



## Non-stoichiometric complexes of cationic starch and 4-sulfophthalic acid and their flocculation efficiency



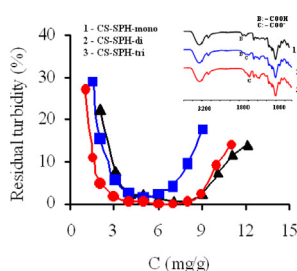
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### HIGHLIGHTS

- Non-stoichiometric complexes (NIC) were formed between cationic starches and 4-sulfophthalic acid.
- Formation of NIC was confirmed by equilibrium adsorption, FT-IR and luminescence spectroscopy experiments.
- Amphoteric properties of NIC determined the better flocculation efficiency.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Non-stoichiometric complexes with an excess of free charges (NIC) were obtained during electrostatic interaction between quaternary ammonium groups of N-(2-hydroxyl)-propyl-3-trimethyl ammonium starch chloride (CS) and multifunctional 4-sulfophthalic acid (SPH). The formation of NIC was confirmed by equilibrium adsorption, FT-IR and luminescence spectroscopy experiments. The Langmuir, Freundlich, Dubinin–Radushkevich and Temkin adsorption models have been used to describe the equilibrium adsorption isotherms. The ratio between the negative and positive charges ( $n^-/n^+$ ) calculated from the values of the Langmuir sorption capacity  $Q_L$  showed that the anionic charges were predominant in the complexes after equilibrium adsorption. NIC with an excess of positive charges were obtained during complex formation between the cationic groups of CS and the anionic groups of SPH. The NIC formed between CS and 25 mol% (according to the cationic groups of CS) of SPH trianions showed the higher flocculation efficiency in destabilization of kaolin suspension in comparison with that of CS only.

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## 1. Introduction

Natural polymers have some advantages over synthetic ones because they are renewable, biodegradable, and non-toxic. Starch is one of the most important, easily available and low-cost natural polymers. Chemically modified starches are widely used in food and non-food industries. Most of the commercially available cationic starch derivatives have a low degree of substitution ( $DS < 0.1$ ) and

are used in the paper industry as retention and dewatering aids. Several studies [1–7] have been performed to examine the flocculation properties of highly cationic starches and their interaction with organic or inorganic matter having a negative charge. Schwarz and co-workers [1–3] investigated the flocculation properties of water-soluble cationic starch derivatives with a high degree of substitution (DS) and have suggested that the flocculation of kaolin dispersion is a combination of the bridging and “charge patch” processes. Moreover, they have shown [2] that cationic starch derivatives induce flocculation of kaolin dispersion at the same minimum doses as do synthetic flocculants with a comparable charge density, but in a broader concentration range. A different flocculation behaviour

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of cationic starches dispersible in cold water was observed in our previously works [4,5]. The cationic starches dispersible in cold water, obtained under conditions preserving the granules of starch unchanged, exhibited a higher flocculation efficiency compared with the soluble ones, and the “charge patch” flocculation mechanism was predominant. Amphoteric polysaccharide flocculants have been developed recently for their multiple applications [8–11]. Amphoteric starch-graft-polyacrylamide was prepared by free radical grafting of carboxymethyl starch [8], by emulsion polymerization in the presence of starch with subsequent hydrolysis and Mannich reaction [9] or cationization with N-(3-chloro-2-hydroxypropyl)trimethylammonium chloride [10]. Cationic starch succinates were prepared by succinylation of starches pre-cationized with EPTMAC [11]. The flocculation efficiency of the obtained amphoteric starches was tested in the destabilization of municipal wastewater [8,9] or kaolin dispersion [10,11]. The obtained results indicated a high flocculation efficiency of amphoteric starches in comparison with only cationic or anionic polyelectrolytes.

The main disadvantage of flocculation with polymers, mainly soluble polycations, is the very small flocculation window, at a small increase of dosage the system being re-stabilized. A number of studies have tried to solve this problem by combining two oppositely charged polyelectrolytes which can be added one after another [12] or as preformed non-stoichiometric polyelectrolyte complexes (NPEC) [13–19]. In the case of NPEC, a substantially wider flocculation window was obtained, although the minimum flocculation dose was higher in comparison with polycations as flocculants. The NPEC dispersions with a different charge excess and hydrophobicity have been formed during electrostatic interaction between poly(diallyldimethylammonium chloride) (PDADMAC) or poly(methacryloyloxyethyltrimethylammonium chloride) as polycations and copolymers of maleic acid with propene or methylstyrene as polyanions [13,14] or between PDADMAC and poly(styrene-*p*-sodium sulfonate) and poly(acrylamide-co-sodium acrylate) [15]. In contrast to PDADMAC alone, the NPEC flocculated silica particles with a higher velocity of sedimentation and in a very broad range of NPEC concentration. Both electrostatic and hydrophobic interactions were important for an effective flocculation of silica with NPEC. The interval up to the beginning of the flocculation optimum was mainly ascertained by electrostatic interaction and depended on the charge density of NPEC, but the broadness of the flocculation window depended largely on hydrophobic interaction. Dragan et al. [16–19] investigated the influence of NPEC characteristics, such as the polycation and polyanion structure, molar ratio between charges, particles morphology and low molecular mass electrolyte content, on the flocculation of model kaolin dispersion. Synthetic polymers with a different content of the quaternary ammonium group in the backbone or/and in side chains, as polycations, and both inorganic (sulfate and persulfate) [16] and organic (poly(sodium 2-acrylamido-2-methylpropanesulfonate) [17–19] anions were used to obtain non-stoichiometric ionic complexes (NIC) or NPEC nanoparticles with an excess of cationic groups. All the formed complexes were more effective in the destabilization of model dispersions than polycations alone, especially as regards the broadness of the flocculant window. Petzold et al. [20] investigated the dye flocculation performance of polyampholytes containing hydrophobically modified cationic, hydrophilic non-ionic and anionic monomer units, always with an excess of positive charges, and compared it with that of homopolymers and with those obtained using NPEC dispersion with an adjustable surface charge density. Both polyampholytes and NPEC successfully removed the disperse dye. The efficiency of dye separation was mainly influenced by the charge of polymers or NPEC, demonstrating that charge neutralization was one of the flocculation mechanisms.

In the last years, water-dispersible NPEC of anionic polyelectrolytes combined with chitosan [18,19] or cationic starch [21–23] have aroused a considerable interest. The results presented in studies clearly shown that nanoparticles of NPEC were more effective in flocculation than polyelectrolytes alone, especially at a low molar ratio between charges. In the case of NPEC obtained by pre-mixing of cationic starch and anionic sodium polyacrylate, the flocculation efficiency strongly depended on the DS of cationic starch [23]. Several mechanisms are involved in the enhanced flocculation induced by polyelectrolyte complexes obtained from modified natural polymers. These mechanisms depend on the ratio between charges and the total amount of polyelectrolytes added. However, interparticles bridging by NPEC and charge neutralization induced by the deposition of the complexes were found to be the main reason for the enhanced flocculation [21].

Cationic starch could form complexes of different stoichiometry during its electrostatic interaction with anionic low molecular weight compounds, such as anionic surfactants [24,25], sodium tripolyphosphate [26], triiodide [27], potassium dichromate [28] as well as anionic dyes [29]. The nature of a complex depended on the state of cationic starch in water (soluble, colloidal dispersion or swollen microparticles). The water-soluble cationic starches acted as a typical soluble polyelectrolyte and formed an insoluble complex with anionic dye only at the optimal concentration, whereas cold-water-dispersible cationic starches or the microparticles of cationic cross-linked starches could adsorb all the dye present in the solution if their amount was sufficient [29].

It was shown [5] that the addition of monosulfo dye to kaolin suspension changed the flocculation efficiency of cold-water-dispersible cationic starches (CS). CS adsorbed the anionic dye and destabilized the kaolin suspension simultaneously. The effect of dye on flocculation efficiency depended on the degree of substitution of CS and the accessibility of CS cationic groups, and was related to the screening of the accessible cationic charges on the surface of CS. However, it is unclear how the complexation with anionic compound possessing both sulfo and carboxylic groups could change the flocculation efficiency of CS. Sulfo groups could always take part in the electrostatic interaction with the cationic groups of polymer, whereas the carboxylic groups could interact when they are in the ionized form mainly. The purpose of the present investigation was to form the non-stoichiometric complexes with an excess of cationic or anionic groups during interaction between quaternary ammonium groups of cationic starches and the acidic group of 4-sulfophthalic acid (SPH). The influence of the amount of introduced SPH and the ionization degree of carboxylic groups of SPH on the structure and the flocculation efficiency of formed complexes also was the aim of investigation.

## 2. Materials and methods

### 2.1. Materials

The Antanavas Starch plant (Lithuania) supplied the native potato starch (intrinsic viscosity  $[\eta] = 0.391/\text{g}$ ). 2,3-Epoxypropyltrimethylammonium chloride (70%) (EPTMAC), epichlorohydrin (99%), 4-sulfophthalic acid (50%) (SPH), 2-(*p*-toluidino)-6-naphthalene sulphonate, and kaolin with particle size of  $\sim 0.9 \mu\text{m}$  were supplied by Sigma–Aldrich. All chemicals were of analytical grade.

### 2.2. Synthesis of cationic starch (CS) and cationic cross-linked starch (CCS)

The starch was cross-linked with 0.1 mol/AGU (anhydroglucoside unit) of epichlorohydrin in the presence of NaOH, washed with cold water and dried.

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