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Factors influencing production of cationic starches

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Abstract

The main factors – the amount of catalyst NaOH, the temperature and composition of reaction mixture – influencing the effectiveness of starch cationization with glycidyltrimethylammonium chloride (GTAC) were investigated. It was found that cationic or cross-linked cationic starches with preserved microgranules, a degree of substitution from 0.2 to 0.85 and reaction efficiency from 82% to 93% could be obtained during etherification of starch or cross-linked starch with a mixture containing GTAC, "free" water and 0.04–0.08 mol/AGU sodium hydroxide in heterogeneous condition. The activation energy of the GTAC main reaction is lower than that of the side reactions, thus starch cationization at a lower temperature proceeds with higher reaction efficiency.

The amount of NaOH in the cationization mixture has a great influence on the rate of the main and side reactions of GTAC. Only the main reaction – cationization of starch – proceeds when all the NaOH present in the reaction mixture is adsorbed from the liquid phase by the starch. The duration of this "first reaction stage" decreases with increasing reaction temperature and the amount of NaOH in the reaction mixture. NaOH present in the liquid phase of the reaction mixture catalyzes the side reactions of GTAC and changes their character.

Keywords: Cationic starch; Chemical modification; GTAC; Reaction efficiency

1. Introduction

In recent years, cationic starches (CS) with a high degree of substitution (DS) are of increasing interest. CS with DS from 0.2 to 0.9 is the most promising candidate to replace synthetic flocculants or sorbents in various industrial applications (Bendoraitiene, Klimaviciute, Sableviciene, & Zemaitaitis, 2005; Crini, 2006; Haack, Heinze, Kulicke, & Oelmeyer, 2002; Klimaviciute, Riauka, & Zemaitaitis, 2007). Due to the use of renewable resources as a main raw material and a higher biodegradability of the products, production of CS becomes the subject of sustainable or "green" chemistry. In economic terms, the microgranular CS as flocculants and sorbents is still competitive with the synthetic products despite the higher doses required. The cost of the native starch is below the cost of synthetic reagents, and the cost of the cationization agent mainly influences the price of CS. Therefore, in the manufacture of modified starch, the ultimate requirement is high efficiency of the cationization reaction.

CS are commonly prepared by the reaction of starch with glycidyltrimethylammonium chloride (GTAC) or 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC) in homogeneous or heterogeneous (water suspension, suspension in organic solvents or mixture of water and organic solvents) conditions or by cationization of starch in the "dry" state (Haack, Heinze, & Rensingm, 2004; Haack et al., 2002). If CHPTAC is used, higher amounts of alkaline agents are required, since part of it is consumed for the formation of epoxy groups. However, starch undergoes pasting if high amounts of alkali are present in the reaction mixture and the structure of starch grains is destroyed. Therefore, CHPTAC might be used only for the synthesis of CS with a low content of quaternary ammonium groups (DS < 0.1).

Heinze and co-workers (Haack et al., 2004) obtained starch derivatives containing high amounts of quaternary ammonium groups (DS up to 1.1) by etherification of

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potato, maize and wheat starch both with CHPTAC and GTAC in heterogeneous and homogeneous conditions. When starch was modified with CHPTAC in ethanol/water suspension the DS of the obtained CS depended on the molar ratio of the reagents and the type of starch and varied between 0.03 and 0.88. However, reaction efficiency (RE) was below 47% in all cases. The higher RE was achieved when starch was modified with GTAC. The DS of CS obtained in heterogeneous conditions (water suspension) varied between 0.38 and 1.05 with the RE from 40% to 76%. When starch was dissolved in dimethylsulphoxide modification with GTAC proceeded in homogeneous conditions, CS with DS from 0.37 to 0.57 was obtained with a similar RE as in the case of the heterogeneous conditions. CS with DS $\sim$ 1.5 was obtained only by two-stage modification, when cationic starch was additionally alkylated with a large amount of GTAC (10 mol GTAC/AGU). An increase in the amount of NaOH as a catalyst of cationization reaction did not enhance the yield, because the side hydrolysis reactions of epoxy groups were intensified when the amount of NaOH exceeded 0.4 mol/AGU.

In comparison with the other methods, “dry” modification of starch has several advantages (Bischoff, Hellwig, & Rubo, 1992). The obtained product does not require washing and filtering, thus starch loss and water pollution are avoided. With special catalysts (Powdercat® Process) the reaction proceeds at room temperature and reduces the energy input. This method allows production of CS with DS up to 0.5 and a satisfactory yield.

Our earlier investigations demonstrated (Bendoraitiene, Kavaliauskaite, Klimaviciute, & Zemaitaitis, 2006) that the reaction of GTAC with starch might proceed in the absence of the external catalyst if a particular quantity of “free” water is present in the system. The reaction is accelerated by alkaline agents, such as NaOH, KOH or other alkalis which act as catalysts for the reaction and deprotonate the hydroxyl groups of starch.

At the same time, alkalis accelerated (Bischoff et al., 1992; Buchberger, Pfeifer, & Schoftner, 2002; Goclik, Stach, & Mischnick, 2004) the side reactions of cationization agents subject to the conditions of the reaction. In an alkaline medium, hydrolysis of epoxy groups occurred and *N*-(2,3-dihydroxy)propyl-*N*,*N*,*N*-trimethylammonium chloride was produced. Water-soluble oligomers of GTAC are also found in the reaction mixture. *N*-(3-Hydroxy-1-propen)-*N*,*N*,*N*-trimethylammonium chloride was produced when starch was modified with GTAC in an organic solvent containing small amounts of alkali even at room temperature. Hellwig et al. (Bischoff et al., 1992) proposed that hydrolysis of GTAC is predominant in water, whereas *N*-(3-hydroxy-1-propen)-*N*,*N*,*N*-trimethylammonium chloride was found in the reaction mixture if starch was modified at a higher than room temperature under alkaline conditions.

The literature has no data about the best methods of obtaining CS with a high DS and are action efficiency above 60%. Furthermore, it was shown that CS with a preserved granular structure of native starch was a better adsorbent (Klimaviciute et al., 2007) and flocculant (Bendoraitiene et al., 2005). For these reasons, the production of CS with a high charge density requires choosing the conditions of cationization that preserve the starch microparticles unchanged, where only the main reaction of polysaccharide with GTAC occurred. The obtained products should contain only minor amounts of by-products and can be used without further purification. Discovery of conditions at which at least 80% of alkylation agent is used in the main reaction would enable to reduce the cost of CS and to compete with synthetic polymers.

The aim of the present work was to estimate the main factors, such as the amount of alkaline catalyst, the temperature and composition of the reaction mixture, that influence the effectiveness of starch cationization with GTAC under conditions preserving the microgranules of highly cationic starches unchanged.

2. Materials and methods

2.1. Materials

The Antanavas Starch Plant (Lithuania) supplied native potato starch (intrinsic viscosity $[\eta] = 390$ ml/g). The aqueous solution of the cationic reagent, 2,3-epoxypropyltrimethylammonium chloride (glycidyltrimethylammonium chloride, GTAC or Quab 151®), was purchased from Degussa (Dusseldorf, Germany). The original solution contained 70% of active, 5% of inactive monomers and 22% of water (molar ratio of GTAC:H_2O was 1:2.645). Epichlorohydrin (99%) was purchased from Sigma–Aldrich. All the other chemicals were of analytical grade.

N-(2,3-dihydroxy)propyl-*N*,*N*,*N*-trimethylammonium chloride was obtained under hydrolysis of GTAC in water at a temperature of 60 °C.

2.2. Preparation of cross-linked starch

The native potato starch was suspended in water in order to obtain the 50% (w/w) slurry. The macromolecules of starch were cross-linked by epichlorohydrin (EPI) in the presence of NaOH added until the pH value of the reaction mixture reached 11. The cross-linking at 45 °C was completed after 24 h. Cross-linked starch, water-washed and dried at 50 °C, was used for cationization.

As a mole of starch, the mole of anhydroglucoside unit (AGU) was used and the amount of EPI ranged from 0.002 to 0.3 mol/AGU. Cross-linked starches were denoted as CLS_x, where x shows the amount of EPI (mol/AGU) used in the cross-linking reaction.

2.3. Preparation of cationic starches

Cationic starches were prepared by modifying native potato or cross-linked starch with a reaction mixture containing Quab 151® under heterogeneous conditions at 45, 60 and 75 °C. Cationic potato starches are denoted as CS and cationic cross-linked starch as $CCLS_x$.

The molar ratio of the reagents was AGU:epoxide:NaOH:H_2O = 1:(0.3–2):(0–0.175):(0–11). The reaction mixture was prepared as follows: a concentrated solution of GTAC, an aqueous solution of NaOH (5%) and H_2O were thoroughly mixed. After preparing the reaction mixture, starch was added, homogenized and left for a certain time in constant temperature conditions. For the evaluation of the reaction efficiency, the reactions were carried out until no 2,3-epoxypropyltrimethylammonium chloride was left (after 24–720 h). After the reaction the cationic starches were washed with isopropanol 5 times and dried at 50 °C.

The nitrogen content in cationic starch was estimated according to the Kjeldahl method after purification by Soxhlet extraction with methanol for 16 h. The degree of substitution (DS) was calculated from nitrogen content:

$$\mathrm{DS} = \frac{162 \times N}{1400 - 151.5 \times N}, \tag{2.1}$$

where N is nitrogen amount estimated according to Kjeldahl, %, 162 is the molecular weight of AGU, and 151.5 is the molecular weight of GTAC.

The reaction efficiency (RE) indicates the percentage of added cationic reagent that has potentially reacted with the starch. RE (%) was calculated from the equation:

$$\mathrm{RE} = \frac{\mathrm{DS}}{\text{Added GTAC mol/AGU}} \times 100\%. \tag{2.2}$$

2.4. Evaluation of amount of epoxy groups

To determine the epoxy groups, an exactly weighed 0.25–0.5 g sample of the cationization mixture was added to a sodium sulphite solution and mixed for 30 min with a magnetic stirrer. The NaOH formed in the reaction of epoxy groups with sulphite was potentiometrically titrated with 0.1 M HCl to pH 9.6. The quantity of NaOH present in the reaction mixture was determined in a similar way, the only difference being that the specimen was added to distilled water instead of a sodium sulphite solution. The amount of epoxy groups E_p (in %) was calculated according to the formula:

$$E_\mathrm{p} = \frac{(V - V_1) \times c \times 43}{m \times 10}, \%, \tag{2.3}$$

where V is the volume of 0.1 M HCl used for determination of epoxy groups, ml; V_1 is the volume of 0.1 HCl used for the determination of NaOH, ml; c is the HCl concentration (0.1 M); m is the mass of the specimen, g.

2.5. Experimental design and statistical analysis

A central composite rototable design was applied to evaluate the influence of $CLS_{0.05}$ cationization conditions on the reaction efficiency. A MODDE 7 programme (demo version) (www.umetrics.com) was fitted to the obtained data.

A five-level, three-factor fractional design was used. Twenty experiments were run consisting of 8 factorial points, 6 axial points and 6 central points. The three independent factors having the greatest influence on starch cationization were NaOH concentration ($Z_{[\mathrm{NaOH}]}$), reaction temperature ($Z_{[\mathrm{t}]}$) and reaction duration ($Z_{[\mathrm{D}]}$). The values of these variables were calculated at five different coded levels: –1.68 (the lowest level), –1,0 (middle level), 1 and 1.68 (the highest level). The highest and the lowest levels of each independent factor were chosen from the results of a preliminary experiment. The correlation between the coded levels and the actual values of the factors are presented in Table 1.

2.6. Analysis of reaction mixture

The etherification mixture containing (in mol) GTAC:NaOH:H_2O 1:0:5.5 or 1:0.04:5.5 was kept at 75 °C. After a certain time the content of compounds according to their molecular mass was determined in the mixture. The etherification mixture was examined with the ZQ2000 mass detector (Waters, Milford, MA). Ionization was positive. The voltage of ion source was 20 V, temperature 120 °C.

2.7. Evaluation of NaOH amount adsorbed from reaction mixture by native starch or $CCLS_x$

Reaction mixtures having a constant molar ratio of AGU:epoxide:H_2O = 1:2:11 and a different molar ratio of NaOH (from 0 to 0.08 mol/AGU) were prepared. The initial amount of NaOH ($NaOH_{initial}$) in the reaction mixture without starch was determined by titration with 0.1 M HCl (phenolphthalein was used as a indicator). Native starch or $CCLS_x$ with DS = 0.3 was added to the mixture and thoroughly mixed for 5 min. After centrifugation (10 min, 2000 rpm), the residual amount of NaOH ($NaOH_{residual}$)

Table 1
Correlation between coded levels and actual values of factors used in three-factor fractional design

Variable	Coded level of variable				
	–1.68	–1	0	1	1.68
NaOH concentration ($Z_{[\mathrm{NaOH}]}$) (mol/AGU)	0.016	0.0	0.05	0.07	0.083
Reaction temperature ($Z_{[\mathrm{t}]}$) (°C)	34.7	45	60	75	85.2
Reaction duration ($Z_{[\mathrm{D}]}$) (h)	0.07	0.75	1.75	2.75	3.43

was determined in the same manner. The adsorbed amount of NaOH ($NaOH_{adsorbed}$) was calculated as a difference between $NaOH_{initial}$ and $NaOH_{residual}$.

2.8. Particle size measurement

The size distribution of native or modified starch particles by volume was measured with a COULTER LS200 particle size analyzer equipped with the Coulter Fluid Module (Beckman Coulter, USA) and expressed as a geometric mean value. To evaluate the influence of temperature on particle size, the suspension of cross-linked starch in water was preheated for 10 min at 75 or 100 °C in a water bath, cooled down and then the particle size was measured.

2.9. Optical microscopy

Optical observations were carried out using an OLYMPUS CX31 optical microscope (Philippines) under a 400× magnification. Photographs were obtained with an OLYMPUS camera. To improve the image, a small amount of Toluidine Blue solution or 0.05 M iodine was added to the suspension of modified starch.

3. Results

After mixing starch, GTAC and water, the starch etherification reaction (main) and side reactions of GTAC begin and proceed. External catalysts, especially NaOH, accelerate these reactions. The influence of parameters such as the NaOH:AGU molar ratio and temperature on the DS of cationic starch, side reactions of GTAC and reaction efficiency were studied.

3.1. Influence of sodium hydroxide concentration

Native potato starch was modified by reaction mixtures with a constant AGU:epoxide:$H_2O = 1:2:11$ molar ratio and the NaOH molar ratio from 0.02 to 0.175 mol/AGU at a constant temperature 45 °C. The kinetic curves of GTAC consumption in the main reaction are depicted in Fig. 1a and in the side reaction in Fig. 1b.

Data in Fig. 1 show that both the modifications of potato starch and side reactions of GTAC proceeded more rapidly with increasing the content of NaOH in the reaction mixture. The duration until all GTAC was consumed shortened from 500 to 9 h when the content of NaOH in the reaction mixture increased from 0.02 to 0.175 mol/AGU. A comparison of GTAC side reactions kinetic curves (Fig. 1b, curves 1–3) shows that some of them are of S-form. When the content of NaOH in the reaction mixture ranged from 0.02 to 0.08 mol/AGU, no side reactions of GTAC proceeded at the initial stages, and within a definite period all GTAC was consumed in the main reaction with starch hydroxyl groups. In the second stage the main reaction continued, but an intensive conversion of GTAC to the side products began. In the third stage when over

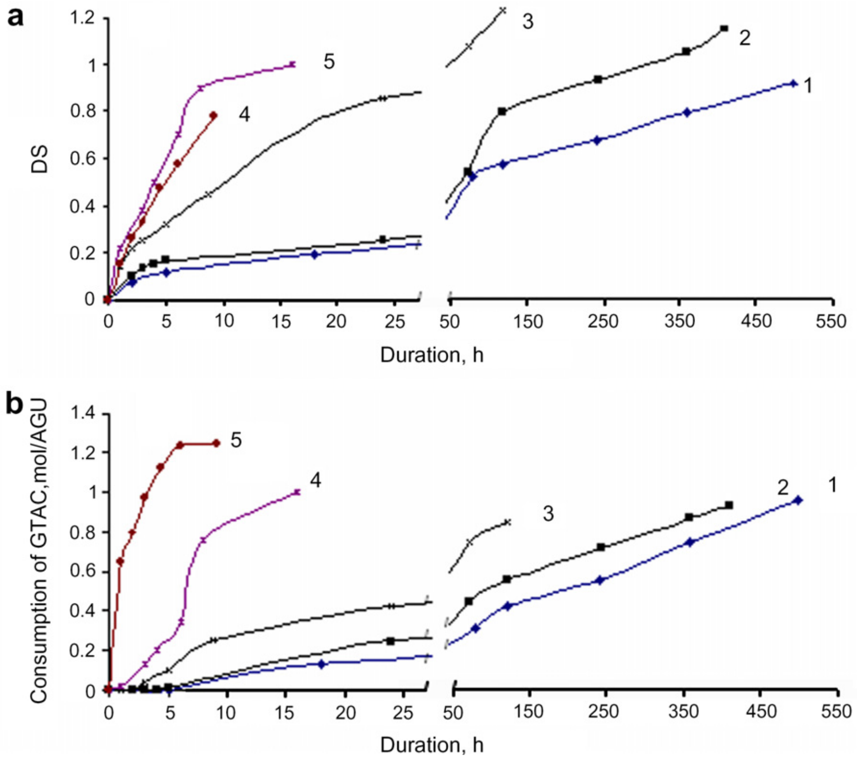


Fig. 1. Consumption of GTAC in the main (DS) (a) and side (b) reactions versus reaction duration when the content of NaOH in reaction mixture was mol/AGU: 1 – 0.02; 2 – 0.04; 3 – 0.08; 4 – 0.12; 5 – 0.175. Native potato starch was modified with (mol) AGU:GTAC:$H_2O = 1:2:11$ reaction mixture. Temperature 45 °C.

Table 2
Dependence of GTAC consumption in the main and side reactions in the first stage and at the end of starch[a] cationization on NaOH content in reaction mixture at 45 °C

Amount of NaOH (mol/AGU)	Duration of first stage (h)	Consumption of GTAC in the main reaction (%) in the first stage/at end	Consumption of GTAC in side reactions (%) in the first stage/at end
0.02	6	6.5/47	0/53
0.04	5	8.2/55	0/45
0.08	2	12.5/59	0/41
0.12	1	10.8/50	0/50

[a] Native potato starch was modified by (mol) AGU:GTAC:H_2O = 1:2:11 reaction mixture.

60% of GTAC was consumed, both the main and side reactions proceeded slowly.

The duration of the first stage of reaction (when GTAC was consumed in the main reaction only) decreased with increasing the amount of NaOH in the reaction mixture. For example, when the content of NaOH was 0.02 and 0.08 mol/AGU, the side reactions of GTAC started after 6 or 2 h (Fig. 1b, curves 1 and 3) and reaction efficiency (RE) was 47% and 59% (Table 2), respectively. If the content of NaOH was 0.175 mol/AGU, both the main and side reactions of GTAC proceeded since the first few minutes. In this case RE was 39% only, and 61% of GTAC was utilized inefficiently (Fig. 1).

The reaction of starch cationization with GTAC is complicated and its mechanism could include many steps. In the kinetic stage the rate of the main and side reactions of GTAC may be satisfactorily described as a pseudo-first-order reaction. The rate constants of the main (k_m) and side (k_s) reactions of GTAC were calculated by fitting the equation to the data in Fig. 1 and presented in Table 3 along with the correlation coefficient.

Data presented in Table 3 indicate that the absence of NaOH in the reaction mixture (autocatalytic starch etherification (Bendoraitiene et al., 2006)) lead to a fourfold increase in the rate of the side reactions compared to the main reaction of GTAC. However, at the end of autocatalytic reactions RE was 45% only and slightly differed from RE when the reaction was catalyzed with NaOH. The results listed in Table 3 unambiguously demonstrated the crucial influence of NaOH on the reactions proceeding during starch cationization. An increase in the amount of catalyst from 0.02 to 0.12 mol/AGU increased the rate constant of the main reaction (k_m) 25 times. An increase of the side reactions rate constants was observed when the content of NaOH exceeded 0.08 mol/AGU. Up to this level of NaOH, the main reaction proceeded more rapidly than the side reactions. If NaOH content increased to 0.175 mol/AGU due to rapid side reactions, the rate of the main reaction decreased and RE reached 39% only. It can be concluded that GTAC was used most effectively (RE = 59%) when NaOH content in the reaction mixture was 0.08 mol/AGU.

3.2. Influence of reaction temperature

An effective way to accelerate epoxide reactions with polysaccharides is to increase the temperature of the etherification reaction (Karim, Norziah, Siau, & Wan Rosli, 2004; Zemaitaitis, 1992). However, investigation of this factor is complicated by starch gelatinization. The gelatinization temperature depends on the nature of starch and ranges within 58–65 °C (Atwell & Thomas, 1999). During gelatinization the state of starch changes – granules of starch are converted into a colloidal solution of amylase and amylopectin in water. Etherification of starch gels differs from etherification of starch granules because in the case of gels the reaction is controlled by diffusion (mass transport).

Forming cross-links between starch macromolecules with epichlorohydrin can prevent decomposition of starch granules during gelatinization. For this reason, cross-linked potato starch (CLS) was chosen as a model to evaluate the influence of temperature on starch reaction with GTAC. As is seen in Table 4, the size of $CLS_{0.1}$ granules in aqueous suspension differed from that of native starch very little. After heating $CLS_{0.1}$ for 5 min at a temperature of 75 or 100 °C, its granules greatly swelled and yet retained their morphology (Fig. 2).

Table 3
Dependence of the GTAC main (k_m) and side (k_s) reaction rate constants on NaOH content in reaction mixture at 45 °C

Reaction mixture (mol) AGU:GTAC:NaOH:H_2O = 1:2:X:11, with X equal to	Main reaction		Side reaction		RE (%)
	$k_m \times 10^5$ (s^{-1})	R^2	$k_s \times 10^5$ (s^{-1})	R^2	
0	0.0167	0.987	0.067	0.992	45[a]
0.02	0.0389	0.993	0.031	0.994	47
0.04	0.0583	0.997	0.050	0.993	55
0.08	0.3250	0.999	0.194	0.994	59
0.12	0.9722	0.986	1.514	0.990	50
0.175	0.8917	0.996	3.778	0.993	39

[a] 10% of GTAC remained in reaction mixture.

Table 4
Size of particles of native starch and $CLS_{0.1}$ in water at 20 °C

Starch	Particle diameter according to the volume (μm)
Native potato	32.9
Native potato after treatment at 100 °C	Gel
$CLS_{0.1}$	30.0
$CLS_{0.1}$ after treatment at 75 °C	52.5
$CLS_{0.1}$ after treatment at 100 °C	53.6

When native and $CLS_{0.05}$ were modified under the same conditions (with the same reaction mixture at 45 °C), an identical dependence of DS and consumption of GTAC in side reactions on reaction duration was obtained (Fig. 3).

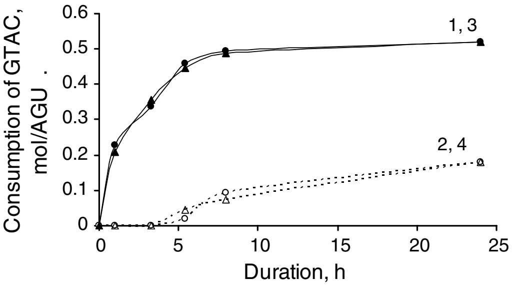


Fig. 3. Dependence of DS (—) and consumption of GTAC in side reactions (---) on reaction duration when modified: 1 and 2 – native starch; 3 and 4 – $CLS_{0.05}$. Composition of reaction mixture (in mol) AGU:GTAC:NaOH:H_2O = 1:0.7:0.08:10. Temperature 45 °C.

In order to study the influence of temperature on the main and side reactions of GTAC, $CLS_{0.1}$ was modified with GTAC at 45, 60 and 75 °C, and the results obtained are shown in Fig. 4. NaOH content in the reaction mixture was optimal and equal to 0.08 mol/AGU. When such level of NaOH was used in modifying native potato starch at 45 °C, the first stage of reaction (when GTAC was used in the main reaction only) lasted 2 h (Table 2). As is seen from Fig. 4, the same results were obtained when $CLS_{0.1}$ was modified at 45 °C. With an increase in reaction temperature, both main and side reactions proceeded faster and the duration of the first stage became shorter.

From the kinetic curves shown in Fig. 4, the pseudo-first-order reaction rate constants of GTAC consumption in the main reaction with $CLS_{0.1}$ (k_m) and side (k_s) reactions were calculated (Table 5). The plot of k_m and k_s as a function of the inverse of temperature shows that the rate constants follow the Arrhenius dependence. The activation energy E_a for both the main and side reactions were also calculated (Table 5).

One can see from Table 5, the activation energy of GTAC side reactions was higher than that of the main reaction: E_a of the side reactions was 84.95 kJ/mol, and E_a of the main reactions 69.64 kJ/mol. The obtained values of E_a clearly indicate starch cationization must proceed at a lower temperature because the influence of temperature on the rate of the main reaction of GTAC is less than on the side reactions. When the reaction temperature was 45 °C, the rate constant of the main reaction was 1.8 times higher than that of the side reaction and at temperature of 75 °C only 1.2 times higher.

3.3. Investigation of GTAC side reactions

The products of GTAC side reactions were determined by mass spectroscopy of the reaction mixture after retention at 75 °C. During etherification not only *N*-(2-hydroxypropyl)-3-*N*,*N*,*N*-trimethylammonium starch chloride but also other compounds containing quaternary ammonium groups can be formed. Their amount depended on the duration of reaction and the composition of reaction mixture. Data presented in Fig. 5a show that if NaOH was absent in the reaction mixture (autocatalytic reactions of GTAC), full conversion of GTAC into side products occurred after 120 h. The predominant compounds of side reactions are *N*-(2,3-dihydroxy)propyl-*N*,*N*,*N*-trimethylammonium chloride (62%) and its adduct with GTAC – 2,6-dihydroxy-4-oxa-1,7-di(trimethylammonium)heptane dichloride (dimer of GTAC) (19%). When NaOH was present in the reaction mixture, the side reaction of GTAC proceeded more rapidly and the full conversion of GTAC into side products took 10 h (Fig. 5b). Predominant compounds of side reactions were also *N*-(2,3-dihydroxy)propyl-*N*,*N*,*N*-trimethylammonium chloride and dimer of GTAC, but in different proportions: 35.5% and 42.3%, respectively. Except these compounds, 6% of 2,9-dihydroxy-4,7-oxa-1,10-di(trimethylammonium)-5-(trimethylammonium)methyldecane trichloride (trimer of GTAC) and 3% of *N*-(3-

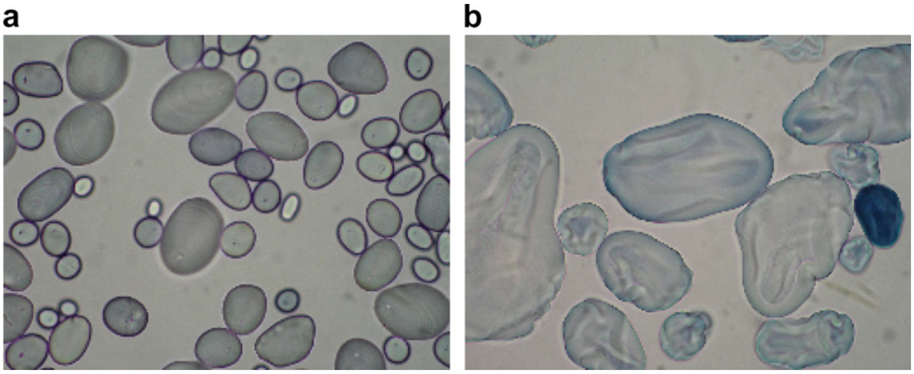


Fig. 2. 400× magnified photographs of $CLS_{0.1}$ granules in water after dispersing at 20 °C (a) and after heating of the dispersion at 100 °C (b).

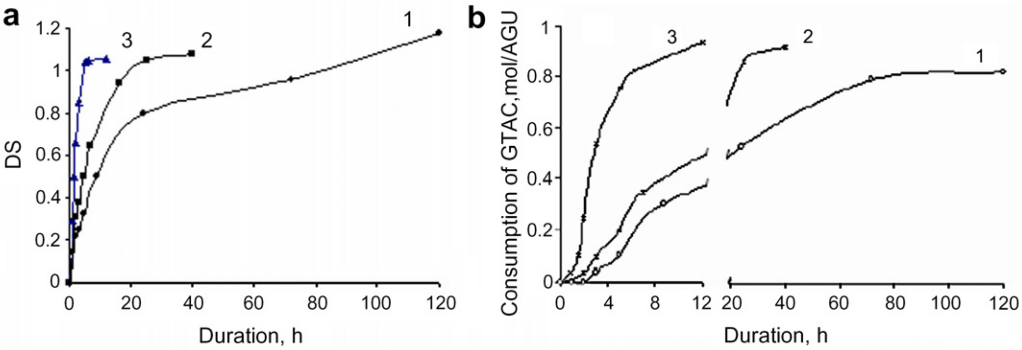


Fig. 4. GTAC consumption in the main (DS) (a) and side (b) reactions versus reaction duration when the reaction temperature was 1 – 45 °C; 2 – 60 °C; 3 – 75 °C. $CLS_{0.1}$ was modified with reaction mixture (in mol) AGU:GTAC:NaOH:H_2O = 1:2:0.08:11.

Table 5
Dependence of GTAC main and side reactions rate on reaction temperature when $CLS_{0.1}$ was modified

Reaction temperature (°C)	Rate constant, $s^{-1} \times 10^{-5}$	Correlation coefficient (R^2)	Activation energy E_a (kJ/mol)
The main reaction			
45	0.353	0.995	69.64 ($R^2 = 0.99$)
60	0.919	0.992	
75	3.161	0.991	
The side reaction			
45	0.197	0.992	84.95 ($R^2 = 0.98$)
60	0.575	0.991	
75	2.633	0.994	

Composition of reaction mixture was AGU:GTAC:NaOH:H_2O = 1:2:0.08:11.

hydroxy-1-propen)-*N*,*N*,*N*-trimethylammonium chloride were formed in the reaction mixture.

The obtained data showed that during starch cationization the side reaction of GTAC started when a certain critical amount of quaternary ammonium salts containing hydroxy groups more active than water was formed in the reaction mixture. This assumption was confirmed when starch was cationized with a reaction mixture containing an additional amount of *N*-(2,3-dihydroxy)propyl-*N*,*N*,*N*-trimethylammonium chloride. As one can see from Fig. 6, differently from starch cationization by a common reaction mixture, when an additional amount of *N*-(2,3-dihidroxy)propyl-*N*,*N*,*N*-trimethylammonium chloride was present in the reaction mixture the main and side reactions of GTAC began together and reaction efficiency decreased from 83% to 75%.

3.4. Optimal conditions of starch cationization

The data presented above indicate that N-(2-hydroxypropyl)-3-*N*,*N*,*N*-trimethylammonium starch chloride with DS more than 1.18 was not obtained even though the reaction mixture of starch cationization contained 2 mol/AGU of GTAC. When CCLS with DS = 0.28 was cationized repeatedly with a reaction mixture containing 2 mol/AGU of GTAC, the DS of the obtained CCLS was only 1.05. These results were similar to those described in Haack et al. (2004). It seems likely that the interaction with GTAC is stopped when the density of the positively charges in the modified cationic starches reaches some critical value.

Three-factor fractional design (TFF) was applied to explain the role of the factors influencing RE when starch

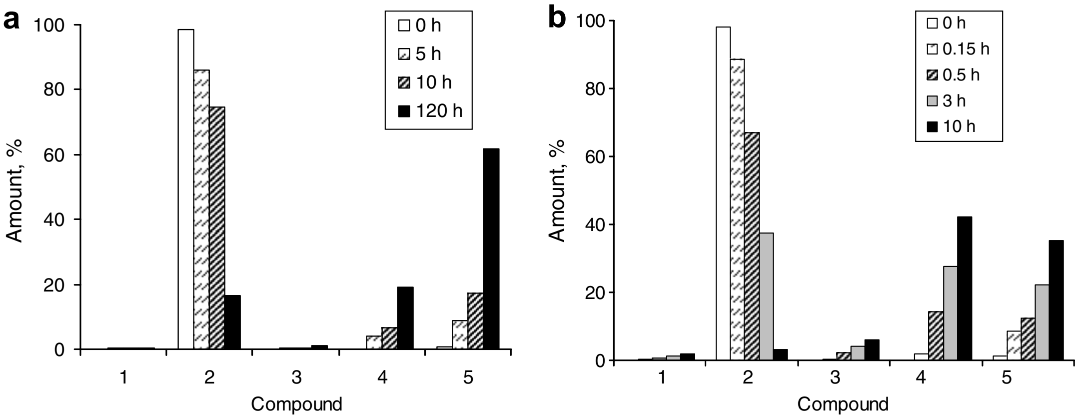


Fig. 5. Dependence of the amount of formed compounds on duration of keeping at a temperature of 75 °C the reaction mixture GTAC:NaOH:H_2O (mol): (a) – 1:0:5.5; (b) – 1:0.04:5.5. Compounds formed: 1 – *N*-(3-hydroxy-1-propen)-*N*,*N*,*N*-trimethylammonium chloride; 2 – GTAC; 3 – dimer of GTAC; 4 – trimer of GTAC; 5 – *N*-(2,3-dihydroxy)propyl-*N*,*N*,*N*-trimethylammonium chloride (glycol).

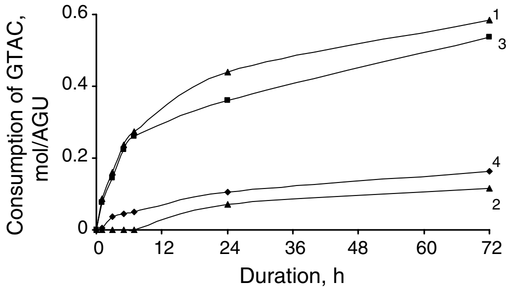


Fig. 6. GTAC consumption in the main (1 and 3) and side (2 and 4) reactions versus reaction duration, when starch was modified with reaction mixture: 1 and 2 – commonly used (AGU:GTAC:NaOH:H_2O = 1:0.7:0.04:3, in mol); 3 and 4 – containing additionally 0.35 mol/AGU *N*-(2,3-dihydroxy)propyl-*N*,*N*,*N*-trimethylammonium chloride. Temperature 45 °C.

was cationized with a reaction mixture having a fixed AGU:GTAC proportion (1:0.6). Cross-linked starch ($CLS_{0.05}$) was modified because the temperature of modification was higher than of the gelatinization of native potato starch at chosen TFF conditions. The content of catalyst in the reaction mixture ($Z_{[NaOH]}$), the temperature ($Z_{[t]}$) and duration ($Z_{[D]}$) of the reaction were chosen as the main factors influencing the effectiveness of starch cationization. The coded levels and actual values of factors are presented in Table 1 (part 2.1).

After mathematical treatment of the results, the regression equations of the GTAC consumption in the main and side reactions were obtained:

$$Y_{DS} = 0.21883 + 0.0666 \cdot Z_{[NaOH]} + 0.10294 \cdot Z_{[t]} + 0.08222 \cdot Z_{[D]} + 0.02338 \cdot Z_{[t],[D]} + 0.0271 \cdot Z^2_{[t]} - 0.01644 \cdot Z^2_{[D]} \quad (3.1)$$

$$Y_{Side\ r.} = 0.00432 + 0.00831 \cdot Z_{[NaOH]} + 0.02496 \cdot Z_{[t]} + 0.01914 \cdot Z_{[D]} + 0.00513 \cdot Z_{[NaOH],[D]} + 0.00113 \cdot Z_{[t],[D]} + 0.00322 \cdot Z^2_{[NaOH]} + 0.01348 \cdot Z^2_{[t]} + 0.01127 \cdot Z^2_{[D]} \quad (3.2)$$

Eq. (3.1) implies that to obtain modified starches with a maximum amount of cationic groups the NaOH content in the reaction mixture and the temperature of the reaction must be increased. On the other hand, as one can see from Eq. (3.2), the increase in the amount of catalyst and temperature increases the side reactions of GTAC. Consequently, cationic starches with a high reaction efficiency must be obtained only with a thoroughly selection of the main factor values. NaOH content in the reaction mixture may be from 0.02 to 0.08 mol/AGU, and the temperature of the reaction should be as low as possible. The results shown in Fig. 7 confirm these conclusions. When NaOH content was lower than 0.08 mol/AGU, the main reaction of GTAC with hydroxyl groups of starch proceeded in the first stage of cationization (Fig. 7b). In these conditions starch was modified very efficiently. A maximum of 3.3% of GTAC (in most cases only 0–2%) was consumed in the side reactions. For example, after all consumption of GTAC, CCLS with DS 0.55 and RE 92% was obtained when NaOH content was 0.08 mol/AGU and the temperature of reaction 75 °C.

A special programme, MODDE 7 (www.umetrics.com), was fitted and a linear relationship was obtained between experimental data and points calculated from three-factor fractional design equations with the correlation coefficient R^2 varying from 0.98 to 0.99. The good agreement was confirmed by RE and DS of native starch (Table 6) and CLS (Table 7) cationized in optimal conditions of reactions calculated from TFF. The cationic native starch derivatives with DS 0.27–0.81 and RE more than 81% were obtained at 45 °C and 0.04 mol/AGU of NaOH (Table 6). The data in Table 7 show that formation of cross-links among macromolecules of starch polysaccharides did not influence the RE. If native starch was cross-linked with 0.002–0.3 mol/AGU of EPI and cationized, the RE was above 92% in all cases.

As it can be seen from Tables 6 and 7, CS and CCLS with DS from 0.27 to 0.56 can be obtained with RE of about 93%. After the reaction, the residual amount of

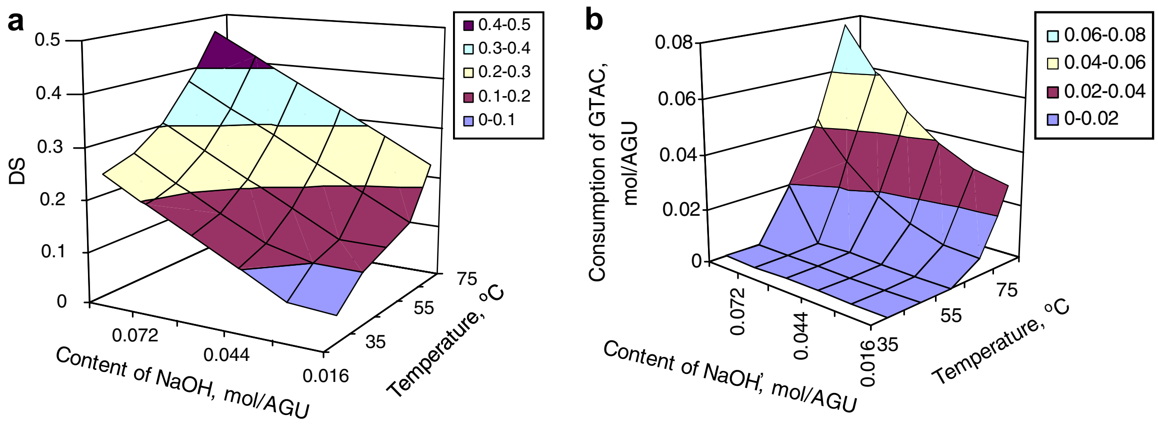


Fig. 7. Consumption of GTAC in the main (DS) (a) and side (b) reactions versus NaOH content in reaction mixture, and reaction temperature. Proportion of other reagents (in mol) AGU:GTAC:H_2O = 1:0.06:10, duration of reaction 1.75 h.

Table 6
Dependence of DS of CS and RE on the reaction temperature and reaction mixture composition

AGU:GTAC:NaOH:H_2O (in mol)	Temperature (°C)	Duration (h)	DS	RE (%)
1:0.3:0.04:1.78	45	24	0.27	97
1:0.6:0.04:2.5	45	24	0.56	93
1:0.7:0.04:2.7	45	48	0.61	87
1:1:0.04:5	45	48	0.81	81

Table 7
Dependence DS of CCLS and RE on the amount of EPI used in cross-linked reaction at different levels of GTAC in cationization mixture[a]

Amount of EPI used in cross-linked reaction (mol/AGU)	RE/DS, when amount of GTAC in reaction mixture (X) (mol/AGU)		
	$X = 0.22$	$X = 0.36$	$X = 0.44$
0.002	93/0.205	92/0.33	93/0.41
0.05	93/0.205	92/0.33	93/0.41
0.15	93/0.205	93/0.335	93/0.41
0.3	93/0.205	93/0.335	93/0.41

[a] AGU:GTAC:NaOH:H_2O = 1:X:0.08:8 (in mol). Temperature 45 °C.

water in the mixture was about 20–25%. Calculations had shown that the content of NaOH and side products of GTAC in the mixture was just about 1%. So, for the technical purposes (such as flocculation of dispersions or adsorption of dyes) reaction mixture could be used without any purification after reaction. For this reason RE will be the same when CS and CCLS are obtained on the industrial scale.

4. Discussion

According to the above, the rate and effectiveness of catalytical starch cationization reaction are closely related with the distribution of reaction components between solid and liquid phases of a heterogeneous reaction mixture, especially NaOH. Therefore, the amount of NaOH adsorbed by native potato starch and $CCLS_{0.05}$ with DS = 0.3 were determined. NaOH was adsorbed from the reaction mixture AGU:GTAC:NaOH:H_2O = 1:2:X:11, where X stands for different amounts of NaOH. The data obtained are presented in Fig. 8.

The data in Fig. 8 show that both native potato starch and $CCLS_{0.05}$ with DS = 0.3 adsorbed from the reaction mixture (where GTAC played a role of electrolyte) about 0.1 mol/AGU of NaOH. When the content of NaOH in the reaction mixture was higher than 0.1 mol/AGU, not the whole amount of it was adsorbed and part of NaOH was in liquid phase. In this case, the side reactions of GTAC started and proceeded faster and in a different mode (Figs. 1 and 5). If reaction mixture had "free" water (Bendoraitiene et al., 2006) NaOH adsorbed on the polysaccharide activated its hydroxyl groups. The amount of activated hydroxyl groups determined the rate of the main reaction because in water the alkoxy ions of starch reacted with GTAC, and N-(2-hydroxypropyl)-3-N,N,N-trimethylammonium starch chloride was obtained (Scheme 1, reaction 1). NaOH determined the conversion of GTAC into cationic side products in the liquid phase. When the liquid phase of the reaction mixture contained no NaOH, a slow autocatalytic hydrolysis proceeded and GTAC was catalyzed by hydroxyl ions, which originated during GTAC interaction with water (Bendoraitiene et al., 2006) (Scheme 1, reaction 6′). Some amount of N-(2,3-dihydroxy)propyl-N,N,N-trimethylammonium chloride formed in this process reacted with GTAC and transformed slowly into the dimer of GTAC (Scheme 1, reaction 4).

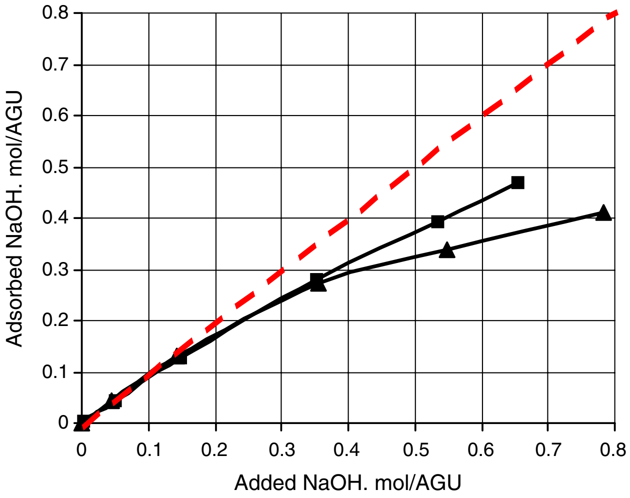
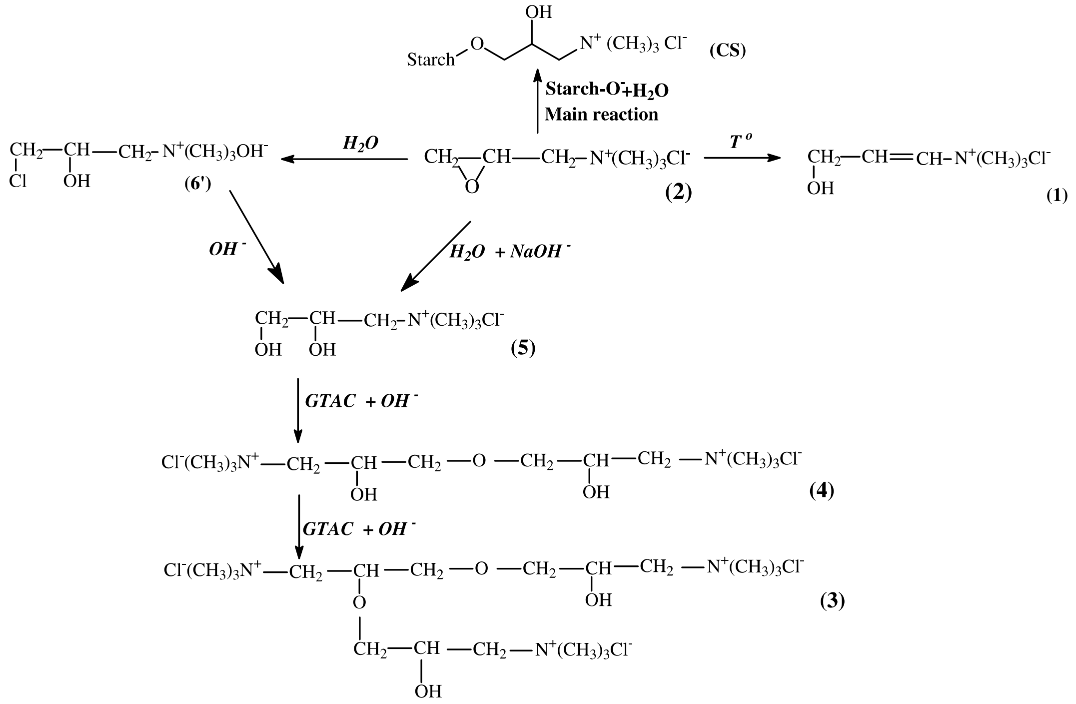


Fig. 8. Amount of NaOH instantaneously adsorbed by native potato starch (▲) and $CCLS_{0.05}$ with DS = 0.3 (■) from reaction mixture AGU:GTAC:NaOH:H_2O = 1:2:X:11 (mol) at 20 °C.

The rate of GTAC reactions catalyzed with NaOH was 60 times higher than that of autocatalytic reactions in the liquid phase (Bendoraitiene et al., 2006). It was not only due to a higher concentration of hydroxyl ions, but also due to formation of glycols in the reaction mixture. An intermediate product, N-(2-dihydroxy)propyl-N,N,N-trimethylammonium chloride (Scheme 1, reaction 5), formed in the first stages of the reactions, was more active than water. In the environment of hydroxyl ions this compound deprotonized, reacted easily with GTAC, formed a dimer of GTAC (Scheme 1, reaction 4) and later a trimer of GTAC (Scheme 1, reaction 3). Thus, the distribution of NaOH among the components of the heterogeneous system "starch – reaction mixture" influenced not only the rate of the side reactions of GTAC, but also their character.

5. Conclusions

1. Cationic or cross-linked cationic starches with preserved microgranules, substitution degree 0.2–0.85 and reaction efficiency 82–93% might be obtained during etherification of starch or cross-linked starch with a mixture con-



Scheme 1. The side reaction of GTAC and the compounds formed: 1 – *N*-(3-hydroxy-1-propen)-*N*,*N*,*N*-trimethylammonium chloride; 2 – *N*-2,3-epoxypropyl-*N*,*N*,*N*-trimethylammonium chloride (GTAC); 3 – trimer of GTAC; 4 – dimer of GTAC; *5* – *N*-(2,3-dihydroxy)propyl-*N*,*N*,*N*-trimethylammonium chloride; 6′ – *N*-(3-chlor-2-hydroxy)propyl-*N*,*N*,*N*-trimethylammonium hydroxide.

taining glycidyltrimethylammonium chloride (GTAC), “free” water and 0.04–0.08 mol/AGU sodium hydroxide in heterogeneous conditions.

2. The activation energy of the GTAC main reaction was lower than that of the side reactions, thus starch cationization proceeded at lower temperature with higher reaction efficiency.
3. The amount of sodium hydroxide in the cationization mixture had a great influence on the rate of the main and side reactions of GTAC and their character:
    - 3.1. Only the main reaction – starch cationization – proceeded when all sodium hydroxide present in the reaction mixture was adsorbed from the liquid phase by starch (the first stage of reaction). The duration of this stage decreased with increasing reaction temperature and the content of sodium hydroxide in the reaction mixture. The side products of GTAC, *N*-(2,3-dihydroxy)propyl-*N*,*N*,*N*-trimethylammonium chloride and 2,6-dihydroxy-4-oxa-1,7-di(trimethylammonium)heptane chloride, were formed in the latest stages when GTAC began to react with water.
    - 3.2. Sodium hydroxide, present in the liquid phase of the reaction mixture, catalyzed the side reactions of GTAC and changed their character. In this case, not only *N*-(2,3-dihydroxy)propyl-*N*,*N*,*N*-trimethylammonium chloride as the side product of GTAC was present, but also the product of its interaction with GTAC – 2,6-dihydroxy-4-oxa-1,7-di(trimethylammonium)heptane chloride – were presented in the reaction mixture.

Acknowledgements

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