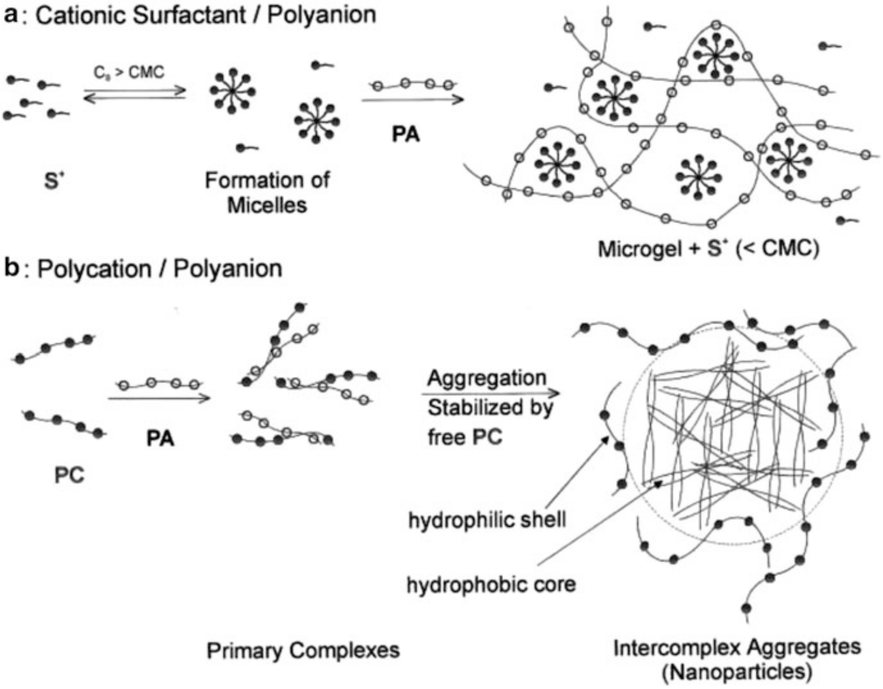


Fig. 14 Scheme of complex formation and possible structures: (**a**) cationic surfactant/PA; (**b**) PC/PA. Adapted from [128]

5 Current Trends and Future Research Directions

5.1 Advanced Characterization Methods

In contrast to previous research in the field of flocculation, which mostly investigated the direct interaction between one substrate and one polymer, today we have to deal with multicomponent mixtures and formulations. Therefore, a direct and efficient method for the characterization of the sedimentation behavior is necessary. It is demonstrated that the separation analyzers LUMiFuge and LUMiSizer can be used for a pre-selection of flocculants [131, 132]. The LUMiSizer is a microprocessor-controlled analytical centrifuge that allows determination of space- and time-resolved extinction profiles during the centrifugation of up to 12 samples simultaneously [133]. This multisample analytical batch centrifugation with optical detection proved to be a versatile tool for the determination of the characteristic material properties related to the sedimentation and consolidation behavior of dispersions. This was demonstrated for the sedimentation and consolidation of rigid non-interacting particles and also for the consolidation of interacting network-forming particles.

The evaluation of ceramic dispersions using analytical centrifugation (STEP-Technology), combined with multisample analytical centrifugation is described [134]. The shear-dependent sedimentation rate, consolidation, and packing behavior are directly analyzed. In addition, the particle size distribution can be obtained with high resolution. Application studies on kaolin, silicon carbide, and silica dispersions show the high potential of this method. The potential of multisample analytical centrifugation for formulation design (stability as well as flocculation) was demonstrated in investigations on the effect of particle (silica, calcium carbonate) and polymer (PAA) concentration on dispersion properties of different stabilized suspensions [135].

The dispersibility of carbon nanotubes (CNTs) was assessed by studying the sedimentation of CNTs dispersed in aqueous surfactant solutions at different ultrasonication treatment times using a LUMiSizer. Different commercially available multiwalled CNTs, such as Baytubes C150P or Nanocyl NC7000, showing quite different kinetics, were compared. In addition, the particle size distributions were analyzed using dynamic light scattering and centrifugal separation analysis [136].

As described, the application of flocculants with two or more components is of growing importance for solid–liquid separation processes, including the dewatering of ultrafine materials (sludge from clay, coal, or gravel pits) or sewage sludge. Through various examples involving the preparation of well-characterized model systems, it has been demonstrated that the removal of detrimental substances such as colored materials (dyes) or stickies is favorable by the formation of PECs. In addition, PECs as well as PSCs can be used as materials for the sorption of hydrophobic materials such as organic compounds.

5.2 Use of Natural Polymers

For many years, in most cases synthetic polyelectrolytes such as PDADMAC or PEI as PC, and PAC, PAMPS, or PSS as PA were used for complex formation. But at present, the application of so-called natural polymers is of growing importance in the field of complex formation. Natural polymers occur in nature and can be extracted. Examples are chitosan as well as polysaccharides such as starch, pectin, or alginate. Natural polymers are used because of their good biodegradability and high biocompatibility in a wide range of applications in industry. They can have cationic charge (chitosan) [137] or can be modified with cationic as well as hydrophobic units [74].

The interaction between modified starch and sticky-containing wastewater was mentioned in Sect. 3.2. of this article [67, 68]. Mihai [141] investigated chitosan-based nonstoichiometric PECs (NPECs) as specialized flocculants. Such NPEC were more effective than chitosan in kaolin separation. Their main advantage is the increase in critical concentration for kaolin restabilization. The NPEC particles were adsorbed on the kaolin surface, protecting them more efficiently against re-dispersion.

The physicochemical properties of biopolymer-based PECs with controlled pH and/or thermoresponsiveness were described by Glampedaki et al. [138, 139]. The study [138] illustrates a novel combination between negatively charged pH- and thermoresponsive microparticles of poly(isopropylacrylamide-*co*-acrylic acid) (PNIAA) and positively charged chitosan chains. Morphological and physicochemical aspects of the stimuli-responsiveness of the complexes were investigated through scanning electron microscopy, polyelectrolyte titration, UV–vis spectroscopy, analytical centrifugation, and tensiometry. The PNIAA thermoresponsiveness kinetics was found to be both temperature- and pH-dependent. Chitosan/PNIAA complexes appeared more hydrophobic below LCST and more hydrophilic above LCST, compared with PNIAA alone. Their demixing behavior revealed that chitosan/PNIAA complexes are more sensitive to pH and temperature changes than their individual components. Finally, complexes were found to be surface-active, with their surface activity lying between those of chitosan and PNIAA. The information obtained about hydrophilicity/hydrophobicity aspects of the studied systems is considered essential, as they are intended for interesting applications such as polyester surface functionalization.

The preparation of pH- or thermoresponsive microgels of NIPAAm copolymerized with acrylic acid, either alone or complexed with chitosan is described [138]. All properties of the microgels are in very good correlation with those expected from the chemical structure of the polymers used for their preparation.

A new type of a dual system using mixtures of chitosan and a thermosensitive polymer has been described in Sect. 2.7 [47–50].

PECs also have been the focus of an expanding number of studies for their wide use in medicine. For instance, biopolymer nanoparticles have been described as very promising nanosized carrier materials with great potential in health care and environmental sciences [140].

Müller et al. [141] described PEC nanoparticles prepared by mixing solutions of oppositely charged PEL, whose size and shape can be regulated by external and media parameters. An improved preparation protocol for PEC nanoparticles based on consecutive centrifugations was elaborated, resulting in better reproducibility and lower polydispersity. Experimental and simulation evidence showed that salt and PEL concentration are sensitive parameters for size regulation of spherical PEC nanoparticles. The authors outline certain advantages of dispersed PEC particles for life science applications due to easy preparation, graded nanodimensions, achievable solid content, and uptake/release properties for proteins and drugs.

The physicochemical and biological properties of DNA and small interfering RNA (siRNA) complexes prepared from a set of maltose-, maltotriose-, or maltoheptaose-modified hyperbranched PEIs [termed (oligo-)maltose-modified PEIs; OM-PEIs] were investigated [142]. The authors showed that pH-dependent charge densities of the OM-PEIs correlate with the structure and degree of grafting and with the length of the oligomaltose. Decreased zeta-potentials of OM-PEI-based complexes and changes in the thermodynamics of DNA complex formation are observed, while the complex sizes are largely unaffected by maltose grafting and the presence of serum proteins.

But, these aspects of complex application in medicine are not addressed in this review and therefore they are not referred to in detail here.

6 Summary and Outlook

Polyelectrolytes and their complexes play a central role in solid–liquid separation processes such as paper making or waste water treatment.

A lot of different products are available – synthetic as well as natural polymers. Worldwide, the use of PECs is a fast growing market for treating water in different spheres of life, such as the supply of drinking water, the purification of wash water, or the dewatering of sludge.

The main message of this review is that many different ideas based on an understanding of colloid–polymer interactions have been developed for solving different problems, at first in the paper industry, but also for other technologies such as the separation of metals (like alumina) or minerals, the dewatering of sludge, or the removal of dyes.

The direct interactions between a flocculant (PC) and a charged particle suspension have been investigated for many years and are not the topic of this review. But, it is important to know (also for dual flocculation) that polymers with low molar mass can flocculate via neutralization or patch flocculation mechanism, whereas polymers with higher molar mass can flocculate via bridging. Decreasing the charge density of polymers makes the flocculation range broader and the flocs bigger.

Because the separation problems have become more and more complex, new principles of flocculation must be used to meet all requirements, such as the removal of heavy metals, dyes, or natural colloids. Instead of monoflocculation with one polycation, pre-mixed PECs (made from PC and PA), which are effective flocculants due to their size and structure, are used. Because hydrophobic interactions are of growing importance for the removal of hydrophobic substances such as oil, it is necessary to introduce hydrophobic parts into the flocculants or, alternatively, to use pre-mixed PSCs.

Last but not least, the flocculation efficiency of synthetic polymers should be compared with natural polymers like chitosan, or with polysaccharides such as modified starch, pectin, or alginate.

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