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Comparative study on the formation and flocculation properties of polyelectrolyte complex dispersions based on synthetic and natural polycations

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Nonstoichiometric interpolyelectrolyte complexes (NIPECs) as colloidal dispersions formed by the interaction of synthetic polycations which possess ammonium quaternary centers attached to an acrylic macromolecular chain, derived from poly(N,N-dimethylaminoethyl methacrylate), or a natural polycation, chitosan, with poly(sodium-2-acrylamido-2-methylpropanesulfonate) (PAMPS), and three random copolymers of AMPS with tert-butylacrylamide or methyl methacrylate, were prepared. The effects of polyelectrolyte characteristics and concentration on the complex features were investigated by turbidimetric titration and dynamic light scattering, the molar ratio between the positive and negative charges ranging between 0.05 and 0.4. The nonstoichiometric complex nanoparticles were tested in the destabilization of kaolin model dispersion and proved to be more efficient than polycations alone, especially as concern the broadness of the flocculation window. The highest efficiency of the NIPECs dispersions was found when they have been prepared at very low molar ratios between charges ($n^-/n^+ < 0.1$).

1. Introduction

A very interesting property of polyelectrolytes is their ability to form complexes with oppositely charged polyelectrolytes, a process known to be very important in biological systems [1]. The properties of the interpolyelectrolyte complexes (IPECs) are influenced not only by the intrinsic characteristics of the polymers (molar mass, stereochemical fitting, charge densities), but also by the experimental conditions like the concentrations of polyelectrolytes, their mixing ratio and addition rate, ionic strength of the solution, mixing order, etc. [1–6]. IPECs can be divided mainly into three types: soluble IPECs, i.e. macroscopically homogeneous systems containing nanoscopic IPEC aggregates [7,8]; turbid colloidal systems with suspended IPEC particles in the transition range to phase separation [9–12]; two-phase systems containing precipitated IPECs [2,13]. Considerable efforts have been lately devoted to the preparation of IPECs as colloidal dispersions because of their widespread applications in chemical engineering, pharmaceutical and biological areas [10,14,15]. The most important parameters for their applications are the polymer concentration, the size of nanoparticles and their storage stability [4,11,16].

To improve the solid/liquid separation process, polymeric flocculants, mainly polycations, have been used [17–19], their main disadvantage being the very small flocculation window, at a small increase of the dosage the system being re-stabilized. The flocculation efficiency has been improved by combination of two (or more) oppositely charged polyelectrolytes that can be added one after another [20,21] or as nonstoichiometric interpolyelectrolyte complexes (NIPEC) [16,22–24]. The main advantage of NIPECs is the substantially wider window for flocculation. Nevertheless, the optimum concentration required for flocculation with NIPECs was found to be higher than the optimum concentration for flocculation with polycations.

In our previous works it was shown that NIPECs nanoparticles, even monodisperse, could be prepared as stable colloidal dispersions by using synthetic polycations having cationic centers in the backbone as starting polyions, and poly(sodium-2-acrylamido-2-methylpropane sulfonate) (PAMPS) or some random ionic/nonionic copolymers of AMPS, as added polyions in a wide range between charges [4–6,25]. Our recent investigations on the influence of the molar ratio between opposite charges on the flocculation efficiency of NIPECs based on chitosan (CS) demonstrated that not only the broadness of the flocculation window could be enlarged but also the optimum dose could be decreased with NIPECs dispersions prepared at a ratio between charges lower than 0.2 [26,27]. Therefore, the objective of this study was the preparation and characterization of novel positively charged NIPECs nanoparticles based on two strong synthetic polycations derived from poly(N,N-dimethylaminoethyl methacrylate) (PDMAEM) by quaternization with benzyl chloride (BC), having quaternization degree of 50 mol%, polycation Q_{50}, and 85 mol%, polycation Q_{85}.

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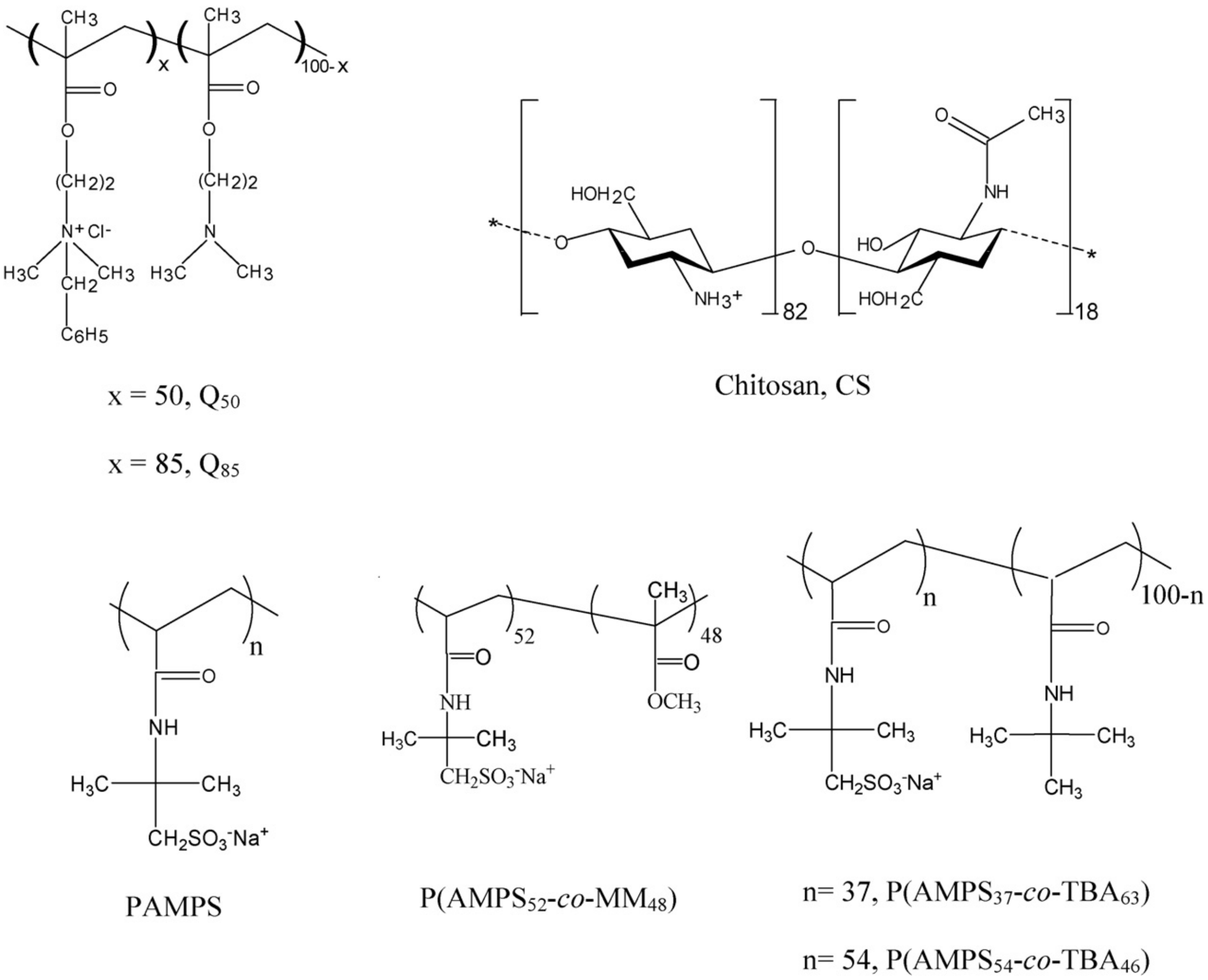

Scheme 1. Chemical structure of polyelectrolytes.

PAMPS and three random copolymers of AMPS with tert-butyl acrylamide, P($AMPS_{54}$-*co*-TBA_{46}) and P($AMPS_{37}$-*co*-TBA_{63}), or with methyl methacrylate, P($AMPS_{52}$-*co*-MM_{48}) were used as polyions in default, being added to the polycations up to a molar ratio between charges, n^-/n^+, of 0.4. Thus, the variables of interest in the preparation of NIPECs were the polyions structure, their charge density, and the molar ratio between charges. The NIPECs dispersions thus prepared were used in the flocculation of model kaolin dispersion compared with polycations used in their preparation. Kaolin suspensions were used as a representative colloidal material because kaolin, which is a well known and widespread thickening agent, is a key component in various industrial fluid formulations and in consequence has received great interest in recent years [26–29]. The results obtained with complex dispersions based on synthetic polycations were compared with those obtained with NIPECs based on CS. To the best of our knowledge, this is the first study on the use of NIPECs dispersions bearing positive charges in excess, prepared at very low molar ratios between charges ($n^-/n^+ < 0.1$), in the flocculation of kaolin.

Table 1
Some characteristics of the polyelectrolytes used in this work.

Sample	M, kDa	M_w/M_n	M_u[d], g/charge	b[e], nm	CD[f], %
Q_{50}	136[a]	1.97	441	0.500	0.50
Q_{85}	136[a]	1.97	311.5	0.294	0.85
CS	334[b]	–	205.5	0.628	0.82
PAMPS	170[c]	2.1	229.0	0.250	1.00
P($AMPS_{52}$-*co*-MM_{48})	285[c]	4.7	321.3	0.481	0.52
P($AMPS_{54}$-*co*-TBA_{46})	175[c]	3.9	350.8	0.463	0.54
P($AMPS_{37}$-*co*-TBA_{63})	–	–	472.5	0.675	0.37

[a] Molar mass of PDMAEM determined by SEC.

[b] Viscometric molar mass.

[c] Molar mass determined by SEC.

[d] Mass per charge, $M_u = [M_{IM} \times f_{IM} + M_{NM} \times (1 - f_{IM})]/f_{IM}$, where M_{IM} and M_{NM} are the molar masses of the ionic and the nonionic monomer and f_{IM} is the molar fraction of the ionic monomer.

[e] Average charge distance.

[f] Charge density.

2. Experimental

2.1. Materials

The chemical structures of the polyelectrolytes used in this work are shown in Scheme 1, some of their characteristics being summarized in Table 1.

The strong synthetic polycations were obtained by the quaternization of PDMAEM with BC according to ref. [30]. CS as powder, purchased from Fluka, with ash content less than 2%, was used without further purification. The viscometric average molar mass (Table 1) and the acetylation degree (of about 18%) of CS were determined as previously shown [31]. PAMPS and copolymers of AMPS with MM and TBA were synthesized and purified according to Refs. [6,32].

Kaolin powder (from Aldrich), used as model substrate for fine particles, had the average particles size of about 600 nm, the polydispersity index of about 0.58 and the particle charge density of 0.067 mequiv g^{-1} [27].

2.2. Methods

2.2.1. Preparation of polyelectrolyte solutions

The stock aqueous solutions of polycations Q_{50} and Q_{85} with a concentration of 1 g/L were prepared at room temperature 24 h before use, and then polymer solutions with a concentration of 0.5 mM was obtained by adequate dilution with distilled water. The CS solution, with a concentration of 1 g/L, was prepared by solving the powder in 1 vol.% acetic acid solution and intensive stirring for at least 48 h. For NIPECs preparation, the concentration of CS solution was adjusted to 0.5 mM (or 1 mM) by dilution with 1 vol.% acetic acid solution. The polyanions solutions with concentration of 5 mM were prepared by appropriate dilution with distilled water of the stock solutions (10 mM). The molar concentrations of all polyelectrolytes were calculated taking into account the mass per charge values (M_u, see Table 1). The concentration of the charged groups in each polyelectrolyte solution was determined by polyelectrolyte titration, with a Particle Charge Detector PCD 03 (Mütek GmbH, Germany), using a standard polyelectrolyte solution, poly(sodium ethylenesulfonate) or poly(diallyldimethylammonium chloride), with a concentration of 10^{-3} mol/L, in dependence on the nature of charges.

2.2.2. NIPECs preparation

Specific volumes of the polyanion solution, having a concentration of 5 mM (or 10 mM), were added dropwise to the aqueous solution of polycation, with a concentration 10 times lower, with a constant addition rate of 3.8 mL polyanion/(mL polycation × h), under magnetic stirring, at room temperature (about 25 °C), until a desired molar ratio between opposite charges, n^-/n^+, has been obtained. After mixing, the formed dispersions were still stirred 60 min and were characterized and used in flocculation testes after 24 h of storage.

2.2.3. Turbidimetry

The NIPECs formation was followed by the optical density at $\lambda = 500$ nm (OD_{500}), with a SPECORD M42 spectrophotometer (standard 1 cm quartz cell), using distilled water as reference. At this wavelength, the polyelectrolytes used in the complex preparation do not absorb, so the OD_{500} values resulted only from the light scattering of the NIPEC nanoparticles.

2.2.4. Dynamic light scattering (DLS)

DLS measurements were carried out at a fixed angle of 90° by means of a Zetasizer 3000 (Malvern Instruments, Worcestershire, UK) equipped with a 10 mW He–Ne laser (operating at $\lambda = 633$ nm) as a light source. DLS measures the diffusion in particle dispersions, which can be interpreted using the Stokes–Einstein equation to yield the particle average hydrodynamic diameter (D_h). At least two independent DLS measurements were averaged to get the D_h values.

2.2.5. Destabilization of a kaolin model suspension with polycations and NIPEC dispersions

The kaolin model dispersions, with a concentration of 1 g/L and pH 6, were prepared by sonication for 15 min using an Ultrasonator Sonics Vibra-Cell. All the flocculation experiments were conducted at room temperature. Volumes of 50 ml kaolin model suspension were stirred at 120–150 rpm in beakers, and then different volumes of flocculant were added. Stirring was continued with the same speed for about 2 min, and then decreased to about 50 rpm for 15 min. After a settling time of about 20 min, which was shown to be the optimum, the reading of OD_{500} was performed, using a SPECORD M42 spectrometer. Distilled water was used as reference. Residual turbidity (RT) was calculated with the following equation:

$$\mathrm{RT} = \frac{\mathrm{OD}_{500\mathrm{s}}}{\mathrm{OD}_{500\mathrm{i}}} \times 100\ (\%)$$

where OD_{500s} was OD_{500} after the addition of flocculant and OD_{500i} was OD_{500} of the initial model suspension. To evaluate and compare flocculation performance of the polycations alone and the corresponding NIPECs as concern the optimum dose, an arbitrary limit of 5% RT was fixed, for RT under this value the system being considered to work as flocculant. The broadness of flocculation window was calculated as the difference between the re-dispersion concentration (the highest polymer dose at which the RT was lower than 5%) and the optimum dose.

3. Results and discussion

3.1. Formation and characterization of NIPEC colloidal dispersions

The formation of positively charged NIPECs between either synthetic polycations or CS and the polyanions PAMPS, P($AMPS_{54}$-*co*-TBA_{46}), P($AMPS_{37}$-*co*-TBA_{63}) and P($AMPS_{52}$-*co*-MM_{48}) was followed first by turbidimetry, plotting the OD_{500} values as a function of the molar ratio between the oppositely charged units, n^-/n^+ (Fig. 1).

As can be observed in Fig. 1a, the common feature for the complex dispersions formed with synthetic polycations was the monotonous increase of OD_{500} values with the increase of the molar ratio, n^-/n^+, for all studied colloidal dispersions. This behavior can be attributed mainly to the formation of an increasing number of particles with further addition of polyanion. The main difference consists of the OD_{500} values of the dispersions formed with polycation Q_{85} were higher than those formed with polycation Q_{50} for any random copolymer of AMPS used as added polyion. These results could be attributed to the differences in the conformation of polycations, induced by their charge density. Thus, in the case of polycation Q_{85} a more extended conformation is expected, comparative with polycation Q_{50}, and a higher availability of cationic charges to interact with anionic charges of polyanion. This may induce the formation of a higher number of particles, reflected in the higher values of OD_{500}. No difference was observed when PAMPS was the polyion in default (the results obtained with polycation Q_{85} not shown in Fig. 1a). A very small increase of the OD_{500} values with the increase of the ratio between charges was observed when CS was the polyion in excess, at the same concentration as in the case of synthetic polycations (Fig. 1b). Increasing twice the concentration of oppositely charged polyions led to a clear increase

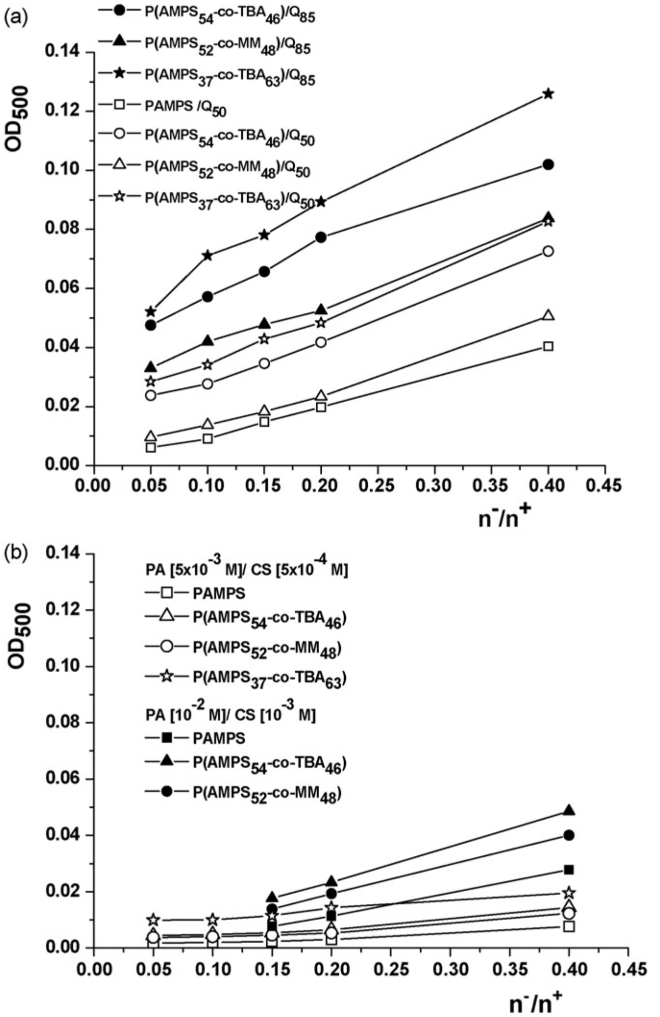

Fig. 1. OD_{500} values of the NIPEC dispersions as a function of the molar ratio between charges, n^-/n^+, prepared with polycations: (a) Q_{50} and Q_{85}, and (b) CS.

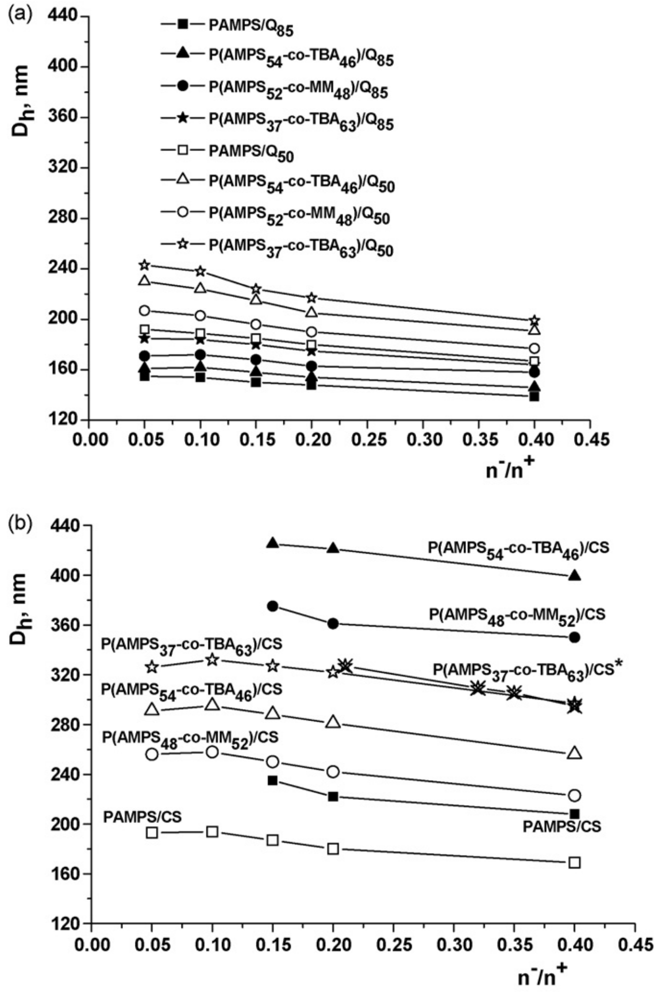

Fig. 2. Hydrodynamic diameter, D_h, of the NIPEC dispersions as a function of the molar ratio between charges, n^-/n^+, prepared with polycations: (a) Q_{50} and Q_{85}; (b) CS: close symbols PA [10^{-2} M]/CS [10^{-3} M], open symbols PA [5×10^{-3} M]/CS [5×10^{-4} M]; CS* sample with M_v = 470 kDa.

of the OD_{500} values. This behavior may be explained taking into account that a higher number of chains were into the solution, and thus a higher number of particles can be formed, leading to the increase of system turbidity.

The influence of the polyanion structure is clearly evidenced in Fig. 1, the turbidity values being always higher when P($AMPS_{37}$-*co*-TBA_{63}) was used as polyanion, i.e., the copolymer with the lowest content in AMPS, for the same molar ratio between charges and polyions concentration, irrespective of the polycation structure. The decrease in the charge density caused the increase of the polyanion amount requested for the charge compensation, which may cause the increase of the turbidity. These results are in agreement with data previously reported [6,26].

The influence of the characteristics of oppositely charged polyelectrolytes on the particle sizes (hydrodynamic diameter, D_h) of the NIPEC dispersions formed by mixing PAMPS, P($AMPS_{54}$-*co*-TBA_{46}), P($AMPS_{37}$-*co*-TBA_{63}), and P($AMPS_{52}$-*co*-MM_{48}) with synthetic polycations or CS are presented in Fig. 2.

As Fig. 2a shows, D_h values slowly decreased, with almost 15 nm, when the molar ratio increased from 0.05 up to 0.4, the values being in the range 140 and 185 nm, when polycation Q_{85} was the polyion in excess, and higher when polycation Q_{50} was the polyion in excess. The small decrease of particles sizes with the increase of the molar ratio between charges was observed for other systems prepared with synthetic polycations [24,25] and can be ascribed to the rearrangements of the chains with the increase of polyanion content into the IPECs particles, and the formation of more compact particles with lower sizes. As Fig. 2a shows, the charge density of polyions influenced the particle sizes of the NIPECs. Thus, D_h values were always higher when polycation Q_{50} was used, compared with Q_{85}, for the same polyanion and molar ratio between charges. Also, the values of D_h were the highest when P($AMPS_{37}$-*co*-TBA_{63}) was used as added polyanion, for any polycation. This behavior can be explained taking into account that at a higher content of the nonionic comonomer, a higher amount of polyion, either polycation, or polyanion, is required, and this may cause the increase of the sizes of complex nanoparticles.

Fig. 2b shows that when CS was the polycation in excess, the particle sizes were much higher for the same concentration of polyions and the same polyion in default. Also, the decrease of the particle sizes with the increase of the ratio between charges was more consistent compared with synthetic polycations, with almost 34–40 nm. For comparison, Fig. 2b includes some results obtained for IPECs prepared with polyanion P($AMPS_{37}$-*co*-TBA_{63}) and a CS sample with a higher molar mass (470 kDa) and a comparable deacetylation degree (80%) [26,27]. As can be observed in Fig. 2b, the particle sizes varied in the same range with the increase of the ratio between charges, irrespective of CS molar mass, supporting the formation mechanism proposed in our previous work [26].

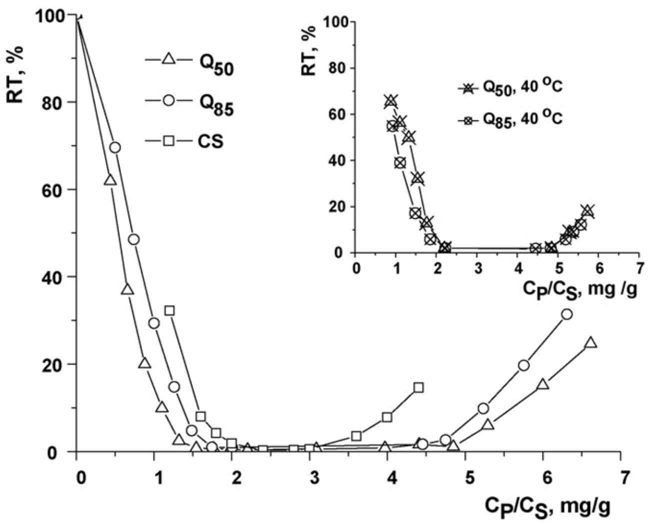

Fig. 3. Residual turbidity, RT, as a function of polymer per substrate, C_P/C_S, in kaolin flocculation at 25 °C; the inset, RT as a function of C_P/C_S, at 40 °C.

The particles sizes increased with the increase of polyelectrolytes concentration as in the case of OD_{500} values (Fig. 1b) because of the increase of complex particles concentration and also to the increase of the collision number with the increase of concentration, the aggregation level being thus enhanced.

3.2. Destabilization of a kaolin model suspension with polycations

The variation of residual turbidity (RT) as a function of the ratio between the amounts of polymer per substrate (C_P/C_S, mg/g) in kaolin flocculation with the polycations used in this study is presented in Fig. 3.

As Fig. 3 shows, the polycation structure strongly influenced the flocculation efficiency. At the optimum dose, the adsorbed polymer reduces the interparticle repulsion and provides attractive forces through charge neutralization, bridging, charge patch, or through their combination [17]. As Fig. 3 shows, the optimum dose (RT = 5%) of CS needed for destabilization and sedimentation of kaolin suspension was achieved at 1.75 mg CS/g kaolin, the flocculation window ranging between 1.75 and 3.75 mg CS/g kaolin. By further increase of CS dose, RT increased, the system being restabilized. The higher flexibility of synthetic polycations enables a better coverage of the kaolin particles, a smaller amount of polymer being required to reach optimum flocculation concentration (1.25 mg polycation Q_{50}/g kaolin and 1.55 mg polycation Q_{85}/g kaolin) and a broader flocculation window up to 4.8 mg Q_{50}/g kaolin and 5 mg Q_{85}/g kaolin being found, compared with CS.

The difference between the flocculation efficiency of the polycations Q_{50} and Q_{85} is assigned to the difference in their charge density. Highly charged polyelectrolytes tend to adsorb at oppositely charged surfaces in a flat conformation, while the decrease of polyelectrolyte charge density leads to the increase of chain flexibility, an increased fraction of segments being adsorbed in loops and tails favoring bridging interactions in colloidal dispersions. If polyelectrolyte adsorbs flat at the surface and possess uncompensated charges, even at low surface coverage, the aggregation of dispersed particles through charge patch mechanism is usually expected. This would be the case of polycation Q_{85}. Decreasing the charge density, the chain flexibility increases, and a combination of bridge and charge patch mechanisms may occur when polycation Q_{50} was used as flocculant.

PDMAEM is a well-known thermo-responsive polymer with a lower critical solution temperature value of around 50 °C [33,34]. As the inset in Fig. 3 shows, increasing the flocculation temperature, performances of polycations Q_{50} and Q_{85} decreased, the optimum concentration being shifted from 1.25 or 1.55 mg polycation/g kaolin, respectively, to 2.2 mg/g irrespective of polycation charge density. When temperature increased from 25 up to 40 °C, the hydrophobic interactions of the side chains increased and the polymeric chains tend to become more compact [33,34], and thus the flocculation efficiency of the kaolin particles diminished.

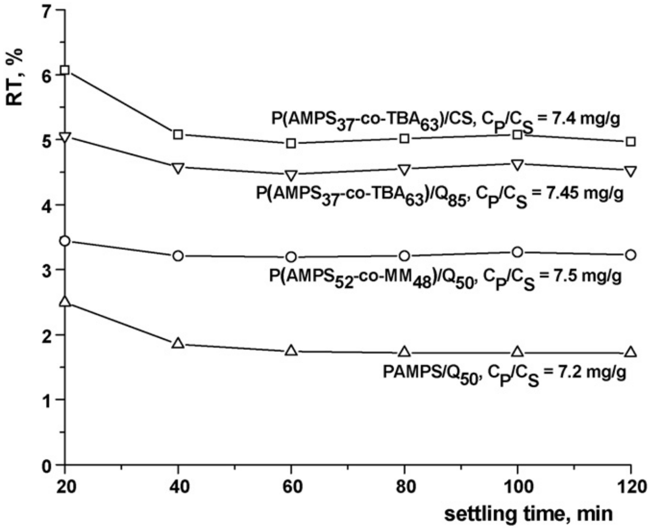

Fig. 4. Residual turbidity, RT, as a function of settling time in the flocculation of kaolin with some NIPECs with the molar ratio between charges, $n^-/n^+ = 0.1$.

3.3. Destabilization of a kaolin model suspension with NIPECs

Fig. 4 shows the RT values as a function of the settling time for the flocculation of kaolin with some NIPECs dispersions prepared with four polyion pairs, at a ratio between charges of 0.1. It is obvious that after 20 min of settling, the RT values insignificantly decreased, with maximum 1% in next 100 min. Therefore, a settling time of 20 min was fixed for all experiments.

Kaolin destabilization produced by NIPECs based on synthetic polycations, Q_{50} and Q_{85}, at two molar ratios between opposite charges is illustrated in Figs. 5 and 6, as RT values as a function

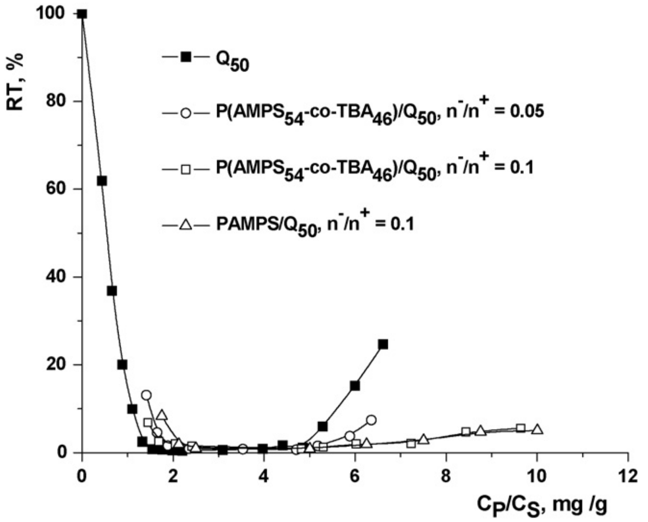

Fig. 5. Residual turbidity, RT, as a function of polymer per substrate, C_P/C_S, in kaolin flocculation with NIPECs based on Q_{50}.

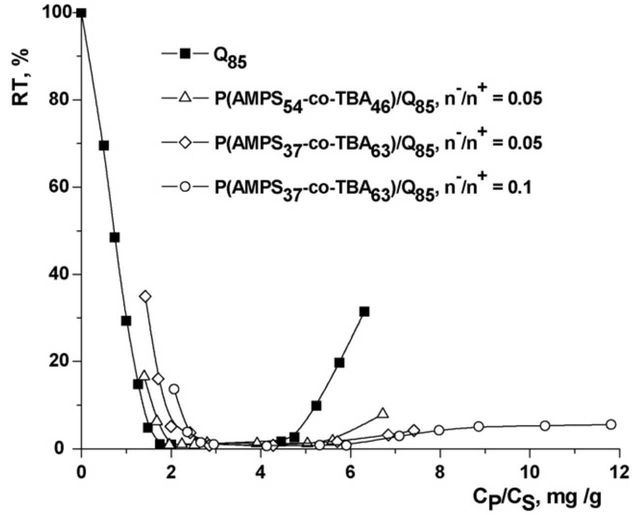

Fig. 6. Residual turbidity, RT, as a function of polymer per substrate, C_P/C_S, in kaolin flocculation with NIPECs based on Q_{85}.

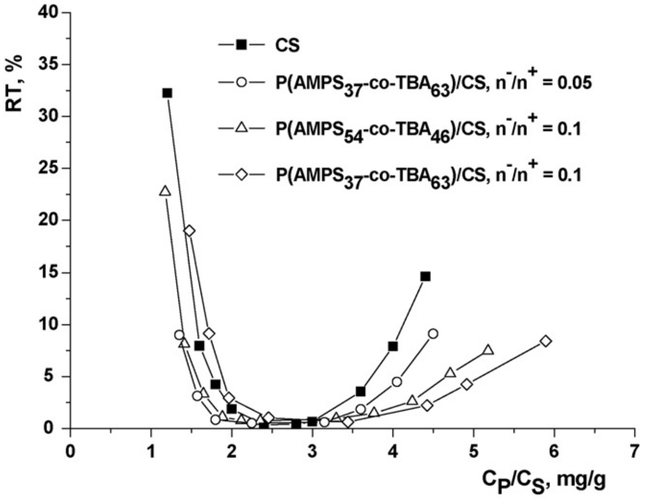

Fig. 7. Residual turbidity, RT, as a function of polymer per substrate, C_P/C_S, in kaolin flocculation with NIPECs based on CS.

of the ratio between the amount of polymer added to substrate (kaolin). In the case of flocculation with NIPECs, the polymer mass (C_P) is the sum of the mass of polycation and polyanion at the molar ratio selected for the complex preparation.

As Fig. 5 shows, NIPEC dispersions present higher broadness of the flocculation window, comparative with the corresponding polycations, which increased with the increase of the molar ratio between charges. The optimum dose has been influenced by the molar ratio between charges and polyanion structure, a small increase being observed compared with polycations. Thus, for kaolin flocculation with NIPECs prepared with polycation Q_{50} at $n^-/n^+ = 0.05$, the optimum dose increased to about 1.7 mg/g, irrespective of the polyanion structure [data for NIPECs prepared with PAMPS, P($AMPS_{37}$-*co*-TBA_{63}) and P($AMPS_{52}$-*co*-MM_{48}) not included here]. Increasing the molar ratio between charges up to 0.1, the charge density and the size of the complex particles decreased, leading thus to the adsorption of a higher amount of flocculant on the particle surface. The thicker layer of NIPEC particles and the higher hydrophobicity of the flocculant protected more efficient the particles against re-dispersation, leading to wider flocculation window.

In the case of flocculation with NIPECs prepared with Q_{85} (Fig. 6) a similar behavior was observed as concern the flocculation window. The optimum dose was 1.8 mg/g for NIPECs with P($AMPS_{54}$-*co*-TBA_{46}) [also for NIPECs with PAMPS and P($AMPS_{52}$-*co*-MM_{48}), data not shown here] and 2.2 mg/g for P($AMPS_{37}$-*co*-TBA_{63}), when the molar ratio was 0.05 and increased up to 2.4 mg/g when the molar ratio was 0.1.

The results obtained in the flocculation of kaolin by NIPEC dispersions based on CS are presented in Fig. 7.

As can be observed in Fig. 7, the CS based NIPECs are effective flocculants even at the low molar ratios between charges selected for this study, the values of optimum dose and flocculation window depending on the polyanion nature and the ratio between charges, n^-/n^+. The main difference between NIPECs based on CS and those prepared from synthetic polycations was the narrower flocculation window. Thus, at a molar ratio between charges of 0.05 the optimum dose decreased from 1.75 mg/g (for CS) at around 1.5 mg/g, for NIPECs prepared with P($AMPS_{37}$-*co*-TBA_{63}). Increasing the molar ratio up to 0.1, the optimum dose slowly increased up to 1.6 mg/g for P($AMPS_{54}$-*co*-TBA_{46}) but were still lower than that of CS. Increasing the nonionic content in polyanion structure [P($AMPS_{37}$-*co*-TBA_{63})], a significant enlarge of the flocculation window was observed, in agreement with the results previously presented [27].

4. Conclusions

Two synthetic polycations derived from PDMAEM, and CS were used to prepare NIPEC dispersions, with positive charges in excess, by adding PAMPS, as well as three ionic/nonionic random copolymers of AMPS differing by the nonionic comonomer structure or content (TBA or MM) as polyanions. Turbidity and DLS have been used to investigate the characteristics of the complex dispersions as a function of the polyion structure, and molar ratio between charges. The OD_{500} values of the dispersions formed with polycation Q_{85} were higher than those formed with polycation Q_{50}, for any random copolymer of AMPS used as added polyion. The higher density of cationic charges may induce the formation of a higher number of particles when Q_{85} was in excess, reflected in the higher values of OD_{500}. The sizes of the complex particles decreased with the increase of the molar ratio between charges, for all studied systems, meaning that more compact structures were formed. The particle sizes were the highest when the polyanion with the highest hydrophobicity was used [P($AMPS_{37}$-*co*-TBA_{63})].

The complexes formed at a low ratio between charges, up to 0.1, were tested in the destabilization of kaolin model dispersion compared with polycations used in their preparation. The complex nanoparticles were more effective flocculants than polycations alone, the critical concentration for kaolin re-dispersion being much higher for NIPECs as flocculants. Also, the higher the hydrophobic content of polyanion was the wider the flocculation window. The main difference between NIPECs based on CS and those prepared from synthetic polycations was the narrower flocculation window. The increase of the flocculation efficiency of NIPECs dispersions bearing positive charges in excess prepared at very low molar ratios between charges ($\leq$0.1), compared with polycations, in the kaolin separation process, has been demonstrated for the first time in this work. The optimum dose in the flocculation with NIPECs was close to that of polycations but the flocculation window was up to three times larger than that of polycations. These aspects are extremely important from the practical point of view, and recommend these complex dispersions as specialized flocculants for solid/liquid separation processes.

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