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Kaolin dispersion destabilization with microparticles of cationic starches

Rima Klimaviciute*, Dalia Sableviciene, Joana Bendoraitienė, Algirdas Zemaitaitis

Department of Organic Technology, Kaunas University of Technology, Radvilenu pl. 19, LT-50254 Kaunas, Lithuania
Tel./Fax +370 37 456081; email: rimakli@ktu.lt.

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ABSTRACT

The flocculation efficiency of microparticles of cold-water-dispersible cationic starches (DCS) in the destabilization of kaolin dispersion in distilled water and anionic dye solution was investigated. DCS could act as both flocculants and adsorbents. The flocculation efficiency of DCS has been changed in the presence of inorganic salt or anionic dye in the kaolin dispersion. These changes depended on the degree of substitution and accessibility of cationic groups, i.e. on the factors that determined both the size of DCS microparticles and charge distribution on their surface. The best flocculation of kaolin dispersion was achieved at the particular size and surface charge density of DCS microparticles. In that case the balanced areas of negatively and positively charged patches were formed on the surface of DCS after adsorption of kaolin particles and during ensuing flocculation heavier floccules were formed.

Keywords: Cationic starch; Flocculation; Flocculation mechanism; Fluorescence

1. Introduction

Although water-soluble synthetic ionic polyacrylamide derivatives find wide applications as flocculating agents, a potential problem associated with their use is the lack of biodegradability and high cost. The development of the substitutes based on natural polymers could be more attractive from the biodegradability point of view, and another important factor here will be matching the performance.

Most of commercially available cationic starch derivatives used in the paper industry as retention and dewatering aid have a low degree of substitution (DS < 0.2) [1–5]. Various cationic starch derivatives with the high DS were prepared and evaluated by Khalil [6,7]. Native and hydrolyzed maize starches were used as parent materials for those derivatives. The flocculation efficiency was found to depend on the amino group type and followed the order: quaternary > tertiary > secondary > primary. The flocculation efficiency increased with an increase of nitrogen content. Nystrom and co-workers [8] investigated the interactions between cationic calcite and highly cationic starches containing quaternary ammonium groups.

Heinze and co-workers [9–13] synthesized water-soluble cationic starch derivatives with a high degree of functionalization and investigated their flocculation properties. The solutions of cationic starches ((2-hydroxy-3-trimethylammonium)propyl starch chloride) with DS up to 1.54 and kaolin or harbour sediment as model dispersions were used in flocculation and adsorption experiments. The flocculation behaviour of cationic starches (CS) showed a strong dependency on both DS and the content of amylopectin [10,13]. CS from amylopectin-rich (waxy maize) starch gave the highest degree of dewatering. Flocculation initiated by CS from potato starch

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* Corresponding author.

was found [11] to occur long before the kaolin surface charge neutralization had been reached. The amount of DS required for complete phase separation decreased with an increase of DS, and dispersion restabilization was observed at CS overdose. It has been suggested that flocculation of kaolin dispersion is a combination of the bridging and "charge patch" processes. The lowest flocculant dosage yielding the maximum dewatering results was determined for the most substituted sample (DS = 1.48) [13]. The molar mass distribution and coil dimensions of CS also greatly influenced the flocculation efficiency, because a 1.5-fold increase in molar mass can compensate a 1.5-fold decrease in DS. Similar results were obtained employing water-soluble cationic starch derivatives with quaternary ammonium groups obtained from hydroxyethylated starch as described in our previous work [14]. The best flocculation with water-soluble CS occurred when the absorbed amount of cationic groups in the dose was sufficient to cover about a half of anionic sites on kaolin particles. In that case, the flocculation of kaolin dispersion followed the charge neutralization mechanism. At a higher than optimal dose, the macromolecules of soluble cationic starch have covered most of the available anionic sites on each kaolin particle and imparted an electric positive charge to them, high enough to cause the mutual repulsion.

More interesting was the observation that cationic starches obtained from native potato starch under conditions of heterogeneous reactions in which starch granules remained unchanged and formed a dispersion of swollen particles in cold water exhibited a more than twice as high flocculation efficiency compared to that of the soluble cationic starches [14]. They were called cold-water-dispersible cationic starches (DCS). The flocculation properties of DCS depended on DS, the state of the particles in water and the accessibility of quaternary ammonium groups to anionic polyelectrolytes. DCS with the DS from 0.27 to 0.37 showed the best flocculation of kaolin dispersion, and the content of accessible cationic groups in a dose of DCS at which the best flocculation occurred was about 0.634×10^{-5} equivalent per g of kaolin.

The flocculation properties of polyelectrolytes were changing in the presence of electrolytes in destabilized dispersion. For example, the addition of the electrolyte reduced the required dose of soluble CS and broadened the flocculation window, although no substantial influence of ionic strength on the adsorption of soluble CS was found [11]. Larsson and co-workers [1–3] investigated the flocculation of nanosized silica particles with water-dispersible cationic amylopectin with DS = 0.04 and the influence of salts on this process. They obtained that electrolyte screened the cationic charges of amylopectin up to an electrolyte concentration of 50 mmol, however the dimensions of macromolecules of cationic amylopectin were changed by the addition of only few mmoll of electrolyte. The increase of the electrolyte concentration increased the flocculation amplitude, moved the maximum of the flocculation amplitude to higher mass ratio nanosized silica/cationic amylopectin and expanded the mass ratio interval with high flocculation amplitude. However, in the literature, there are no reports on the influence of electrolytes on the flocculation properties of water-dispersible cationic starches with a high DS.

Textile wastewater polluted with auxiliaries and dyes is discharged into municipal outlets. Most of dyes in textile wastewater are anionic compounds, and can therefore interact with cationic polyelectrolytes. Besides dyestuff, textile wastes contain other negatively charged compounds such as thickeners, dispersing agents, anionic detergents etc. which could help to facilitate the flocculation of ionic and disperse dyes [15]. Under controllable conditions the cationic polymer and textile auxiliaries form polyelectrolyte complexes (PECs) that would incorporate the dyes and then precipitate. It was shown [16] that during the interaction of poly(diallyldimethylammonium chloride) and potato starch, non-stoichiometric PECs are formed. Such PECs have an appreciable amount of free quaternary ammonium groups and effectively eliminate acid dye from the water solution. Adsorption of anionic dyes on cross-linked starches containing quaternary ammonium groups was, also, evaluated and compared with that of CS [17]. The effectiveness of dye binding decreased with the increase of DS of DCS due to the increase of solubility of DCS and the soluble part of DCS was binding the dye as a typical soluble polyelectrolyte. A tannin-based coagulant and a vegetable protein extract derived from *Moringa oleifera*, were, also, investigated both as flocculants and adsorbents [18,19]. Therefore the interactions of organic low-molecular weight ions with the polyelectrolyte used for the flocculation may change the flocculation properties of both dispersion and polyelectrolyte.

The aim of the present work was to determine the influence of organic (anionic dye) and inorganic (NaCl) ions on the flocculation efficiency of highly-charged water-dispersible cationic starches in kaolin dispersions. Also, some peculiarities of the flocculation mechanism in such systems are discussed.

2. Materials and methods

2.1. Materials

Native potato starch was supplied by Antanavas Starch Plant (Lithuania), native maize starch by Cerestar (Holland) and hydroxyethylated starch Kollotex 1250 by Avebe (The Netherlands).

Cationic polyacrylamide Zetag 7652 was obtained from CIBA. 2,3-epoxypropyltrimethylammonium chloride (EPTMAC) and 2-(p-toluidino)-6-naphthalene sulfonate (TNS) were purchased from Sigma-Aldrich.

The kaolin used in flocculation experiments was obtained from Gluchovici (Ukraine). The average diameter of kaolin particles was 0.6 μm in distilled water and 0.65 μm in NaCl solution (50 mmol/l). The zeta-potential of aqueous kaolin dispersion at pH 5.5 was –37 mV.

2.2. Synthesis of cationic starches

Cationic starches were prepared by the reaction of potato, maize or hydroxyethylated starches with EPTMAC in the presence of sodium hydroxide (the molar ratio of starch : epoxy compound : NaOH was 1 : (0.4–0.7) : 0.04) at 45°C for 3–24 h [20]. After the reaction, the cationic starches were washed (3 times) with isopropanol and dried at 50°C. The nitrogen content (N, %) in cationic starch derivatives was estimated by the Kjeldahl method after the purification by Soxhlet extraction with methanol for 16 h. The degree of substitution (DS) was calculated from nitrogen content:

$$\mathrm{DS} = \frac{162 \times \mathrm{N}}{1400 - 151.5 \times \mathrm{N}} \tag{1}$$

The cationic starches washed and purified by Soxhlet extraction were applied in experiments of fluorescence measurement and only washed in experiments of flocculation.

2.3. Preparation of cationic starch dispersions

The dispersions of cationic starches in distilled water (0.2–0.4 wt.%) were prepared by stirring with a magnetic stirrer at the room temperature for 1 h and then were left to stay for 6–8 h. In some experiments, the dispersions were heated up in an autoclave at 126°C for 60 min.

2.4. Flocculation of kaolin dispersions

Different methods can be used to evaluate the flocculating properties of polyelectrolytes. Larsson with co-workers [1–3] studied the flocculating kinetics in a stopped flow apparatus and flocculating amplitude as a change in turbidity during the first 30 ms was defined. The flocculation of calcite dispersion with cationic starches was determined by measuring the particle size [8]. Often the flocculating activity is determined as a difference in absorbance of the supernatant after sedimentation of dispersion with and without the flocculant [6,7]. In the wastewater treatment it is important that the flocculated particles of dispersion could settle down fast. The more effective the flocculant, the larger floccules are formed and they settle down faster. In this case the sedimentation rate of the flocculated disperse phase can be examined and the flocculating efficiency D can be calculated [21]:

$$D = \frac{V}{V_o} - 1 \tag{2}$$

where V and V_o are the sedimentation rate of disperse phase with and without the flocculant, mm/min.

An assay of the flocculation efficiency of cationic starches in kaolin dispersion was carried out as follows: 12.5 g of kaolin and 150–200 ml of distilled water were stirred for 10 min with a magnetic stirrer and poured into a test cylinder (diameter 40 mm, height 300 mm). The cylinder was calibrated in millimeters. The line of zero mm corresponded to the line of 250 ml volume of the cylinder. A dispersion of cationic starch was added in different doses, and then distilled water was poured to get exactly 250 ml (the final concentration of kaolin in the dispersion was 50 g/l). The pH value of the dispersion was 5.5. The dispersion was slowly mixed for 30 s and allowed to sediment. A clear layer of liquid was formed in the upper part of the test cylinder. The height of the clear layer of liquid in mm, depending on the sedimentation time, was measured. The experiments were carried out at room temperature (18–20°C).

In some flocculation experiments, a solution of C.I. Acid blue 25 (Boruta, Poland) was used instead of distilled water.

The curves that represented the height of the clear layer vs. time were defined. The initial parts of these curves were straight lines for which the linear equations were calculated with the correlation coefficient $R^2 > 0.99$. The rate (V, mm/min) of sedimentation were computed from the slope of these lines, and the flocculation efficiency D was calculated from Eq. (2).

The standard deviation of D was from 1.5 to 2 in the flocculation with water-dispersible cationic starches.

2.5. Evaluation of accessibility of cationic groups

The accessibility (A) of cationic groups of modified starches was evaluated by polyelectrolyte titration with dextran sulphate as describe in [14]. It was assumed that accessible cationic groups were the ones titrated until the first change of the indicator color.

2.6. Particle size measurements

The size distribution of the cationic starch and kaolin particles in water by number was measured with COUTER LS200 Particle Size Analyzer equipped with the Couter Fluid Module (Beckman Couter, USA) and expressed as a geometric mean value of particles diameter.

2.7. Fluorescence measurements

Fluorescence spectra were recorded on an MPF-4 spectrophotometer (Hitachi, Japan). 2-(*p*-toluidino)-6-naphthalene sulphonate (TNS) was used as a fluorescence probe and the excitation wavelength of 280 nm was employed. The concentration of TNS in all experiments was 0.04 mmol/l. To the aqueous solution of TNS the cationic stach solution or dispersion was added. When the influence of the electrolyte was examined, NaCl solution was added before the addition of the solution or dispersion of cationic starch.

2.8. Optical microscopy measurements

The optical observations were carried out using the Olympus CX31 optical microscope (Philippines) under 100-time magnification. The photographs were taken with an Olympus camera.

3. Results and discussion

The object of this investigation was the flocculation efficiency of microparticles of dispersible in cold-water cationic starches (DCS) containing quaternary ammonium groups obtained from native potato starch under conditions of heterogeneous reactions and preserving morphologic structure of starch granules unchanged [22]. When DCS were dispersed in cold water, only 26% of cationic groups were accessible to anionic macroanions (A = 26%). The accessibility of cationic groups was increased up to 100% (A = 100%) after the heating of DCS dispersions at 126°C for 60 min.

The maximum flocculation efficiency (D_{max}) of DCS with different DS and A = 26% in destabilization of aqueous kaolin dispersions is presented in Table 1 along with the data obtained for cold-water-dispersible cationic starch from maize starch (CMS). As could be predicted from our previously work [14], DCS with DS in the range from 0.27 to 0.36 showed the best flocculation efficiency. The amount of accessible cationic groups in dose at which the highest value of D_{max} was obtained was in the range from 0.64×10^{-5} to 0.68×10^{-5} equivalent per g of DCS (eq./g). With the increase of DS D_{max} of DCS decreased and the number of accessible cationic groups in dose at D_{max} increased. The lowest flocculation efficiency was obtained when CMS was used to destabilize the aqueous kaolin dispersion.

The differences in flocculation efficiency between DCS and CMS with different DS could be related to different size of swollen microparticles of cationic starches (Table 1). DCS with the best flocculation efficiency existed in water as the largest particles.

According to the obtained data (see Table 1) DCS with DS 0.36 represented high flocculation efficiency and the latter of DCS with DS 0.48 was lower. Therefore those two samples were chosen for the investigation of the influence of organic and inorganic anions on the flocculation properties of cationic starches.

3.1. Influence of NaCl on flocculation properties of DCS

The flocculation properties of both DCS with a low number of quaternary ammonium groups [3] and water-soluble cationic starches (SCS) with a high number of quaternary ammonium groups [11] have been changed when the electrolytes were added into the dispersions. However, there are no data in the literature on the influence of the electrolytes on the flocculation properties of DCS with a high DS.

The flocculation efficiency of DCS with different DS (0.36 and 0.48) and different level of accessibility of cationic groups (26% and 100%) in the destabilization of aqueous kaolin dispersions and kaolin dispersions containing 50 mmol/l of NaCl was tested and is presented as a function of DCS concentration (expressed in mg of DCS per g of kaolin) in Fig. 1. The influence of NaCl on D_{max}, the dose of DCS that is required to achieve D_{max}, the amount of accessible cationic groups in the dose and the diameter of DCS particles are shown in Table 2. It is obvious, that the influence of NaCl on flocculation efficiency of DCS depended on both DS and the level of accessibility of cationic groups. In the case of 26% accessibility the flocculation efficiency of DCS with DS = 0.36 slightly decreased when 50 mmol/l of NaCl was added to the dispersion, whereas the flocculation efficiency of DCS with DS = 0.48 increased 1.5 times. In both cases, the dose required to achieve D_{max} increased 1.5–1.75 times compared to that required to destabilize the aqueous kaolin dispersion. When DCS with fully accessible cationic groups were used to destabilize NaCl kaolin dispersion, the D_{max} of DCS with DS = 0.36 increased almost two times, while that of DCS with DS = 0.48 increased only

Table 1
Influence of DS on flocculation efficiency of DCS (A = 26 %) and CMS (A = 24%) in destabilization of aqueous kaolin dispersions

Type of cationic starch	DS	D_{max}	Dose of DCS (mg/g) at D_{max}	Amount of accessible cationic groups in the dose at D_{max}, ($\times10^{-5}$ eq./g)	Diameter of particles (μm)
DCS	0.27	37.8	19.2	0.64	18
	0.36	42.1	16	0.68	22
	0.48	30.4	16	0.85	18
	0.56	16.2	16	1.09	2
CMS	0.22	5.9	22.4	0.63	4
	0.34	7.8	22.4	0.89	3
	0.53	10.8	19.2	1.05	7

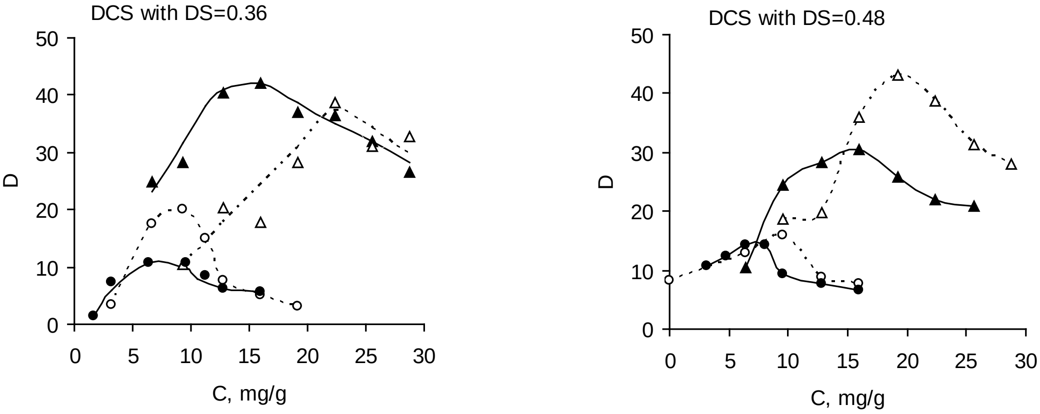

Fig. 1. The influence of DCS dose in the aqueous kaolin dispersions (solid line) and kaolin dispersions containing 50 mmol/l of NaCl (dashed line) on the DCS flocculation efficiency (*D*). The accessibility of cationic groups was 26% (triangle) and 100% (circle).

Table 2
Flocculation efficiency of DCS with different DS and A in the destabilization of aqueous kaolin dispersions and kaolin dispersions containing 50 mmol/l of NaCl

DS	*A* (%)	Concentration of NaCl (mmol/l)	D_{max}	DCS dose (mg/g) at D_{max}	Amount of accessible cationic groups in the dose at D_{max} ($\times 10^{-5}$ eq./g)	Diameter of DCS microparticles (μm)
0.36	26	0	42.1	16	0.68	22
		50	38.7	22.4	0.96	13
	100	0	11	7.4	1.22	Couldn't be estimated
		50	21.4	9.6	1.59	
0.48	26	0	30.4	16	0.85	18
		50	43.1	19.2	1.01	12
	100	0	14.2	6.4	1.30	Couldn't be estimated
		50	16.0	9.6	1.96	

very slightly. The dose required to achieve the Dmax increased almost 1.3–1.5 times.

Along with an increase of the dose of DCS required to achieve D_{max}, the number of accessible cationic groups in this dose increased proportionally (Table 2). That increase could be related to the screening of the charges of some DCS cationic groups by the electrolyte ions. Consequently, screened cationic groups couldn't interact with negatively charged kaolin particles and participate in the flocculation process.

On other hand, the screening of cationic charges changed the conformations of the macromolecules and the dimensions of the polymer particles. It was aimed to assess the particle diameter of tested DCS when their dispersions were prepared in both water and in NaCl containing solution. After the heating of the dispersions (A = 100%) the size of DCS colloidal particles couldn't be measured because large swollen particles of DCS were transparent and "invisible" to particle size analyzer. The data in Table 2 show that the diameter of DCS microparticles decreased 1.5–1.7 times in the NaCl solution compared to that in water and became the same for both DCS with DS = 0.36 and DS = 0.48. However, despite the same size of the microparticles the flocculation efficiency of DCS with DS = 0.48 was higher than that of DCS with DS = 0.36 (comparing D_{max} values obtained when accessibility of cationic groups was 26%). It could be concluded that the change in the size of DCS particles after adding of NaCl have a minor influence on the changing of flocculation efficiency of DCS.

3.2. Influence of anionic dye on the flocculation properties of DCS

Organic low-molecular weight ions present in wastewater could interact with the polyelectrolytes used for flocculation and/or with particles of destabilized dispersion, and, consequently, can change the flocculation efficiency of the flocculants. It was shown in our previous work [17] that anionic dyes can be adsorbed onto DCS.

For that reason C.I. Acid Blue 25 (AB25) was selected as a model compound of organic low-molecular weight ion and its influence on the destabilization of kaolin dispersion with DCS was investigated. Almost 22% of the added dye was adsorbed by kaolin. Due to the interactions between the positive charges of DCS and the negative ones of the dye anions, a part of the dye was removed during the precipitation of kaolin and DCS flocks. The addition of DCS increased the amount of removed dye from 27% to 49% depending on the amount of DCS, its DS and the initial concentration of the dye. The obtained results indicated some surface charge changes of particles of dispersion components: the kaolin particles became more negative and the amount of free charged DCS cationic groups decreased. These changes had a great influence on the flocculation efficiency of DCS which depended on DS (Table 3). When DCS with DS = 0.36 and anionic dye were present in the kaolin dispersion, the flocculation efficiency was decreased and the dose of DCS required to achieve the D_{max} was increased comparing to values of those obtained for destabilization of aqueous kaolin dispersion. In the case of DCS with DS = 0.48 the value of D_{max} depended on the concentration of dye in the kaolin dispersion. The similar values of D_{max} were obtained when 0.05 mmol/l or lower concentration of the dye was used. By further increase of the dye concentration the D_{max} increased 1.3 times. Simultaneously the dose of DCS needed to reach the D_{max} decreased.

We found [14] that kaolin particles were flocculated effectively when the amount of accessible cationic groups in the optimal dose of DCS was approximately 0.64×10^{-5} eq./g. By the increase of the number of those groups the flocculation efficiency decreased. When kaolin dispersion without dye was destabilized with DCS with DS 0.48 the concentration of accessible groups in the dose at D_{max} was 0.85×10^{-5} eq./g (Table 3). The increasing addition of anionic dye into kaolin dispersion decreased the content of accessible cationic groups in dose at D_{max} until the optimal level of 0.65×10^{-5} eq./g was reached and whereupon DCS with DS = 0.48 exhibited better flocculation efficiency. These results supposed that the changes in flocculation properties of DCS after the addition of anionic dye to kaolin dispersion were related to the screening of the accessible cationic charges on the surface of DCS. The flocculation efficiency of DCS increased if after screening the quantity of cationic charges of DCS participated in the formation of floccules with kaolin particles became optimal.

3.3. Influence of NaCl on interaction of DCS with TNS

To investigate the influence of inorganic electrolytes on the interaction of DCS with dye anions, luminescence spectroscopy was employed and TNS as a fluorescence probe was used. When TNS molecules were added to the polymer solution, chains of cationic polymers constituted a specific non-polar environment, and the fluorescence emission in the typical wavelength interval of 450–650 nm [23] was observed. The fluorescence spectra of DCS with DS = 0.36 and accessibility of 26% and 100% are shown in Fig. 2. When all cationic groups of DCS were accessible the maximum fluorescence intensity at 510 nm increased with the increase of the concentration of DCS added (Fig. 2a). Such fluorescence dependence was, also, observed for other soluble cationic polyelectrolytes [23,24]. Several maxima were observed in the fluorescence spectra (Fig. 2b) when DCS containing only 26% of accessible cationic groups was added to TNS, although the total fluorescence intensity increased with the increasing amount of DCS in the system. All cationic groups of DCS interacted with anionic dyes [17]. Similarly, TNS as an anionic compound could also interact with all cationic groups of DCS. Several fluorescence maxima in the spectra of TNS in DCS with partially accessible cationic groups might be explained by the different accessibility of cationic groups and the formation of different environments where molecules of the probe were trapped. These differences might be releated to the uneven modification of starch.

The influence of NaCl on the interactions between TNS and DCS with DS 0.36 and 0.48 and the different accessibility (26% and 100%) of cationic groups was investigated. The relative fluorescence intensity (I/I_o,

Table 3
Influence of AB25 dye concentration in kaolin dispersion on flocculation properties of DCS with different DS (A = 26%)

Concentration of AB25, (mmol/l)	DS = 0.36			DS = 0.48		
	D_{max}	Dose of DCS (mg/g) at D_{max}	Amount of accessible cationic groups in the dose ($\times10^{-5}$ eq./g)	D_{max}	Dose of DCS (mg/g) at D_{max}	Amount of accessible cationic groups in the dose ($\times10^{-5}$ eq./g)
0	42.1	16	0.68	30.4	16	0.85
0.025	29	19.2	0.82	29.4	19.2	0.98
0.05	29	19.2	0.82	33.6	16	0.82
0.1	30.5	19.2	0.82	40.5	12.8	0.65
0.3	31.5	19.2	0.82	43.3	12.8	0.65

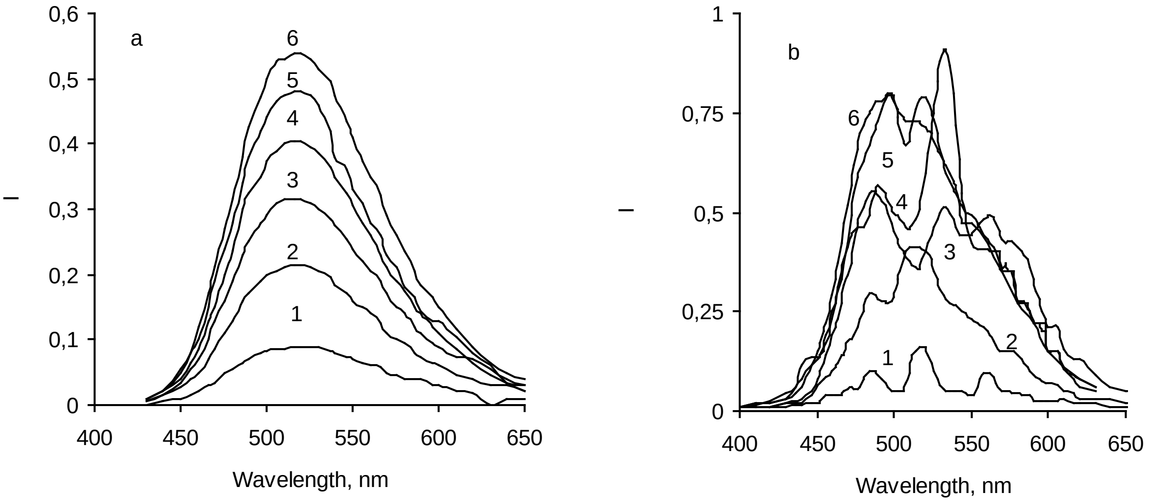

Fig. 2. Fluorescence spectra of TNS in DCS (DS = 0.36) with *A* = 100% (a) and *A* = 26% (b) when the concentration of DCS in solution was, mmol/l: 1 – 0.01; 2 – 0.02; 3 – 0.03; 4 – 0.04; 5 – 0.05; 6 – 0.06. Concentration of TNS was 0.04 mmol/l.

where I and I_o were fluorescence intensities in presence and in the absence of NaCl, respectively) at 510 nm was calculated from the spectra of the probe in DCS with all accessible cationic groups (Table 4). However, the several maxima present in the spectra of TNS in DCS with 26% accesability prevented the use of fluorescence intensity at this particular wavelength for the unambiguous evaluation of the interactions between the macromolecules and probe. Thus only a tendency, i.e. increase or decrease in the fluorescence intensity with the increase of the amount of added salt to this system was assessed.

The influence of electrolyte on the fluorescence intensity of TNS depended on both DS and accessibility of DCS. In the case of DCS with DS = 0.36 by the addition of negligible quantity (0.1–0.25 mmol/l) of NaCl the fluorescence intensity increased for the system with fully accessible cationic groups and decreased when 26% of cationic groups were accessible. Subsequent increase of NaCl concentration led to further decrease of fluorescence intensity. The inverse dependence was observed for DCS with DS 0.48: the fluorescence intensity of TNS was higher in the whole range of NaCl concentrations when accessibility of cationic groups was 26% and less when all cationic groups of DCS were accessible.

The increase or decrease in the fluorescence intensity of TNS in the presence of DCS with a different accessibility of cationic groups when NaCl was added to the system indicated satisfactory role of electrolyte in the interactions between cationic groups of starch and negatively charged compounds. In some cases, the rearrangements of DCS particles affected by NaCl could strengthen their interactions with TNS, while in other cases the effect could be negative.

It should be pointed out that the conditions of the described flocculation (see Section 3.1) and fluorescence experiments were different. In the fluorescence experiments the concentrations of DCS and NaCl were fifty times lower although the ratios of DCS to NaCl were al-

Table 4
Influence of NaCl on the change of TNS fluorescence intensity in dispersions of DCS with different DS and *A*

Concentration of NaCl, mmol/l	Change of TNS fluorescence intensity		Relative fluorescence intensity (I/I_o)	
	DCS with *A* = 26%		DCS with *A* = 100%	
	DS = 0.36	DS = 0.48	DS = 0.36	DS = 0.48
0	1	1	1	1
0.1	decrease	increase (2 times)	2.18	0.35
0.25	decrease	increase (2 times)	1.39	0.74
0.5	decrease	increase (2 times)	0.74	0.63
0.75	decrease	increase (1.5 times)	0.61	0.46
1.0	decrease	increase (1.5 times)	0.45	0.55

most the same as in the flocculation experiments. Despite the differences in the conditions of those experiments the comparison of the results presented in Tables 2 and 4 could be done. The addition of NaCl to kaolin dispersion or to the solution of TNS had the same influence on both the change of the flocculation efficiency of DCS and TNS interactions with DCS. It is important to emphasize that the addition of electrolyte could greatly improve the flocculation properties of DCS compared to those without additives, i.e. in the case of DCS with DS = 0.48 and A = 26%.

3.4. Peculiarities of kaolin dispersion destabilization with DCS

The destabilization of the dispersions using the polyelectrolytes can be achieved by employing a bridging mechanism, by charge neutralization or by formation of "charge patches" on the surface of the particles. Which of the mechanisms will predominate mostly depends on the molecular weight and charge density of the polyelectrolyte. The information about the mechanism, that was predominant in the destabilization of the aqueous kaolin dispersions with DCS microparticles might be obtained from the microphotographs of kaolin floccules and compared to those obtained with cationic polyacrylamide (Zetag 7652) which is commonly used in sludge dewatering (Fig. 3).

A soluble high molecular weight Zetag 7652 incorporated kaolin particles into the large fast-settling floccules and flocculated the dispersion by a bridging mechanism as expected (Fig. 3a). The floccules were quite different when cationic starch derivatives were added into the aqueous kaolin dispersion (Figs. 3b–f). The shape and size of the floccules depended on the kind of cationic starches. Soluble cationic starch (SCS) obtained from hydroxyethylstarch bound kaolin particles into fine floccules (Fig. 3b). Larger floccules were obtained when kaolin dispersion was flocculated with the CMS microparticles (Fig. 3c). The largest floccules were formed when the microparticles of DCS with DS = 0.36 destabilized kaolin dispersion (Fig. 3d). Other increase in the DS of DCS decreased the size of formed kaolin-cationic starch floccules (Fig. 3e). In the case of DCS with DS = 0.56 both large and small floccules were formed (Fig. 3f).

The destabilization of aqueous kaolin dispersion occurred due to an interactions between positive charged microparticles of cationic starch and small negatively charged particles of kaolin. The diameter of kaolin particles in water was 0.6 μm and they were much smaller compared to microparticles of DCS or CMS (Table 1). Therefore, large swollen microparticles of DCS were covered by small solid kaolin particles (darker areas on the surface of DCS or CMS particles in Figs. 3c–f). The positive charges on the surface of DCS microparticles, in particular when DS = 0.36, were not uniformly displayed. To the different areas of the surface the different number of kaolin particles was bound and darker or lighter patches in the microphotograph were observed (Fig. 3d). It seems likely that not all negatively charged surface of rigid kaolin particles took part in the interaction with positively charged DCS microparticle. Consequently, the patches of negative charges could be formed in some particular places on the surface of DCS microparticle, although the overall charge of a particle remained positive. For this reason, one DCS microparticle with negative patches could bind another positively charged DCS microparticle, i.e. DCS flocculated kaolin dispersion according to the mechanism of charge "patches". The larger swollen microparticles of DCS, the greater quantity of kaolin particles were bound, the larger and heavier floccules were formed and precipitated more rapidly. It could be pointed out that negatively charged kaolin particles were the binding elements in the flocculation of kaolin dispersion with DCS. A similar conclusion was done by Larsson with co-workers [3] when they investigated the flocculation of nanosized silica particles with water-dispersible cationic amylopectin with DS = 0.04. In their opinion, silica nanoparticles were the binding elements in the destabilization of silica nanoparticles with cationic amylopectin and the "patch" flocculation was occurred.

When DS of DCS was 0.36, the amount of accessible cationic groups which took part in the destabilization of kaolin dispersion was 0.68×10^{-5} eq./g, meanwhile for DCS with DS 0.56 this amount was much higher – 1.09 $\times10^{-5}$ eq./g (Table 1). For this reason the surface of the colloidal particles of DCS with DS=0.56 was covered by kaolin particles densely, no light patches were observed in the photographs (Fig. 3f) and it was more difficult for the "patch" flocculation to occur. Furthermore, the part of the microparticles of DCS with DS = 0.56 was small, subsequently, small floccules were formed which settled down slowly. The latter two facts can explain why DCS with higher DS and CMS had lower flocculation efficiency. The "patch" mechanism can, also, explain the increase in the flocculation efficiency of DCS with DS = 0.48 after the addition of sufficient amount of acid dye. The interactions between the cationic groups of starch and anionic groups of dye eliminated some of the cationic groups from participation in the flocculation. Then the balanced areas of negatively and positively charged patches were formed on the surface of colloidal DCS particles and heavier floccules were formed (comparing photographs e and g in Fig. 3).

4. Conclusions

The flocculation properties of the microparticles of cold water-dispersible cationic starches (DCS) with DS 0.36 and 0.48 and different accessibility (*A*) of cationic groups (*A* = 26% and *A* = 100%) in the destabilization of kaolin dispersions containing NaCl or anionic dye (C.I. Acid blue 25) have been investigated. DCS with DS =

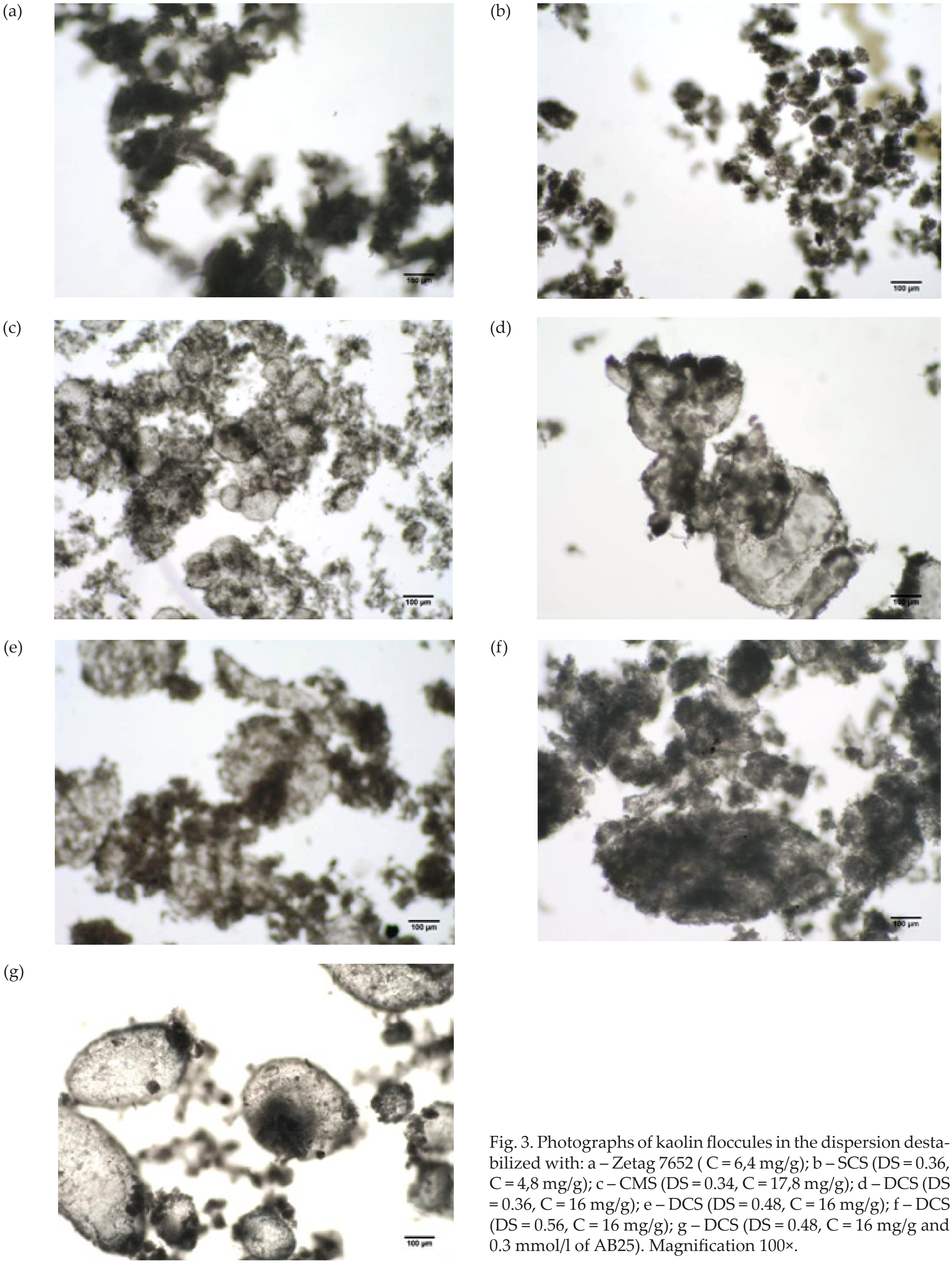

Fig. 3. Photographs of kaolin floccules in the dispersion destabilized with: a – Zetag 7652 (C = 6,4 mg/g); b – SCS (DS = 0.36, C = 4,8 mg/g); c – CMS (DS = 0.34, C = 17,8 mg/g); d – DCS (DS = 0.36, C = 16 mg/g); e – DCS (DS = 0.48, C = 16 mg/g); f – DCS (DS = 0.56, C = 16 mg/g); g – DCS (DS = 0.48, C = 16 mg/g and 0.3 mmol/l of AB25). Magnification 100×.

0.36 and A = 26% possessed high flocculation efficiency and that of DCS with DS = 0.48 and A = 26% was lower when aqueous kaolin dispersions were flocculated. The increase in the accessibility of cationic groups led to the decrease in the flocculation efficiency. The addition of NaCl or acid dye to kaolin dispersion decreased the flocculation efficiency of DCS with DS = 0.36 and partially accessible cationic groups. The flocculation efficiency increased by the addition of electrolyte or acid dye, when kaolin dispersion was destabilized with DCS with DS = 0.48 and A = 26%.

Luminescence spectroscopy was employed to investigate the influence of NaCl on the interaction of DCS with 2-(*p*-toluidino)-6-naphthalene sulfonate (TNS). The influence of electrolyte on the fluorescence intensity of TNS depended on the DS and accessibility of cationic groups of DCS and changed in the same manner as the flocculation efficiency of DCS.

It was supposed that NaCl and anionic dye present in kaolin dispersion changed both the size of DCS microparticles and the charge distribution on their surface. These changes depended on the DS and A of DCS. The best flocculation of kaolin dispersion was achieved at the particular size and surface charge density of DCS microparticles. In that case the balanced areas of negatively and positively charged patches were formed on the surface of DCS after adsorption of kaolin particles and during ensuing flocculation heavier floccules were formed. The destabilization of kaolin dispersion with DCS occurred according to the mechanism of "charge patches".

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