

Dye Flocculation Using Polyampholytes and Polyelectrolyte-Surfactant Nanoparticles

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ABSTRACT: In this article, we report on the dye flocculation performance of polyampholytes containing hydrophobically modified cationic, hydrophilic nonionic, and anionic monomer units, always with an excess of cationic charges. The results are compared with homopolymers and with those obtained using nonstoichiometric polyelectrolyte-surfactant complex (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 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 bit better and the so-called flocculation window is broader as in the case of charge neutralization. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1342–1349, 2007

Key words: flocculation; dye; terpolymers; polyelectrolyte complex

INTRODUCTION

Conventional techniques for purification of dye-containing wastewaters that were also used in combination with other methods are the treatment with inorganic salts (aluminum or ferric oxides)^{1,2} or dye removal using adsorbents such as activated carbon, peat, bentonite clay, or fly ash.^{3–6} The most essential drawbacks are the large amount of dye-containing sludge and the low efficiency with respect to some dyes. So, Marmagne and Coste⁵ studied color removal by the addition of activated carbon and compared the results for different types of dyes. Although color removal efficiency was over 90% for mordant, cationic, and acidic dyes, it was about 40% for direct or dispersed dyes.⁵

Among the commercial textile dyes, particularly disperse dyestuffs are of environmental interest because of their widespread use for dyeing hydrophobic fibers, such as nylon or polyester, and their low removal rate during aerobic waste treatment as well as advanced chemical oxidation.¹ Therefore, new concepts for separation such as the effective removal of disperse dyes have been attracting attention.^{7,8} One option is the application of polymers or polymer combinations. It was found^{9,10} that complexes, formed by

electrostatic interaction between polycation and poly-anion could incorporate the dye particles. Buchhammer et al.¹⁰ investigated the flocculation behavior of two polycations (PDADMAC, PMADAMBQ) in comparison with the premixed polyelectrolyte complex nanoparticles. These results show that the depolarization of the dye solution can be achieved with the polycations as well as with the complex dispersions depending on the type and quantity of the respective flocculant used. However, significant differences with regard to the removing efficiency and the usable range for effective flocculation exist. For both polycations used, which differ markedly in terms of their structure and chain length, a relatively narrow flocculation window was found. It was also interesting that the concentration rate $c_{\text{dye}}/c_{\text{polymer}}$ is determined essentially from the properties of the polycation. It was shown that 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 these are 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.¹⁰ 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 suffi-

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TABLE I
Composition and Properties of Polymers (Terpolymers and Homopolymers)
in Aqueous Solution (1 g/L)

Polymer	MADAMBQ (mol %)	MAS (mol %)	AAM (mol %)	Charge ^a (mmol/L)	Molecular weight (g/mol)
TP1	73	7	20	+2.4	2,020,000
TP2	83	5	12	+2.9	1,830,000
TP3	14	13	73	+0.94	1,820,000
MADAM	100% poly-MADAM			+5.1	390,000
MADAMBQ	100% poly-MADAMBQ			+4.5	720,000

^a Polyelectrolyte titration (PCD 02, Müttek, Germany).

cient 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 polyelectrolyte backbone.^{11–13}

In this article, we report on the dye flocculation performance of polyampholytes containing hydrophobically modified cationic, hydrophilic nonionic, and anionic monomer units, always with an excess of cationic charges. Because of the possible intra- and intermolecular Coulombic interactions within these macromolecules, we assume an increase of the aggregation tendency leading to improved flocculating properties. The results are compared with those obtained using nonstoichiometric polyelectrolyte–surfactant complex (PSC) dispersions with adjustable surface charge density as new dye flocculants.

MATERIALS AND METHODS

Polymers

The synthesis of the polyampholytic terpolymers (TP) of *N*-methacryloyloxyethyl-*N,N*-dimethyl-*N*-benzylammonium chloride (MADAMBQ), acrylamide (AAM), and methacrylic acid (MAS) was performed in two steps. At first, copolymers of MADAMBQ and AAM were synthesized by free radical polymerization of different ratios of the monomers in aqueous solution at 30°C under nitrogen using 10^{−2} mol/L 2,2′-azobisobutanamide dihydrochloride as an initiator. The overall monomer feed was 2 mol/L. Second; purification takes place by ultrafiltration (Minisette Omega, Pall Filtron, cut off 30 × 10³ g/mol) and freeze drying. After several hours, a small increase of the pH was observed during the ultrafiltration process. This leads to a slight hydrolysis of the MADAMBQ units leading to the formation of MAS units. Thus, increasing time of ultrafiltration results in an increasing amount of the anionic parts in the now-formed polyampholytic TP.

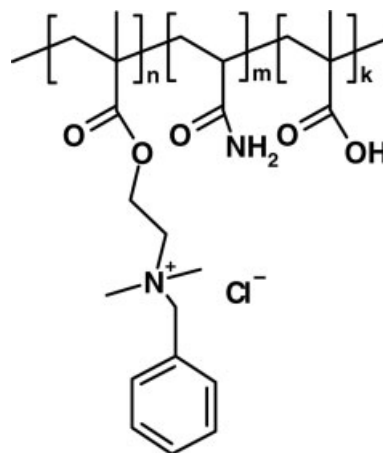
The easily adjustable composition was determined by ¹³C NMR (400 MHz) spectroscopy (inverse gated

decoupling, without NOE decoupling) using a Unity 400 (Varian) (Table I).

The weight-average molar masses of the samples were determined by multiangle light scattering gel permeation chromatography (TSK columns by Tosohaas; laser light scattering detector Dawn DSP, 632.8 nm, 18 detectors from 22.5° up to 147° from Wyatt; eluent 0.2 mol/L Na₂SO₄ and 1% (w/w) acetic acid in deionized water).

M_w values of the TPs were detected as 1,800,000–2,000,000 g/mol.

Probably, these values are something too large, because some association between the oppositely charged parts of different macromolecules cannot be excluded (Table I).



The synthesis of homopolymers of MADAMBQ and of *N*-methacryloyl-*N,N,N*-trimethylammonium chloride (MADAM), which were used for the comparison of flocculation behavior, was carried out by free radical polymerization in aqueous solution according to the literature,¹⁴ followed by purification as described for the TPs.

Dynamic light scattering (DLS), also known as photon correlation spectroscopy (PCS), was applied to determine the hydrodynamic particle size. We used two different devices. At first, the measurements were carried out with ALV/DLS/SLS-5000 (ALV GmbH, Langen, Germany) equipped with an ALV-5000/EPP

TABLE II
Characterization of the Flocculated Substance/Dispersion

Dye blue	Concentration	Average particle size (nm)	Charge ^a	pH
Cellitone fast blue (Disperse blue 3)	80 mg/L	280	-0.074 mmol/L	6.25
anthraquinone-type C.I. 61505			-0.0925 C/g	

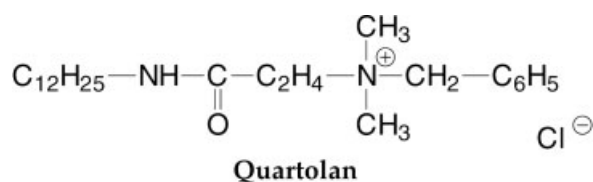
^a Polyelectrolyte titration.

multiple digital time correlator and laser goniometer system ALV/CGS-8F S/N 025. The light source was a 22 mW Helium Neon laser ($\lambda = 632.8$ nm). The light scattered by particles is recorded at angles of 60° and 90°.

The second device was Zetasizer Nano S (ZEN1600) from Malvern Instruments, UK. The instrument is equipped with NIBS[®]-technology (patent from ALV GmbH, Germany), an avalanche photodiode, Q.E. > 50% at 633 nm. A 4 mW Helium Neon laser is used as a light source. For the regulation of light intensity, the device has a movable sample cell and an attenuator.

Polyelectrolyte–surfactant complexes

Polyelectrolyte–surfactant complexes (PSC) with different properties (varying from positive charge to negative) can be easily formed by the interaction between the surfactant Dodecylamidoethyl-dimethylbenzylammoniumchloride (Quartolan) that carries positive charge and the sodium salt of the polyanion poly(styrenesulfonate) (P-SSNa), obtained by Aldrich; molecular weight 70,000 g/mol.



Different amounts of the polyanion (as 0.01 mol/L aqueous solution) were slowly added to the solution of Quartolan (0.005 mol/L) under stirring. The ratio n^-/n^+ represents the molar ratio of the anionic and cationic charged groups in the entire mixture.

After preparation, the PSCs were characterized with the following methods:

The stability of complex dispersions was characterized by using Nephelometric turbidity measurement 2100 AN IS (Hach, Germany).

The charge of the polymer and the surfactant solution as well as the charge of mixtures were determined by polyelectrolyte titration with particle charge detector PCD 02 (Mütek, Germany). This system, working according to the streaming potential principle, was

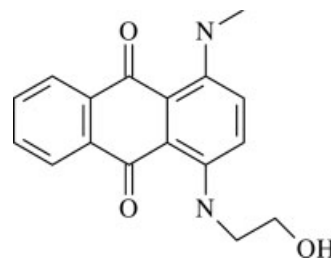
used to detect the isoelectric point of the titration process. An aqueous solution of the cationic polyelectrolyte PDADMAC (0.001 mol/L) was used as titrant for anionically charged mixtures and sodium polyethylenesulfonate (0.001 mol/L) for dispersions with cationic charge.

DLS with Zetasizer Nano S—see description in the part Polymers section.

All DLS measurements were repeated at least five times to get sufficient results.

Flocculation trials—dye removal

The dye Cellitone Fast Blue or “dye blue” (Table II) was dispersed in distilled water by ultrasonic treatment (1 h) and stirring.



After a dispersing time of 24 h, the light absorption (595 nm) of the unflocculated dye solution (80 mg/L) was 0.29.

Different quantities of the polymers (as 1 g/L aqueous solution) or of the preformed complex dispersions were added to 20 mL of the dye solution under gentle mixing. The separation was accelerated by using centrifuge (10 min; 10,000 rpm), because the velocity of dye sedimentation in most cases was low—also with flocculants. Then, the absorbance of the supernatant was measured again at the dye’s absorption maximum (595 nm) with the Lambda 900 spectrophotometer (PerkinElmer).

RESULTS AND DISCUSSION

Dye removal

The disperse dye Cellitone Fast Blue was used as a model to investigate the flocculation properties of the new TPs. As already mentioned,¹⁰ the removal of this



Figure 1 Flocculation of the dye solution (80 mg/L) after adding different quantities of TP1 (without centrifugation); 1–0.3 mL = 187.5 mg/g dye; 2–0.6 mL = 375 mg/g; 3–0.7 mL = 437.5 mg/g; 4–0.8 mL = 500 mg/g; and 5–1.0 mL = 625 mg/g. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

dye with two polycations, (polydiallyl-dimethylammoniumchloride (PDADMAC) and polymethacryloyl-dimethylbenzyl-ammonium-chloride (P-MADAMBQ)), differing in their structure and molar mass (2.4×10^5 and 4.1×10^6 g/mol), was ineffective, especially at low dye concentration. The degree of dye removal was not better than 85%.

The results described here were obtained with new flocculants (TPs and PSCs) and are demonstrated in the figures given below. In contrast to some tested commercial flocculants (high molecular weight AAm type with cationic charge), which are not so effective, the addition of, for instance, TP1 leads to spontaneous

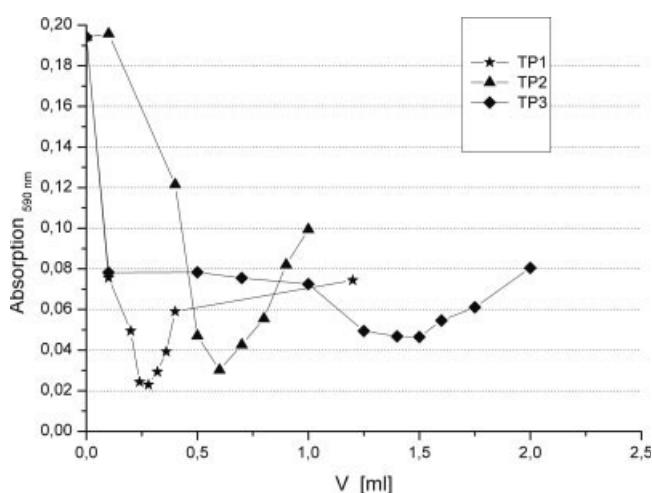


Figure 2 Removal of dye blue (80 mg/L) with TPs; light absorption of the supernatant at 595 nm in dependence on the volume of flocculant (polymer concentration 1 g/L).

precipitation of the dye (within 30 min) and dye reduction in the supernatant. In Figure 1, the influence of polymer concentration is shown. As we also found for the flocculation of inorganic particles,^{7,8,12} a clear separation is obtained only at the “optimum flocculation concentration” (ofc) (see glass 2 in Fig. 1). The so-called flocculation window is very small so that the efficiency of dye removal decreases at higher polymer concentrations. The flocculation mechanism, which is responsible for this behavior will be discussed later, together with Figure 2.

The concentration of flocculant, necessary for the removal of Cellitone Fast Blue from diluted solutions, is very high compared with the flocculation of inorganic particles. The dye separation effect can be further improved by centrifugation so that the supernatant is clear and colorless and the (small) amount of sludge is compact.

In Figure 2, dye removal with different TPs (Table I) is compared. The most effective polymer (about 95% dye removal at the lowest polymer amount) is TP1, followed by TP2. Both polymers have “medium” cationic charge density and certain amount of uncharged AAm units. About 90% removal was obtained with TP2. Polymer 3 with low cationic charge and a high content of uncharged units has a very broad flocculation window, but is not as effective (78.5% dye removal) as the other polymers. This confirms our result¹⁵ that the charge of the flocculant as well as those of the system to be flocculated is the most important parameter that influences the flocculation behavior. Cationic sites or “islands” with a high charge density are formed on the (negatively charged) dye particles by the adsorption of the cationic parts of TPs. Flocculation will then take place through electrostatic attraction between the oppositely charged parts

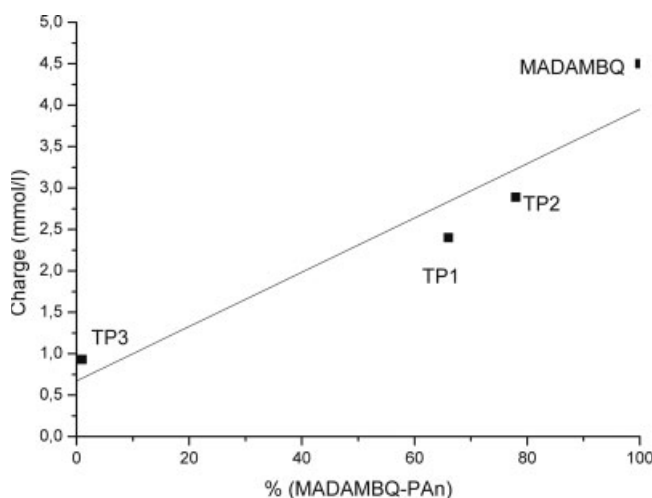


Figure 3 Titrated charge of polymer solutions (1 g/L) in dependence on their (polycation–polyanion)-content (see Table I).

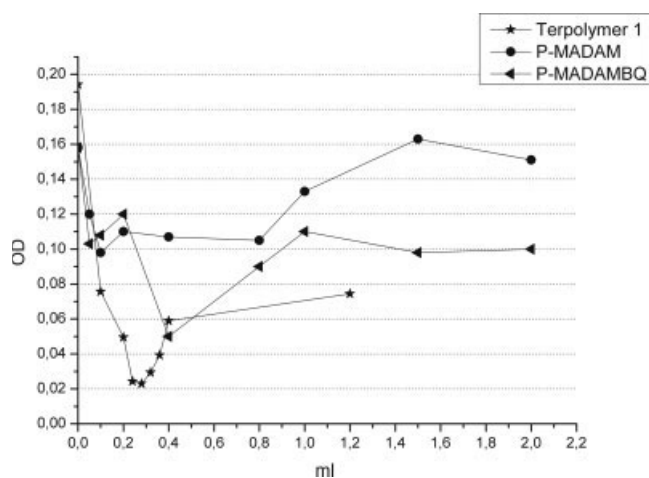


Figure 4 Removal of dye blue (80 mg/L); terpolymers compared with homopolymers; light absorption of the supernatant at 595 nm in dependence on the amount of flocculant (polymer concentration 1 g/L).

on the dye, especially with TP1 and TP2. At higher polymer dosage (higher than the ofc), the dye solutions were restabilized leading to decreased removal. The situation is different in case of TP3 because of the fact that this polymer has only 20% of cationic charges, compared with TP1. Therefore, the ofc is about five times higher than for TP1, the flocculation window is broader, but the degree of dye removal is lower.

Figure 2 also indicates that the ofc of TP2 (with higher charge) is twice that of TP1. We do not have an explanation for this unexpected result. Because TP2 has higher charge and the molecular weights of both polymers are in the same order of magnitude, the flocculation efficiency of TP2 should be better than that for TP1. But the same results were obtained by repeating the experiment.

The differences of polymer charge will be demonstrated after that.

The cationic charge of polymer solutions raises with increasing amount of the cationic unit MADAMBQ. In Figure 3, the "effective" cationic charge, which is calculated by the content of cationic–anionic charge, versus the measured cationic charge is shown. However, as we can demonstrate by using the homopolymers of MADAMBQ and of *N*-methacryloyl-*N,N,N*-trimethylammonium chloride (MADAM) as flocculants (Fig. 4), the flocculation mechanism is more complex because these homopolymers (with higher cationic charge than the TPs in Table I) are less effective in dye removal. The flocculation process is influenced not only by the charge density of the flocculants but also by hydrophobic interactions between different aggregates (dye, polymers). The charge of homopolymers is about twice of the TPs 1 and 2, but MADAM and MADAMBQ are not successful in complete dye removal. As shown in Figure 4, both homopolymers

have a small flocculation window at a very low volume (0.1 mL), but the supernatant is colored dark blue. We can also see differences between MADAM and MADAMBQ. Because of the presence of hydrophobic parts, the latter shows better flocculation properties; similar as TP1. But, in contrast to the homopolymers, the TPs are able to induce spontaneous flocculation of the dye (as shown in Fig. 1).

This can also be explained with new results obtained by Mende.¹⁵ By measuring the floc size of silica particles, flocculated with polyelectrolyte complexes (PEC), she found that the higher the hydrophobicity of the flocculant (PEC), the larger the formed flocs. In case of the hydrophobic TPs, very large flocs are formed immediately, resulting in spontaneous sedimentation. And also MADAMBQ, with lower molecular weight than the TPs, but with hydrophobic parts too, is better than the homopolymer MADAM.

On calculation, we found that the negative charge of the dye (−0.074 mM) can be partly or completely neutralized by adding certain amount of polymer, for instance by 0.25 mL of TP1. So, patching or neutralization is assumed as flocculation mechanism for charged polymers. The degree of neutralization is different for the polymers: only 40% in case of TP1 (patching), but higher for TP2, confirming that not only the measured cationic charge of flocculant is essential for the flocculation, but also a lot of other parameters such as the size and the shape of polymer molecule, or the balance between hydrophobically modified cationic, hydrophilic nonionic, and anionic monomer units. Because of the possible intra- and intermolecular Coulombic interactions within these macromolecules, we assumed an increase of the aggregation tendency leading to improved flocculating properties of the TPs compared with homopolymers. This is confirmed by

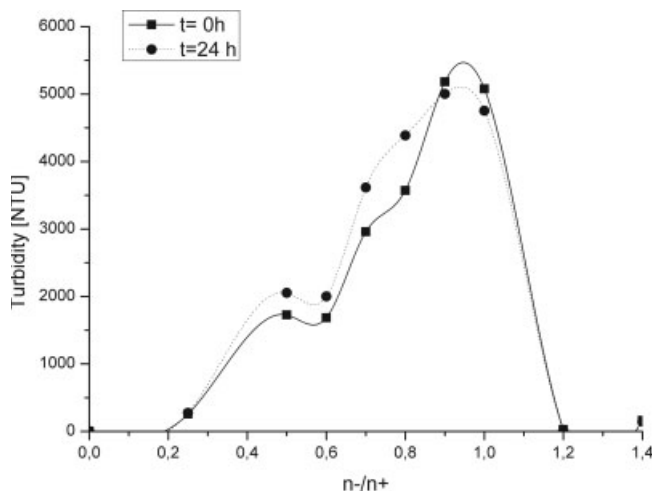


Figure 5 Turbidity of premixed polyelectrolyte surfactant complexes in dependence on the ratio of charges (n^-/n^+) in the mixture.

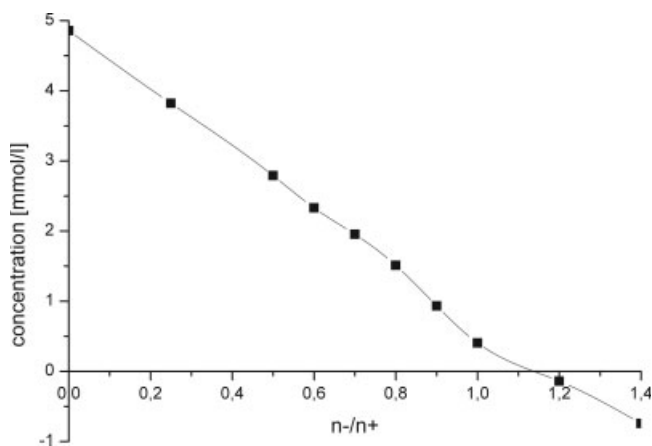


Figure 6 Charge of premixed polyelectrolyte surfactant complexes in dependence on the ratio of charges ($n-/n+$) in the mixture.

the results shown in Figures 2 and 4. But, the reason for differences between TPs 1 and 2 are not yet clear. Both have “medium” charge density and, as was measured with light scattering, they both have large particles with broad particle size distribution (maxima at 70–80 and 300–500 nm). Maybe the higher content of uncharged units is responsible for better decolorization with TP1.

Now, let us compare the TPs with polymer–surfactant complexes. At first, the properties of mixtures between aqueous solutions of the surfactant and poly(styrenesulfonate-sodium salt) (PSS) as polyanion are shown in Figures 5 and 6 and in Table III. As described,¹⁶ the properties of complexes depend on different factors such as:

- The type of polymer and surfactant.
- The concentration and molecular weight of polymer.
- The cmc of the surfactant.
- The composition and preparation of the mixture.

Complexes that are relatively stable can be easily prepared for example with Quartolan/PSS (Fig. 5).

The cationic charge of the surfactant decreases by adding the polyanion so that complexes with definite charge can be prepared (Fig. 6).

The size of complex particles is about 120 nm at the ratio $n-/n+ = 0.2$ and increases to about 200 nm at the ratio $n-/n+ = 0.8$. Near the isoelectric point (very low charge), big agglomerates (larger than 500 nm) with high polydispersity index (PI) were formed.¹⁷

As shown in Figure 5, the turbidity increases when the polyanion is added to the surfactant, demonstrating a strong interaction between both components. The turbidity reaches a maximum, followed by precipitation. It can be also shown that complex dispersions are stable for a long time. In Table III, the properties of complexes are summarized.

As clearly demonstrated (Fig. 7), the polymer–surfactant complexes are also effective in removing the dye. The necessary amount is larger than for the best TP (TP1), but the degree of dye removal is a little bit better (absorption lower than 0.02). The charge of complexes decreases with increasing $n-/n+$ (Table III) so that the need of complex is the lowest at the ratio $n-/n+ = 0.6$. Further, the complex particle size increases with $n-/n+$ and large aggregates (>500 nm) with high polydispersity were found at the ratio $n-/n+$ of about 1. These large particles are very effective in binding the dye because of their size and structure.

The flocculation window of complexes is broader, compared with the highly cationic TP1, especially for the complex with the lowest charge. This result is a bit surprising, because the light scattering investigation of highly diluted TPs with ALV/DLS/SLS-5000 seemed to show very large aggregates with broad particle size distribution too. But, by characterizing these polymers with Sigma and Nanosizer, it was not possible to confirm this and to obtain reproducible results. Compared with PSCs, the measured particle size (intensity) of TPs was significantly lower (<100 nm) and the PI higher than that of the PSC (by measuring the polymers in 0.1M NaCl). Without NaCl (in aqueous solution), the intensity was too low to obtain clear results for the polymers.

Comparison between polymers and complexes

In Figure 8, the “flocculation efficiency” of complexes is compared. The higher the charge, the lower is the ofc. This was found for complexes as well as for polymers.

TABLE III
Properties of PSCs

$n-/n+$	Turbidity (NTU)	Average particle size intensity ^a (nm)	PDI	Charge (mmol/L)
0.6	1684	200	0.14	+2.33
0.8	3570	215	0.14	+1.51
1.0	5078	548	0.61	+0.41

^a Measured with Zetasizer 3000.

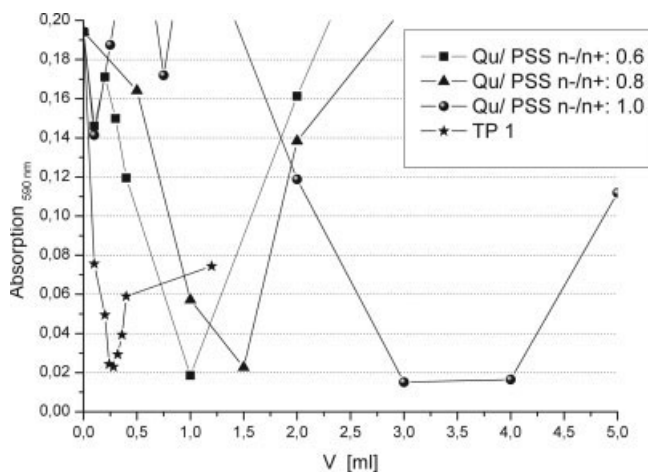


Figure 7 Removal of dye blue (80 mg/L) with polyelectrolyte surfactant complexes; light absorption of the supernatant at 595 nm; absorption in dependence on the complex composition and the amount; TP1 is shown for comparison.

But, whereas TP3 (with low, but higher charge than complex 1.0) is not effective in dye removal, very good results were obtained with all complexes, especially with complex particles with the ratio $n-/n+ = 1.0$. These are large insoluble aggregates with very low charge. The enhanced performance of such complexes cannot totally be described to patch flocculation or to bridging. As already described for polymers,¹⁸ the necessary energy for flocculation arises from the hydrophobic interaction of polymer molecules adsorbed onto dye particles. This demonstrates that not only the charge of the flocculant is essential for separation. Another aspect is the size and structure of polymer(s) in solution. As found with DLS and already described, the polymer-surfactant complexes are compact particles with diameter in the range between 100 and more than 500 nm (in dependence on the type of

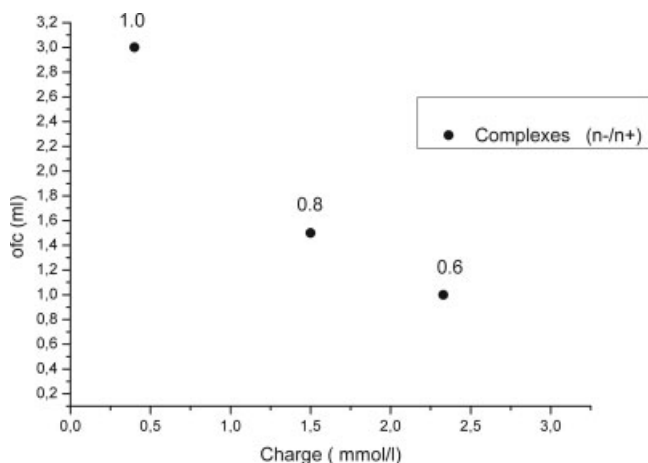


Figure 8 Comparison between different complexes; ofc in dependence on complex charge.

polymer and the ratio $n-/n+$) whereas the size of the prepared polymers is assumed to be smaller. As already mentioned, the size of polyelectrolytes is difficult to characterize with the Zetasizer/Nanosizer. We were not successful to measure significant differences in average particle size between the prepared polymers. But, according to light scattering experiments with ALV/DLS/SLS-5000, the polymers can form aggregates.

The structure and the “balance” between charged and uncharged units as well as the influence of hydrophobic groups are responsible for the flocculation efficiency. It seems that the combination of strong cationic charge with low anionic charge and uncharged units (as in TPs 1 and 2) is most effective in removing the dye blue. Complex nanoparticles from cationic surfactant and polyanion can also interact by electrostatic as well as hydrophobic interaction. In case of the “neutral” complex ($n-/n+ = 1.0$), the flocculation mechanism seems to be different because the charge is very low. The dye molecules can be adsorbed on the hydrophobic parts of the very large complex particles. Because of the compactness of complex particles, the sedimentation process is faster than in case of homopolymers.

CONCLUSION

We were able to show that the dye Disperse blue 3 can be removed from wastewater by new polyampholytes containing hydrophobically modified cationic, hydrophilic nonionic, and anionic monomer units, always with an excess of cationic charges. Because of the possible intra- and intermolecular Coulombic interactions within these new macromolecules, we assume an increase of the aggregation tendency leading to improved flocculating properties.

Similar results were obtained by using positively charged nonstoichiometric PSC dispersions. All these flocculants can partly or completely neutralize the charge of dye whereas big complex aggregates with very low charge seem to interact mostly via hydrophobic forces.

All the tested new TPs and complexes are better (higher degree of dye removal at the same polymer concentration) than homopolymers with comparable molecular weight or than positively charged commercial flocculants with high molecular weight.

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