

Aggregation of Aqueous Kaolin Suspensions in the Presence of Cationic Polyelectrolytes, Anionic Polyelectrolytes and their Mixtures

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Article info

Received:

24 September 2015

Received in revised form:

10 November 2015

Accepted:

9 March 2016

Abstract

The influence of anionic, cationic synthetic polyelectrolytes and their mixtures on the aggregation of kaolin hydrosuspension has been studied by means of spectrophotometry, electrophoresis and dynamic light scattering (DLS). An enhancement of the flocculating property of the cationic polyelectrolyte FO 4650 in accordance with its consumption increases from 0.77 mg/g to 7.7 mg/g has been found. At these conditions the relative size of floccules (R) increases from 1.0 to 13.0. The increase of the flocculating property accordingly to the increasing charge of anionic polyelectrolyte is observed in mixtures of cationic and anionic polyelectrolytes. The time dependences of R in presence of the weakly charged cationic polyelectrolyte mixtures reach a plateau region. This can be associated with the formation of electrostatic contacts between the solid surface and the polymer mixtures, as well as with stabilizing equilibrium conformation of macromolecules. It has been found that mixtures of oppositely charged polyelectrolytes lead to more efficient aggregation of particles than individual polyelectrolytes. This process is enhanced by the introduction primarily of the cationic polyelectrolyte and then the anionic one (R = 6–10). Use of the pre-formulated mixtures of polymers leads to the marked increase in degree of particle aggregation (R = 12). The reason is an interaction of kaolin particles with inter-polymer complex formed by electrostatic attraction of oppositely charged polyelectrolytes.

1. Introduction

One of the major problems related to the natural and waste water treatment by using the layered silicates is to accelerate the separation of dispersed particles from the dispersion medium. For this purpose, various coagulants and flocculants are more appropriate. Notwithstanding that the general regularities of coagulation and flocculation of fine particles are summarized in some well-known papers [1–4]; interest in these systems continues to be in focus of many research group.

In particular, the coagulation and flocculation method has been used in the work [5], which involves polyelectrolytes containing sulfur-groups to remove basic and acid dyes used in the textile industry. The efficiency of the method is shown in removing not only dyes but also ions Cu^{2+} , Pb^{2+} , Fe^{3+} from the water. Dyes and ions were bound with a

natural sorbent due to the ion-exchange mechanism.

The high efficiency of a new composite flocculant, which is a mixture of chitosan and thermosensitive poly-N-vinylcaprolactam, in separating clay particles from their aqueous suspension has been demonstrated [6].

The important role of adsorption by the macromolecular flocculant and the determination of the flocculant's equilibrium conformation in the adsorption layer in the dispersed phase flocculation kinetics was shown in [7]. A new approach to the search for ecologically clean flocculant is considered in [8]. It was found that individual organelles coupled with protease K and diethyl ether can be used as an effective biodegradable flocculant.

The derivatives of *Opuntia ficus – indica* are direct flocculants for biomaterials and heavy metal ions when they are used for purification of polluted water [9].

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In the previous works [10–12], we showed a high sorption activity of the Kazakhstan bentonite clay (montmorillonite of the Monrak Deposit in the East Kazakhstan Region) to the heavy metal ions (Cu^{2+} , Pb^{2+} , Cd^{2+} , Zn^{2+}). The treatment of waste water from the Belousov Ore Mining and Processing Mill with a thermal-acid activated montmorillonite via its flocculation with a flocculant ensures 95–98% of waste water purification enabling the same to be discharged to Irtysh River [10].

In addition, we have shown that the flocculating power of the oppositely charged flocculant mixtures depends strongly on the structure of a mixed adsorption layer [11] of the mentioned polyelectrolytes. The thickness of the mixed adsorption layer has a significant impact on the electrokinetic potential value of the kaolin particles. While the anionic polyelectrolyte charge density increases in its mixtures with a cationic polyelectrolyte, the thickness of the mixed adsorption layer increases, and the flocculating power of such composite flocculant increases as well.

The work [12] analyzes the effect of electrolytes with monovalent, divalent or trivalent metal cations as well as cationic and anionic surfactants on the electric surface properties of kaolin and bentonite. It was found that while the electrolyte concentration increases the ζ -potential of the particles of both minerals reduces significantly. The effect increases while the cation valency increases. The cationic surfactants recharge and the anionic ones increase markedly the negative ζ -potential of kaolin and bentonite particles.

The influence of cationic, anionic polyelectrolytes and their mixtures on the stability of kaolin suspensions has been studied in this paper.

2. Experimental

2.1 Materials

We used kaolin (Light kaolin BP, United Kingdom) dispersed in water at $\text{pH} = 7$ and fractionated by the sedimentation method. The fraction with the average particle diameter of $1.9 \pm 0.2 \mu\text{m}$, stable for one day, was used. The particle size was measured using the DLS spectrometer Zeta Sizer Nano ZS (Malvern) instrument [16].

Products of SNF (France) – Company, the cationic and anionic polyelectrolytes, synthesized on the basis of polyacrylamide, were used as the water-soluble polymers (WSP). Characteristics of the polyelectrolytes used in the study are shown in Table 1.

Table 1
Characteristics of used polyelectrolyte

Product's name	Type	Molecular mass / 10^6 Da	Charge density (content of the functional groups mol.%)
FO 4115	Cationic	6–7	5
FO 4650	Cationic	6–7	35
AN 910	Anionic	8–9	5
AN 945	Anionic	8–9	30
AH 956	Anionic	8–9	60

2.2. Methods

The influence of polyelectrolytes and their mixtures on the stability of water based kaolin suspensions was studied by monitoring the kinetics of the changing optical density of suspensions and by changing sizes of floccules (aggregates of kaolin particles). The floccule dimensions were determined by means of the Zeta Sizer instrument, using a PDA 2000 (particle dynamics analyzer) (Rank Brothers Ltd, United Kingdom) flow system with constant mixing rate of 90 rpm with a magnetic stirrer.

The parameter $R = \frac{V_{rms}}{V_{dc}}$, which is the ratio of the root-means-square (rms) value of the fluctuating light signal (V_{rms}) to the light transmission of the original system V_{dc} (dc – direct current), was used to assess the degree of flocculation [13]. The principle of this instrument has been well described in several papers [14, 15], but basically the larger R the more flocculated the suspension is. The optical density of the clay suspension was determined by means of spectrophotometric method, using the spectrophotometer PD – 303 at a wavelength of 490 nm.

Electrophoretic mobility of kaolin particles was measured with DLS (dynamic light scattering) spectrometer Zeta Sizer Nano ZS at room temperature, within 6–15 V/cm range of external electric field gradient values. We used the average values from five measurements of the ζ -potential. Deviations of the ζ -potential values from the average do not exceed 5%.

3. Results and discussion

In order to optimize the flocculation process of kaolin particles, the effect of the cationic, anionic polyelectrolytes and their mixtures on the aggregation of dispersed phase particles was studied. Factors such as polymer concentration, composition of their mixtures, density of positive and negative charges of polyelectrolytes, and the method

of feeding the components of the mixture into the suspension, which influences this process, were studied as well.

0.05% kaolin suspension proved to be quite stable, as its optical density is practically unchanged for 40 min. Figure 1 shows that increasing concentration of the cationic polymer FO 4650, leads to a significant decrease in the suspension optical density. This may be due to increasing aggregation of particles and their sedimentation.

For more information on the kaolinite particles aggregation in the presence of polyelectrolytes, an influence of the latter on the R parameter has been studied. For small (up to a few microns) particles, this method is about 100 times more sensitive than the method of turbidity [14, 15].

Figure 2 shows that the cationic flocculant FO 4650 does not significantly increase the aggregation degree ($R \sim 3-4$) at low concentrations (0.77 mg/per 1 g of solid phase), while the increase in its content from 1.5 mg/g to 7.7 mg/g leads to the noticeable rise in degree of particles aggregation over time ($R \sim 7-13$). In this case the kaolin particles aggregation may be caused by the decrease of the negative surface charge of particles due to the flocculant polycations adsorption and by reducing electrostatic repulsion between the clay particles [13]. This is evidenced by the kinetics of varying ζ -potential of kaolin particles in the presence of cationic polyelectrolyte FO 4650, anionic polyelectrolyte AN 945, and their mixtures (see Fig. 3). As is seen from this figure, with increasing concentration of FO 4650, the inversion of ζ -potential sign of kaolin particles takes place.

In the presence of the anionic polyelectrolyte, firstly the slight increase in the negative ζ -potential of particles is observed, probably due to the formation of the polymer adsorption layer [16].

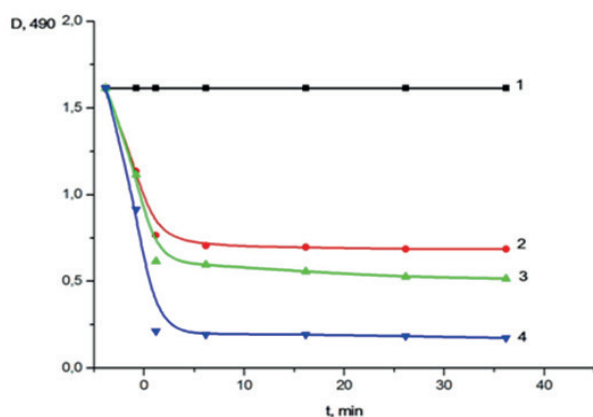


Fig. 1. The kinetics of change in optical density of 0.05% kaolin suspension without flocculant (1) and in the presence of the cationic polyelectrolyte FO.

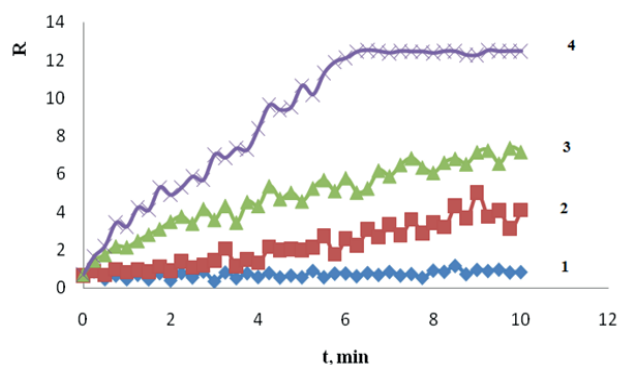


Fig. 2. The kinetics of change in the factor R of 0.05% kaolin hydrosuspension in the presence of the cationic polyelectrolyte FO 4650 at concentrations: 0.77 mg/g (2) 1.5 mg/g (3) and 7.7 mg/g (4).

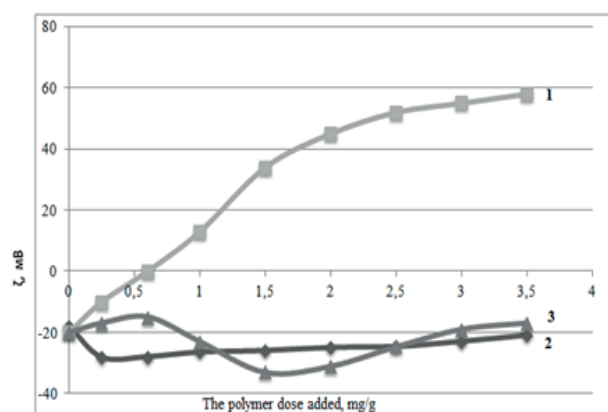


Fig. 3. Dependence of particle zeta potential on the concentration of cationic kaolin FO 4650 (1), AN 945 anionic (2) polyelectrolytes and mixtures thereof of 1:1 by weight (3).

The decrease of ζ -potential of kaolin particles caused by the further rise in concentration of anionic polyelectrolyte may be associated with compression of the electrical double layer (EDL) of particles possessing the polyelectrolyte adsorption layer. While increasing the addition of mixture (up to 1:1 by weight) of FO 4650 and AN 945 polyelectrolytes to the hydrosuspension, the reduction of the negative ζ -potential is initially observed and then its growth (Fig. 3, curve 3).

Of great interest is the study of the influence of the mixtures of oppositely charged polyelectrolytes on suspension stability. This is due to the possibility of changing the charge and conformation of macromolecules, when they interact. In this regard, the flocculation of kaolin particles by the mixture of cationic polyelectrolyte FO 4650 with anionic polyelectrolytes having different densities of negative charge was studied (Fig. 4).

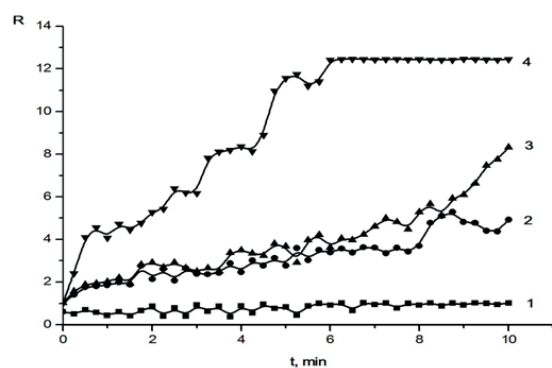


Fig. 4. Kinetics of R factor changes in a 0.05% kaolin hydrosuspension in the presence of (1 mg/g) cationic polymer (FO 4650) (1) and its compositions with anionic polyelectrolytes: AN 910 (2), AN 945 (3), AN 956 (4) at a weight ratio of 1:1.

As is seen from the figure, the mixtures of oppositely charged polyelectrolytes enhance the aggregation of the particles. This phenomenon has been revealed for dispersions containing the increasing concentrations of individual polymers [2, 17]; in this case, the regularity has been found to be the rule for mixtures of polymers as well. While treating kaolin suspensions with mixtures of oppositely charged polyelectrolytes, firstly the layer of cationic polyelectrolyte, adsorbing macromolecules of anionic polyelectrolyte, is formed on the particle surfaces [13].

Formation of the mixed layer of cationic and anionic polyelectrolytes on the particle surfaces has a very important practical value [16, 18]. It always begins with formation of the polyelectrolyte monolayer, charged oppositely to the surface [11].

In this regard, the flocculation of kaolin suspensions by mixtures of weakly charged cationic polyelectrolyte FO 4115 with anionic polyelectrolytes, having different charge densities, was studied (Fig. 5).

The considered dependences display initial plateau which length decreases in accordance with increasing charge density of anionic polyelectrolyte, namely: if the R values start to increase after 4 min in the presence of FO 4115 – AN 910 mixtures, the introduction of FO 4115 and AN 956 mixtures leads to the flocculation rise, visible already in 2–2.5 min. The appearance of the plateau in the R growth kinetics curves may be associated with formation of inter-polymer complex between oppositely charged polyelectrolytes.

Studying the flocculation action of the mixture of oppositely charged polyelectrolytes on kaolin hydrosuspension, is important to clarify the impact of the rate of the components feeding into the disper-

sion system on the particles aggregation. Individual cationic (FO 4115) and anionic (AN 910) weakly charged polyelectrolytes do not possess significant flocculation effect (Fig. 6, curves 1 and 2, respectively). When entering into hydrosuspension firstly anionic polyelectrolyte AN 910, and then, after 30 sec, cationic polyelectrolyte FO 4115, the particles aggregation is enhanced ($R \sim 6$, curve 3). Reordering the mixture components feeding, the first introduction of cationic polyelectrolyte FO 4115, then, after 30 sec, followed by anionic polyelectrolyte AN 910 (Fig. 6, curve 4), leads to the larger degree of particles association ($R \sim 10$).

Addition to the kaolinite suspension of a preformed mixture of oppositely charged polyelectrolytes results in the maximum particle aggregation ($R \sim 12$).

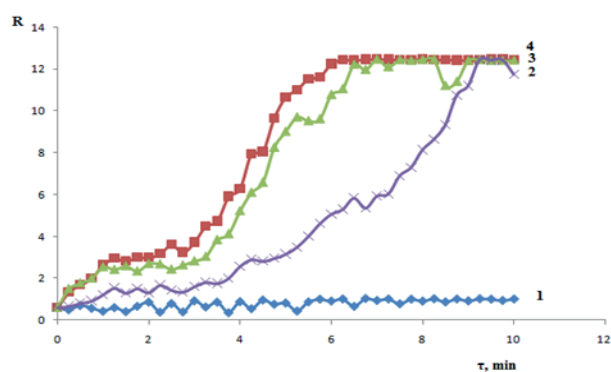


Fig. 5. Kinetics factor R changes of kaolin hydrosuspension in the presence of a weakly charged cationic polyelectrolyte FO 4115 (1) and its composition with anionic polyelectrolytes: AN 910 (2); AN 945 (3); AN 956 (3) at a weight ratio of 1:1.

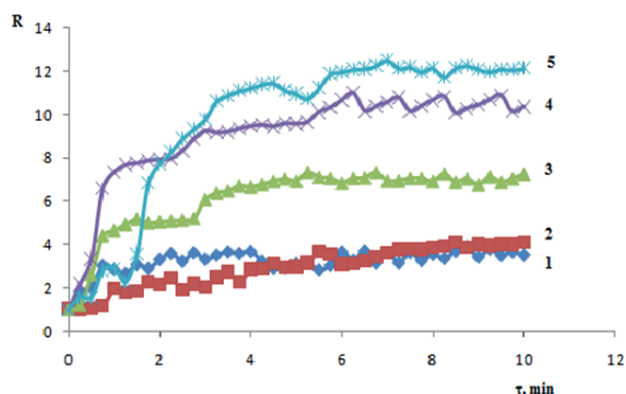


Fig. 6. The kinetics of formation of the kaolin particles flocculate in its 0.05% hydrosuspension in the presence (1 mg/g) of the anionic polyelectrolyte AN 910 (1); cationic polyelectrolyte FO 4115 (2); mixtures (1:1) anionic polyelectrolyte AN 910 + after 30 sec. FO 4115 (3); cationic polyelectrolyte FO 4115 + after 30 sec. AN 910 (4); GRP previously prepared mixture (5).

Interpretation of the experimental results concerning the effect of WSPs and their mixtures on the stability of the kaolin hydrosuspension can be carried out on the basis of existing concepts of stability of polymer-containing dispersed systems [2], taking into account the chemical structure peculiarities of the mineral particles under consideration [19], as well as the characteristics of formation of the polymer adsorption layer [20].

Kaolin is a bi-layered clay mineral where layers of tetrahedral silicon-oxygen structures are neighboring with octahedral aluminum-oxygen-hydroxyl ones [19]. Polymer adsorption and, more specifically, polyelectrolyte adsorption, on the surface of clay particles greatly varies with sign and value of the electric charge of the particles, which very significantly depending on pH. At neutral pH clay particles, as a rule, are negatively charged [21].

Therefore, the significant flocculating effect on the kaolin suspension is caused by the cationic polyelectrolyte FO 4650 (Fig. 2). This effect rises in accordance with increasing concentration of the cationic flocculant. The observed effect may be due to flocculation of clay particles as a result of neutralization of the negative charge of colloidal particles ("neutralization mechanism") or formation of polymer bonds ("bridges") between the dispersed phase particles ("bridge mechanism") [2].

Flocculation action caused by mixtures of oppositely charged polyelectrolytes and associated with formation of interpolymer complexes (IPC). At low relative concentrations of the oppositely charged components, this process is accompanied by decrease in the charge density and hydrodynamic size of IPC. With further increase in concentrations of the second component, charge reversal and the growth of the hydrodynamic size of IPC are observed [22]. The IPC formation in "loops" and "tails" of the adsorbed macromolecules [2, 20] may lead to the formation of larger floccules that reflects on the R values (Fig. 5). The growth of polyelectrolytes charge density can strengthen this phenomenon.

4. Conclusions

Thus from the research results it can be concluded following:

- mixtures of oppositely charged polyelectrolytes on the basis of polyacrylamide are more effective flocculants compared to the individual components;
- flocculation action of polyelectrolytes, both in the individual state and within the mixtures rises in accordance with increasing of their charge density;
- the pre-formed mixture of cationic and anionic polyelectrolytes is the most efficient flocculant.

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