

Flocculating Properties of Water-Soluble Polymer-Colloid Complexes of Aluminoxane Particles with Weakly Charged Cationic Polyelectrolytes¹

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Abstract

The flocculating properties of polymer-colloid complexes (PCCs) formed via noncovalent interactions of positively charged aluminoxane particles (APs) with macromolecules of weakly charged cationic acrylamide copolymers from the Praestol and Organopol series have been studied. The PCCs that spontaneously formed during mixing of sols of a high-basicity aluminum polyhydroxochloride (APHC) with aqueous solutions of the copolymers exhibit high flocculating ability under the conditions of gravity sedimentation of the model kaolin dispersion with $C_d = 8 \text{ g/dm}^3$, and their efficiency exceeds both that of the copolymers and the earlier obtained PCCs with nonionogenic polyacrylamide (PAA). In contrast to weakly charged polycationites, the fully charged KF-99 polyelectrolyte does not form PCCs and the products of its mixing with APHC do not reveal an increased flocculating effect.

Keywords: Polymer-Colloid Complexes of Aluminoxane Particles, Weakly Charged Cationic Polyelectrolytes, Kaolin, Flocculation

1. Introduction

At present, the problem of water supply acquires a global strategic significance since, firstly, water turned out to be the main deficit of the XXI century, and, secondly, control over high quality and safety of consumable water became urgent. The latter factor is associated with the task to remove particles less than $10 \text{ }\mu\text{m}$ in size from water because precisely these particles may adsorb contaminants, pathogenic microorganisms, and viruses that occur in open water reservoirs. It is noteworthy that, among a great diversity of methods for natural water purification, coagulation based on the use of special reagents is the most economically attractive and large-scale. The conventional water treatment technologies make use of aluminum and iron salts, and aluminum basic chlorides (ABCs) have found wide use in recent years. The growing requirements on the content of harmful contaminants in water, including the demand for reduction in the residual amounts of aluminum, which is a neurotoxic substance, stimulate the search for more

complicated reagent compositions ensuring a high degree of water purification at minimal doses of such compositions.

In practice of water treatment, the joint use of polyvalent metal salts and polymer flocculants, above all of polyacrylamide (PAA), has long been in use. These compositions are mainly applied to improve flocculation in sedimentation chambers and to reduce the time of water clarification. However, during the course of hydrolysis of salts, metal ions may form ion-coordination bonds with ion-exchange groups of flocculant macromolecules, thereby changing the conformational and hydrodynamic parameters of macromolecules [1,2]. That is why depending on the regime and order of reagent addition, both synergetic and antagonistic effects may occur in the purification process [3,4]. In [5-10], more complicated compositions based on polymer inorganic salts or their mixtures with organic polymers are developed. Such compositions often involve rather complex preparation procedure and are mostly intended for sewage purification.

A new type of composition reagents has been designed in recent years. These reagents are formed on the

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nanosized level as polymer-particle and polymer-colloid complexes (PCCs) [11-17]. Such systems are distinguished by easy preparation: they spontaneously form through intermolecular association via noncovalent bonds. As a result, well-defined thermodynamically stable supramolecular structures arise with sizes from 10 nm to 100 μm [18]. As regards use in practice, the PCCs based on sols of high-basicity aluminum polyhydroxochloride (APHC) and polyacrylamide have been studied most extensively [19-21]. The composition of such polycomplexes suggests their use as stability regulators for dispersed systems among which are both natural waters and sewages. It was shown that these polycomplexes offer promise as high-efficient reagents in water treatment for household water use [22-24] and in purification of sewages [25-27]. The said PCCs are prepared on the basis of nonionogenic PAA. At the same time, the ion-active acrylamide copolymers are used for water purification. These copolymers differ both in the sign of charge and in the content of ionogenic groups. The feasibility of formation of PCCs of such copolymers with positively charged particles of APHC sols is obviously determined by the chemical structure of the polymer reagent.

Generally, the ability to form PCCs arises from the fundamental property of macromolecules—a high cooperativity of a system of weak interactions (electrostatic, hydrogen-bonding, hydrophobic, and donor-acceptor) between linear polymers and the surface of colloid particles. Therefore, the area of this surface plays the decisive role on condition that reactive centers occur on it. As it was shown in [15], that is why low-molecular-mass aluminum salts do not form PCCs with polyacrylamide, while high-basicity APHC sols, which represent the dispersed system of aluminosilicate particles (APs) mostly composed of species with a size of 4.6 nm and a specific surface area of $3 \times 10^2 \text{ m}^2/\text{cm}^3$ [28,29] form soluble PCCs with the nonionogenic PAA.

The realization of noncovalent interactions that provide the stability of the polycomplexes being formed and their solubility in water is another significant condition of PCC formation. In terms of adopted ideas about the cooperativity of noncovalent interactions in the polymer-particle system, we have recently studied the formation of PCCs during interaction of positively charged APs in APHC sols with weakly charged cationic polyelectrolytes (WCPEs) from the Praestol and Organopol series [30]. It was found that PCCs are formed if the content of cation-active groups in the polymer chain is small. In this case, at a high molecular mass of flexible-chain acrylamide copolymers, in diluted aqueous solutions, a appreciable quantity of lengthy uncharged segments of the polymer chain exists which form cooperative bonds with

the surface of APs as in the case of PAA-based polycomplexes [20,21].

The goal of this work is to study the flocculating properties of water-soluble PCCs based on the weakly charged cationic polyelectrolytes and aluminosilicate particles of aluminum polyhydroxochloride hydrosols.

2. Experimental

APHC was prepared from the aluminum alloy as described in [31] in the form of aqueous solution. The content of aluminum was 12.6 wt %, and the atomic ratio was $\text{Cl}:\text{Al} = 0.46$.

According small-angle X-ray scattering, the aqueous suspension of APHC was the mixture of two types of colloid particles with significantly different sizes (4.6 and 60 nm). The volume content of 60 nm particles did not exceed 1% with respect to the volume of all scattering particles. The 4.6 nm particles were the dense subunits of the thread-like spatial structure with a fractal dimensionality of $d_f \approx 1.0$ [29].

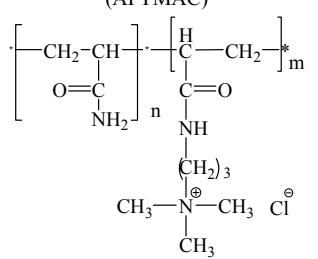
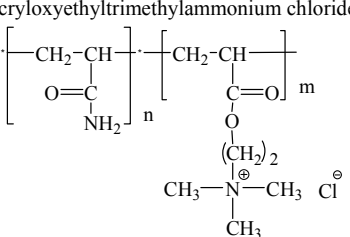
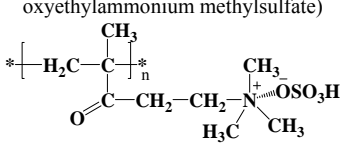
As weakly charged cationic polyelectrolytes, the samples of acrylamide copolymers from the Praestol and Organopol series were used. These samples differed in the chemical structure, molecular mass, and content of cationic (quaternary ammonium) groups. In contrast to weakly charged polyelectrolytes, a strong cationic KF-99 polyelectrolyte, poly(N,N,N,N -trimethylmethacryloyloxethylammonium methylsulfate), was also used in this study. This choice was associated with a wide application of these copolymers in practice and their high molecular mass. Since the copolymer samples used in this study were commercial and their characteristics were of approximate character, we have studied their physicochemical properties. The quantity of cationic groups in WCPEs was determined through the potentiometric titration with AgNO_3 solution using a silver indicator electrode. The viscosity of WCPE solutions was measured at a temperature 30°C in aqueous and aqueous-saline solutions by means of a Cannon-Ubbelohde-75/008 viscometer with $D_{\text{cap}} = 0.54 \text{ mm}$. The characteristics of WCPEs are summarized in the **Table 1**.

To prepare the PCCs, the aqueous solutions of WCPEs ($C = 0.05 \text{ g/dl}$) were mixed with the calculated weighed portion of APHC (at different Al^{3+} : WCPE unit molar ratios), and the mixture was allowed to stand for 1 day at room temperature.

The flocculating ability of PCCs was estimated with the use of the model kaolin suspension in the gravity sedimentation regime.

The kaolin dispersion (the concentration of the dispersed phase was 8 g/dm^3) was prepared from kaolin of the technical grade and tap water; the dispersion was

Table 1. Characteristics of the copolymers.

Commercial trademark	Manufacturer	Structural formula	Properties of WCPEs in aqueous solutions				
			Manufacturer data		Determined experimentally		
			Molecular mass	Cationic charge, % (molar)	$[\eta]$ in 10% NaCl	Content of cationic groups	C_{cross} , g/dl
Praestol 611 BC	JSC "Moscow-Stockhausen-Perm" (Russia)	Copolymer of acrylamide with N-acrylamidopropyl-N,N,N-trimethylammonium chloride (APTMAC)	$\sim 6 \times 10^6$	3 - 10	7.54	6.52	0.13
Praestol 851 BC			$\sim 9 \times 10^6$	3 - 10	9.76	6.97	0.10
Organopol 6400	Ciba Specialty Chemicals (USA)	Copolymers of acrylamide with acryloxyethyltrimethylammonium chloride	High molecular mass	Weakly cationic	7.69	2.94	0.13
Organopol 6405					11.71	1.65	0.08
KF - 99	NPP "KF" (Russia)	Poly(N,N,N,N-trimethylmethacryloyl oxyethylammonium methylsulfate)	1×10^6	Strong	-	100	-
							

allowed to stand for 1 h for swelling, then it was thoroughly stirred and poured into cylinders with $V = 250 \text{ cm}^3$. A certain volume (a dosage) of reagent solution was added in every cylinder; the mixture was stirred with a circular stirrer for 30 s and allowed to settle for 20 min. The upper clarified layer was collected, and its optical density was measured on a Specol-1300 spectrophotometer ($\lambda = 540 \text{ nm}$, and $L = 1 - 3 \text{ cm}$).

3. Results and Discussion

As is known, the removal of mechanical suspensions and colloid particles is the first step in the flow chart of water

purification. In many cases, colloid particles carry the surface negative charge. Hence, due to mutual electrostatic repulsion, such dispersions are sufficiently stabilized. For the same reason, the neutralization of the surface charge is the necessary step in destabilization of colloid dispersions. Moreover, owing to the aggregation of particles, flocs are formed. This process is favored by the addition of polymer flocculants to water during purification. Coagulation and the early stage of flocculation are rapid processes, and their separation presents a challenge. The enlargement of flocs (flocculation) proceeds at a smaller rate. In practice, both separate successive addition of reagents and their simultaneous

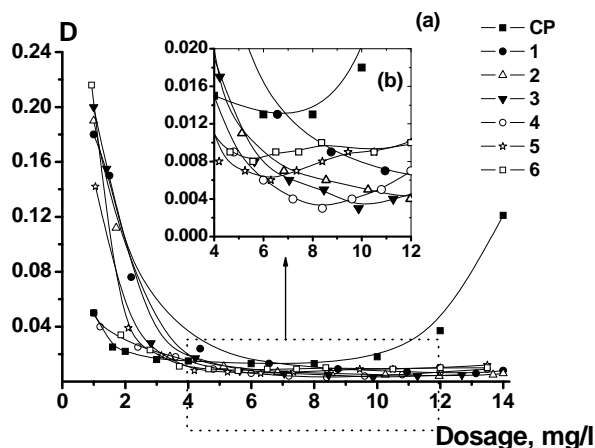


Figure 1. Dependence of the optical density (D) of the kaolin dispersion during flocculation on the dosage of copolymer (CP) (Praestol 611BC) and the related PCCs at different Al^{3+} :CP unit molar ratios in the initial reagent mixture.

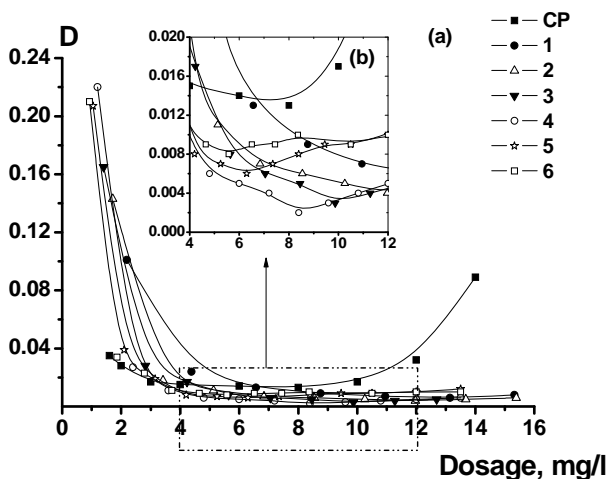


Figure 2. Dependence of the optical density (D) of the kaolin dispersion during flocculation on the dosage of copolymer (CP) (Praestol 851BC) and the related PCCs at different Al^{3+} :CP unit molar ratios in the initial reagent mixture.

addition are employed.

In this connection, in what follows, we present our experimental data on the flocculating properties of polycomplex reagents, PCCs, and on separate effects of the coagulant (the inorganic aluminum salt) and the flocculant (the copolymer of acrylamide) under different regimes of their introduction into the purified model system. Aluminum sulfate (AS) and low-basicity aluminum chloride (ABC), which are conventionally employed in water treatment, were used in this study. The kaolin dispersion in water with a content of the dispersed phase 8 g/dm^3 was employed as a model dispersion. All experiments were performed at a temperature $25 - 27^\circ\text{C}$ (the natural environment indoors). To get comparative data, flocculation was examined with the use of individual

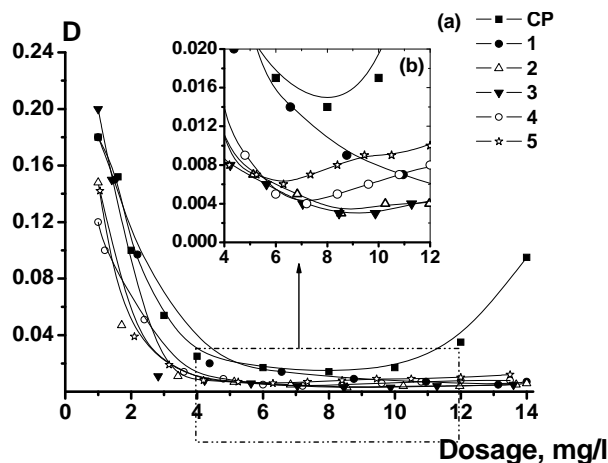


Figure 3. Dependence of the optical density (D) of the kaolin dispersion during flocculation on the dosage of copolymer (CP) (Organopol 6400) and the related PCCs at different Al^{3+} :CP unit molar ratios in the initial reagent mixture.

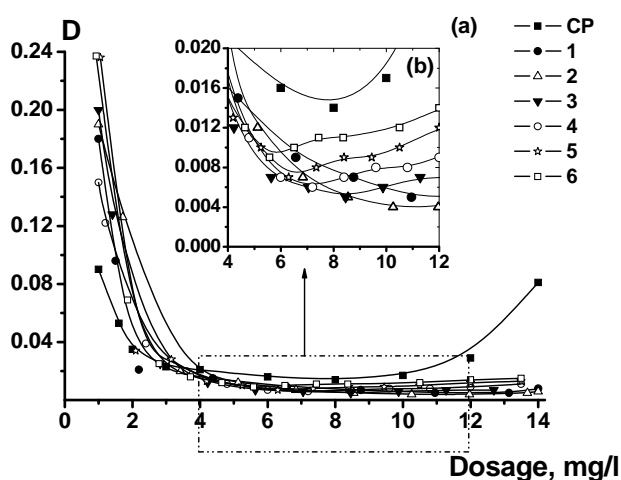


Figure 4. Dependence of the optical density (D) of the kaolin dispersion during flocculation on the dosage of copolymer (CP) (Organopol 6405) and the related PCCs at different Al^{3+} :CP unit molar ratios in the initial reagent mixture.

copolymers and PCCs based on nonionogenic PAA and APHC [24]. **Figures 1-4** demonstrate a variation in the optical density of kaolin dispersion during flocculation with different dosages of polycomplexes of various compositions and individual cationic copolymers.

The following designations are used in **Figures 1-4**: CP is copolymer; 1, 2, ..., 6 refer to the PCCs with Al^{3+} to CP unit molar ratios in the initial mixture equal to 1:1, 2:1, ..., 6:1, respectively.

As follows from the above data, the behavior of all CPs (Praestol and Organopol) is typical for high-molecular-mass polyelectrolytes; that is, they are characterized by the optimal dosage interval (4 - 6 mg/dm^3) in flocculation. An excess of these dosages leads to stabili-

zation of dispersions. On the contrary, the PCCs demonstrate a wider dosage interval and in terms of their efficiency surpass the initial CPs and decrease the optical density to a minimum level of 0.003 - 0.004. A certain difference is observed for the PCCs of different compositions (**Figures 1b-4b**). In all cases, the highest activity is demonstrated by the PCCs prepared at the Al^{3+} : CP elemental unit (molar) ratio in the range from 3:1 to 4:1. A further increase in the amount of Al^{3+} in the reagent mixture brings about a certain decline in the flocculating ability (curves 5 and 6 in **Figures 1-4**).

As was mentioned above, under the combined use of inorganic coagulants and polymeric flocculants, the synergistic effect may be observed. In our opinion, a high activity of the PCCs cannot be associated with this phenomenon but results from the individual nature of poly-complexes. To confirm this suggestion, special experiments on flocculation with mechanical mixtures of CPs with aluminum salts ($\text{Al}_2(\text{SO}_4)_3$ and ABCs) were performed at various orders of their addition to the dispersion, namely, first the coagulant (the salt) and then the flocculant (CP) and vice versa.

Figures 5 and **6** display variation in the optical density of the kaolin dispersion during its treatment with different dosages of individual Praestol 611BC and Organopol 6400, the related PCCs, and the mixtures of Praestol 611BC and Organopol 6400 with ABCs and $\text{Al}_2(\text{SO}_4)_3$. With a small difference, similar dependences were obtained for other copolymers, Praestol 851BC and Organopol 6405.

These data show that the PCCs provide the most pronounced clarification at the same dosages and reveal no stabilizing effect under overdosing. It is noteworthy that a similar behavior is observed for the mixtures of the CPs with ABCs. This circumstance is evidently associated with the fact that the ABCs is an equilibrium mixture of aluminum oxychlorides, including those with high basicity and capable of forming PCCs [31]. Thus, during the mixing of ABCs with the CoaPs, the PCCs are formed in the corresponding small amount and these PCCs play a certain role in flocculation.

The synergistic effect that appears, when the coagulant-flocculant mixtures are used, depends on the order of addition of these reagents to water being treated. **Figures 7** and **8** demonstrate the data on clarification of the kaolin dispersion at different orders of addition of CP (flocculant) and inorganic salt (coagulant).

With small differences, similar relationships were obtained for other copolymers, Praestol 851BC and Organopol 6405. In this case, the best results were achieved for the PCCs as well. As might be expected, the order of addition of reagents flocculant + coagulant gives the smallest effect. As was shown in [30], the strong polyelectrolyte KF-99 does not form PCCs during its mixing

with APHC sols. **Figure 9** demonstrates the results of flocculation with pure KF-99 and its mixtures with the APHCs. These data show that all combinations are characterized by smaller effects than those in the case of the PCCs. The effects due to the said combinations are approximately equal and correspond to the use of the KF-99 solely. This circumstance indicates the absence of interaction between KF-99 macromolecules and aluminonoxane particles.

To elucidate a difference in the flocculating properties of the PCCs of various compositions, the spectrophotometric technique [32] was employed since the conventional technique used to estimate the flocculation effect based on the accumulation of the mass of dispersion precipitating on a torsion balance pan turned out to be inapplicable. In our case, a high rate of floccule sedimentation coagulated with the PCCs caused a high scatter in the experimental data. In the spectrophotometric technique, the optical density of the supernatant taken a certain time after dispersion settling with and without reagent addition was measured. Then, the dimensionless parameter, the clarification effect, was calculated:

$$E_{\text{clar.}} = \frac{\tau_D^0}{\tau_D} - 1 \quad (1)$$

where τ_D^0 and τ_D are the optical turbidities of the supernatant without and with the addition of reagent, respectively.

$$\tau_D = \frac{2,3D}{L} \quad (2)$$

where D is the optical density of a liquid and L is the thickness of the liquid layer in the spectrophotometer cell.

Figure 10 depicts relationships for the clarification effect E_{clar} of the PCCs based on the copolymers under study obtained at different Al^{3+} : CP unit (molar) ratios in the initial mixtures and of the individual copolymers determined at the optimal reagent dosage (6 mg/dm³).

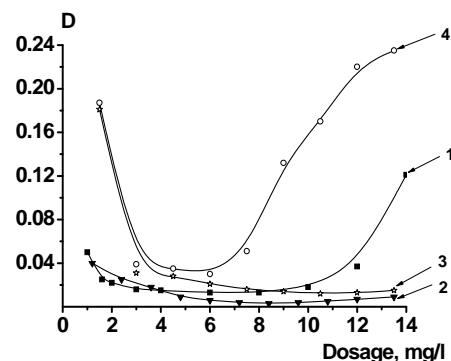


Figure 5. Flocculation of the kaolin dispersion (8 g/dm³). Curves 1, 2, 3, and 4 refer to Praestol 611BC, the related PCC, Praestol 611BC + ABC, and Praestol 611BC + $\text{Al}_2(\text{SO}_4)_3$, respectively, at various reagent dosages (mg/dm³). D is the optical density.

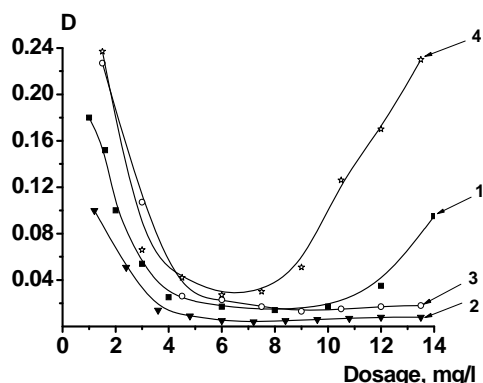


Figure 6. Flocculation of the kaolin dispersion (8 g/dm^3). Curves 1, 2, 3, and 4 refer to Organopol 6400, the related PCC, Organopol 6400 + ABC, and Organopol 6400 + $\text{Al}_2(\text{SO}_4)_3$, respectively, at various reagent dosages (mg/dm^3). D is the optical density.

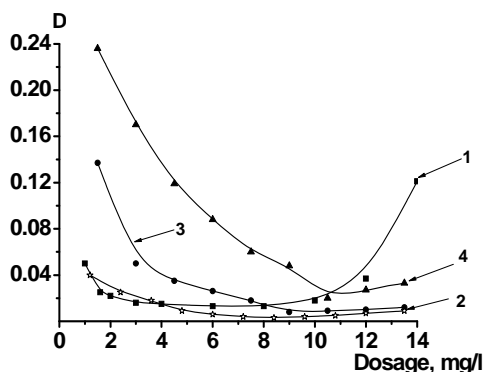


Figure 7. Flocculation of the kaolin dispersion (8 g/dm^3) at different orders of addition of reagents and different reagent dosages (mg/dm^3). The numbering of the curves is as follows: 1) Praestol 611BC, 2) the related PCC, 3) coagulant + flocculant, and 4) flocculant + coagulant. D is the optical density.

Figure 11 compares the values of Eclar obtained for the individual copolymers, the related PCCs at the optimal Al^{3+} : CP unit molar ratio in the initial mixtures, and mixtures. This figure also demonstrates the data obtained for the PCCs of the nonionogenic PAA and APHC sols [24].

The data described above give us grounds to infer that a high flocculating ability of the PCCs is associated with the individual nature of the polycomplexes that combine the properties of the inorganic coagulant and of the polymer flocculant.

4. Conclusions

1) It has been found that the water soluble polymer colloid complexes of weakly charged cationic copolymers of acrylamide with aluminosilicate particles of aluminum polyhydroxochlorides sols demonstrate a high flocculating ability.

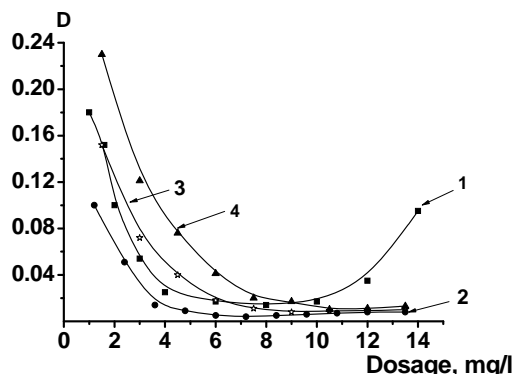


Figure 8. Flocculation of the kaolin dispersion (8 g/dm^3) at different orders of addition of reagents and different reagent dosages (mg/dm^3). The numbering of the curves is as follows: 1) Organopol 6400, 2) the related PCC; 3) coagulant + flocculant, and 4) flocculant + coagulant. D is the optical density.

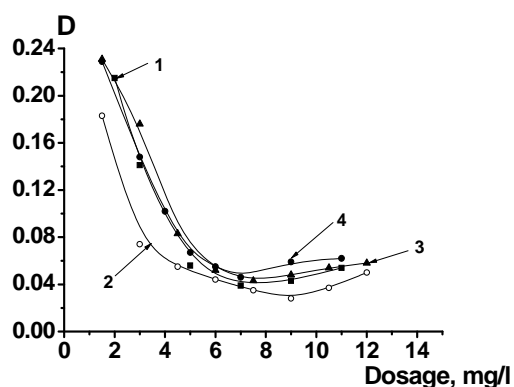


Figure 9. Flocculation of the kaolin dispersion (8 g/dm^3) at different orders of addition of reagents and different dosages of reagents (mg/dm^3). The numbering of the curves is as follows: 1) KF-99, 2) mixture of KF-99 and APHC (the PCC analog), 3) coagulant + flocculant, and 4) flocculant + coagulant. D is the optical density.

culating ability. In terms of flocculating activity in the separation of model kaolin dispersion under the regime of gravity sedimentation of the polycomplexes, they surpass the initial cation-active copolymers and the PCCs based on the nonionogenic polyacrylamide.

2) The flocculating activity of the PCCs depends on the ratio of reagents in the initial mixtures and achieves the maximum value for the Al^{3+} : copolymer unit molar ratios in the range from 3:1 to 4:1 for different copolymers.

3) A high flocculating activity of the PCCs does not result from the synergetic effect of the mutual action of coagulant (APHCs) and flocculant (WCPEs) but is explained by the original nature of the polycomplexes formed during their interaction via nonelectrostatic forces.

4) The fully charged cation-active KF-99 polymer

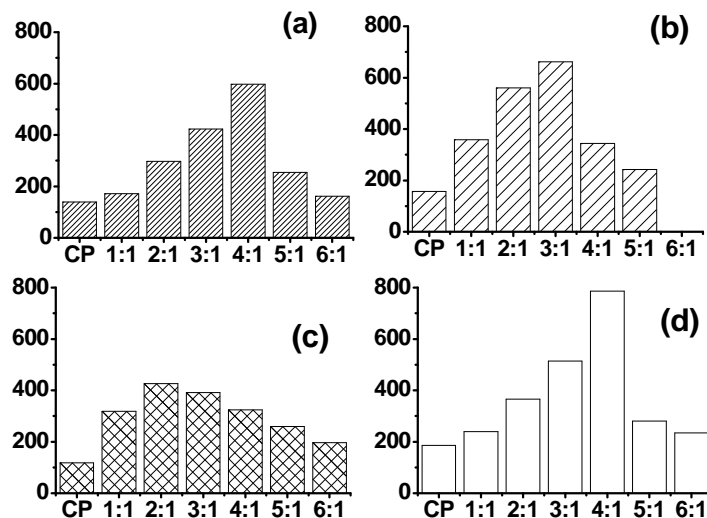


Figure 10. Clarification effects (E_{clar}) for the CPs and the related PCCs of different compositions: (a) Praestol 851BC, (b) Organopol 6400, (c) Organopol 6405, and (d) Praestol 611BC. Designations 1:1, 2:1, etc. refer to Al^{3+} :CP unit molar ratios in the initial reagent mixture.

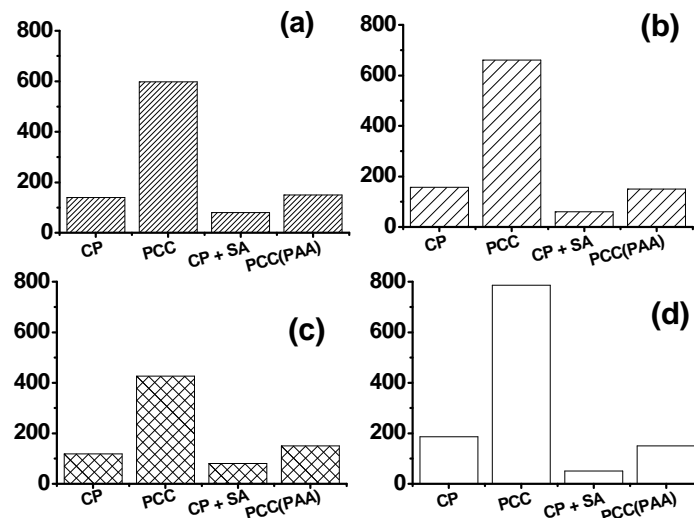


Figure 11. Clarification effects (E_{clar}) for the individual CPs, the related PCCs at the optimal Al^{3+} :CP unit molar ratios in the initial mixtures, mixtures (CP + AS), and the PAA-based PCCs: (a) Praestol 851BC, (b) Organopol 6400, (c) Organopol 6405, and (d) Praestol 611BC.

does not interact with the positively charged APs because of a strong electrostatic repulsion, and their mechanical mixture exhibit no increased flocculating effect.

5. References

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