Modification of cellulose in the solution of methanesulfonic acid

M. A. Akhmedov,[a,b]★ Sh. Sh. Khidirov,[b] and Kh. S. Khibiev[b]

[a] *Dagestan Federal Research Center of the Russian Academy of Sciences, Analytical Center for Collective Use, 45 ul. M. Gadzhieva, 367000 Makhachkala, Russian Federation. Fax: +7 (872 2) 674 965. E-mail: muhamadahmedov@mail.ru*
[b] *Dagestan State University, Department of Chemistry, 43a ul. M. Gadzhieva, 367000 Makhachkala, Russian Federation. Fax: +7 (872 2) 682 326*

Chemical modification of cellulose in solutions of methanesulfonic acid (MSA) is studied. It was found using IR spectroscopy, capillary electrophoresis, and scanning electron microscopy that by treatment of cellulose in 10 and 15 *M* methanesulfonic acid solutions, cellulose is hydrolyzed to form soluble forms of cellulose (cellobiose) and insoluble products (microcrystalline cellulose and nanocellulose). It was also shown by IR, UV, and Raman spectroscopy that the interaction of OH groups of the studied carbohydrate molecules with MSA leads to the formation of mesylates esters.

Key words: hydrolysis, methanesulfonic acid, modification, molecular spectroscopy, microcrystalline cellulose, nanocellulose, cellobiose.

Cellulose is the most demanded natural high-molecular weight biopolymer.[1,2] The products of cellulose modification are used to obtain composite materials,[3—6] films, fibers, membranes,[7—10] nanofibers, nanogels, hydrogels, *etc.*,[1—15] which are widely used in medicine (tissue engineering, drug delivery systems), biotechnology, and other industries.[16—21] A great contribution to the development of fundamental research in the field of synthesis, structure, and properties of cellulose derivatives was made by the Russian scientists.[22—32]

Many authors note[16,20] that the main problem preventing the widespread industrial use of cellulose modification products is the difficulty of their dissolution, including in aprotic organic solvents.[2,32] The solvents for cellulose known to date are classified into aqueous and non-aqueous, and by the nature of the interaction with cellulose are divided into true, complex, and derivatizing solvents.[32,33]

Modification of cellulose in solutions of toluenesulfonic acid has been studied in details.[34] Various medical and biotechnological products have been obtained from cellulose tosylates using nucleophilic substitution reactions.[34—36] A mixture of solvents consisting of a 0.4 *M* solution of methanesulfonic acid (MSA) and a 2 *M* solution of dimethyl sulfoxide (DMSO) was also used to dissolve cellulose.[37,38] However, the complexity of the purification process and the separation of the final product from the solvent, namely, toluenesulfonic acid and DMSO should be noted. In this regard, the search for more effective solvents for cellulose and its subsequent modification is one of the most important tasks in the study of the chemistry of this biopolymer.

The modification of cellulose in MSA solutions was studied by methods of physicochemical analysis in the present work. There are no literature data on the solubility and the possibility of cellulose modifcation in MSA solution.

Experimental

Paper filters (Filtrak, degree of polymerization (DP) was 1200) were use as cellulose samples. Methanesulfonic acid (MSA-70 and MSA-100, BASF) was used as received.

Method for preparation of cellulose solutions. Mechanically ground initial cellulose (up to 1—3 mm) was dissolved in 10 and 15 *M* MSA solutions. The dissolution of cellulose was carried out under vigorous stirring (1500 rpm) using a magnetic stirrer at a temperature of 20—25 °C and atmospheric pressure for 5—10 min. Complete dissolution of cellulose was observed only in a 15.0 *M* MSA solution. In this case, the solution was brown, which is due to the formation of cellulose dehydration products containing chromophore groups. MSA solutions with a cellulose concentration from 1 to 100 g L^{-1} were used for the study.

Method of product isolation and purification. The isolation of dissolved products of chemical modification of cellulose from concentrated MSA solutions was carried out by neutralizing solutions with NaOH solutions. Then the resulting solution (liquid phase) was evaporated at 100—115 °C until the dry residue, sodium methanesulfonate (CH_3SO_3Na), was isolated and treated with hot ethyl alcohol (96 wt.%). After cooling, the mixture was passed through a Nutsche filter, CH_3SO_3Na was separated, the filtrate was evaporated and dried at 50—60 °C.

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The remaining insoluble solid residue of cellulose from the MSA solution was also first neutralized with an alkaline solution of NaOH, thoroughly washed with bidistilled water, and dried at 50—60 °C in an oven.

Research methods. Obtained solutions of modified cellulose were investigated by capillary electrophoresis, molecular (UV, IR, and Raman) spectroscopy, and scanning electron microscopy.

A capillary electrophoresis (CE) system Kapel-105M (LUMEX, Russian Federation) with negative high voltage polarity was used to analyze the composition of the products after hydrolysis of cellulose in a concentrated solution of MSA. Inner capillary diameter d_{in} was 75 μm, full capillary length L_{tot} was 75 cm, effective length L_{eff} was 65 cm. Preparation and analysis of samples was carried out according to known methods.[39,40] The measurement results were processed using a MultiChrom 1.5 software (Ampersend, Russian Federation).

IR spectra were recorded using a VERTEX70 FTIR spectrometer (Bruker, Germany) using an ATR attachment with a ZnSe prism. The spectral resolution of the device was 2 cm^{-1}, the number of scans was 32. To record the IR spectra, the sample under study was repeatedly filtered in the presence of bidistilled water, dried in an oven at 40—50 °C, and mixed with KBr (Alfa Aesar). The obtained values of the absorption bands of functional groups in the IR spectra were analyzed using reference literature.[41—44]

The modification of cellulose in MSA solutions was also studied using a Raman spectral system DXR Smart Raman Research (Thermo Scientific, USA) and a UV-3600 spectrometer (Shimadzu, Japan). The analyzed sample was placed in a quartz cuvette to measure the spectra in the UV and near IR regions. To obtain Raman spectra, the samples were placed in a quartz ampoule, from which air was first evacuated using a vacuum pump, and then the ampoule was filled with an inert gas (argon) and sealed. Analysis and identification of the obtained substances were also carried out using reference information.[43]

A scanning electron microscope SEM Leo-1450 (Carl Zeiss, Germany) with an energy-dispersive X-ray analysis system EDX Inca-100 (Oxford Instruments) was used for the studies by scanning electron microscopy (SEM). The samples were secured to holders using a double-sided conductive carbon tape. Micrographs were obtained at an accelerating voltage of 20 kV in the mode of recording secondary electrons with a magnification from 200 to 25000 at several points. A Pd/Ag alloy was magnetron sputtered onto nonconductive cellulose samples using a Quorum Q150T ES setup (Quorum Technologies, Great Britain).

Results and Discussion

The solutions under study were divided into two parts, namely, liquid filtrate and solid residue of reacted cellulose in order to clarify the nature of the products formed as a result of cellulose hydrolysis in MSA solutions.

The presence of water-soluble low-molecular-weight carbohydrates formed during acid hydrolysis of cellulose was determined by capillary electrophoresis, as well as UV and NIR spectroscopy.

An electroforetogram of a 10.0 *M* MSA solution containing 10 g L^{-1} of cellulose is shown in Fig. 1, *a*. It can be seen that there is already at the sixth minute a clear peak associated with the presence of a forming water-soluble carbohydrate. However, in terms of release time, it does not coincide with the peaks of fructose, glucose, and sucrose. We assumed that this peak may be due to the formation of cellobiose, a disaccharide, which is the main structural unit of the cellulose molecule. Cellobiose consists of two glucose residues linked by an β-glycosidic bond (or 4-(β-glucosido)-glucose) and containing an aldehyde group. Cellobiose is characterized by reactions involving an aldehyde (hemiacetal) group and hydroxyl groups, as a result of which glycosides with alcohols, amines, and other monosaccharides can be formed. The cellobiose is cleaved to form two glucose molecules during further acid hydrolysis or under the action of the enzyme β-glucosidase.[45]

It was also found by the method of capillary electrophoresis (see Fig. 1, *b*) that cellobiose decomposes to glucose when heated to 110—120 °C in the presence of MSA. The release of the glucose peak occurs already after 7 min. The exit time of each of the peaks depends on the electrophoretic mobility of the particles and the electroosmotic flow in the capillary. The sample was diluted by a factor of 500 to increase the mobility of the test substances in the sample.

The quantitative yields of the products formed in the liquid and solid phases after the treatment of cellulose in 10 and 15 *M* MSA solutions were determined by the gravimetric method and are shown in Table 1. As can be seen from Table 1, the deeper hydrolysis of cellulose proceeds in a 15 *M* MSA solution.

It should be noted that after neutralization of a 15 *M* MSA solution containing 1—100 g L^{-1} cellulose, insoluble

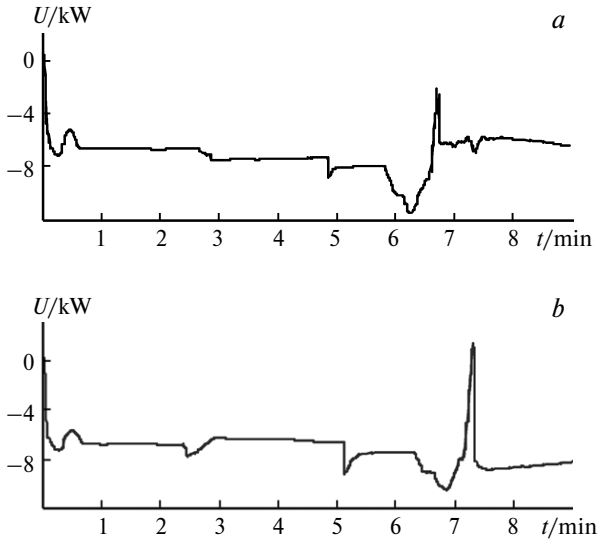


Fig. 1. Electropherogram of solutions of cellobiose (*a*) and glucose (*b*) obtained after hydrolysis of cellulose in 15 *M* MSA solution.

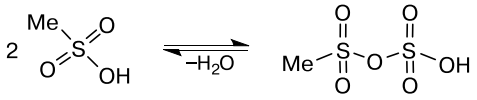
Table 1. The yield of cellulose hydrolysis products

Run	*m*/g (cellulose)	Yield of products (wt.%) after cellulose processing			
		10 *M* MSA solution		15 *M* MSA solution	
		Liquid phase	Solid phase	Liquid phase	Solid phase
1	1.0	7.5	92.5	59.2	40.8
2	10.0	8.8	91.2	57.6	42.4
3	20.0	9.1	90.9	55.4	44.6
4	40.0	10.7	89.3	53.2	46.8
5	100.0	12.2	87.8	50.3	49.7

cellulose (more than 40 wt.%) precipitated from the solution. This indicates that the hydrolysis of cellulose in a 15 *M* MSA solution is incomplete.

The spectra were recorded in the UV and near IR regions (Fig. 2) to elucidate the nature of the formed chromophore groups upon dissolution of cellulose in 10 and 15 *M* MSA solutions. As can be seen from Fig. 2, *a*, in the spectrum of the initial 15 *M* MSA solution in the UV region, there are two absorption maxima at 245 and 312 nm. Numerous absorption bands are observed in the near-IR region at 887, 1000, 1224, 1136, 1159, 1345, 1354, and 1372 nm. These are associated with complex molecular vibrations (overtones) of MSA functional groups. Apparently, such a combination of absorption bands can be due to the fact that at a concentration of more than 15 *M*, MSA molecules, by analogy with concentrated sulfuric acid, are capable of forming methanesulfonic anhydride (Scheme 1).

Scheme 1



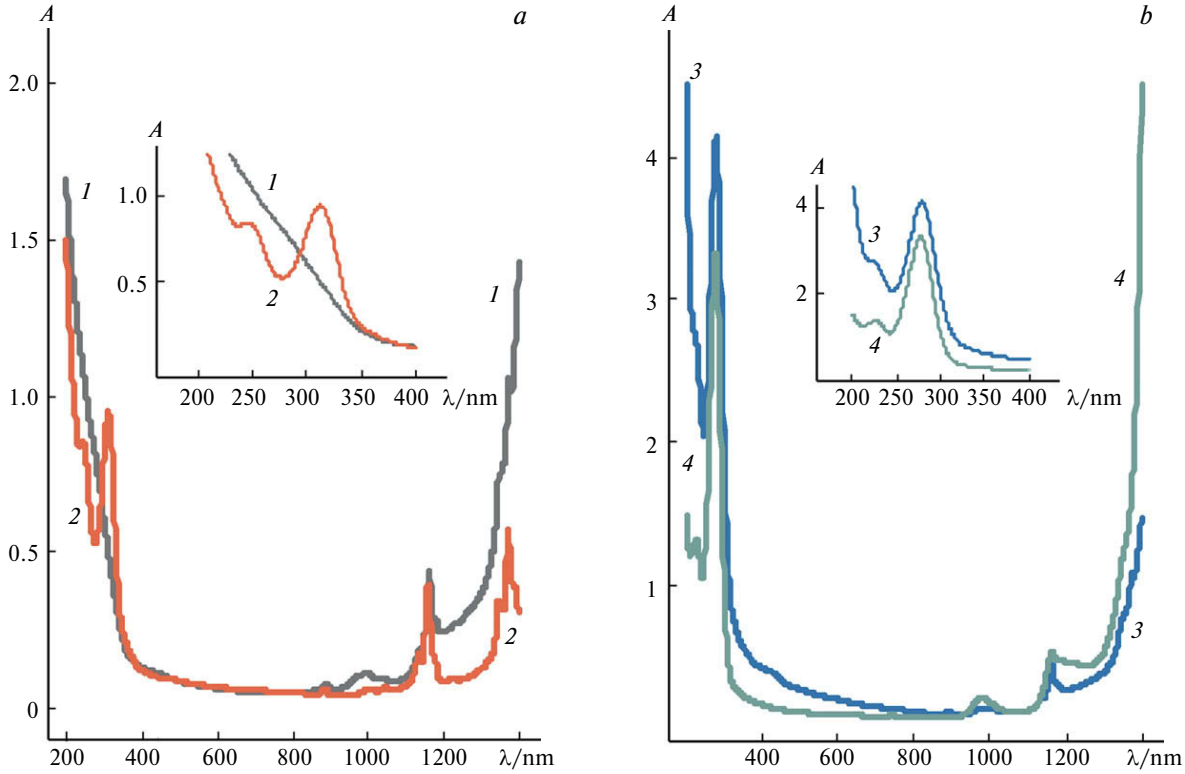


Fig. 2. Spectra in the UV and near-IR region: *a*, starting 10 (*1*) and 15 *M* (*2*) MSA solutions; *b*, cellulose solutions (10 g L^{-1}) in 10 (*3*) and 15 *M* (*4*) MSA solutions (insert shows UV absorption spectra on a larger scale).

Note. Figures 2—4 are available in full color on the web page of the journal (https://link.springer.com/journal/volumesAndIssues/11172).

We assumed that the absorption band with a maximum at 312 nm may be due to the vibration of the mesyl ($CH_3—S(O)_2—O$) group, and the band at 245 nm is due to the vibration of the SO_2 group. Note that in the spectrum of a 10 *M* MSA solution, the above absorption bands are not observed in the UV region, but they are blurred in the near IR region due to the superposition of absorption bands of OH groups from water molecules.

A noticeable shift of the absorption bands of the mesyl (279 and 277 nm) and sulfo groups (224 and 226 nm) is observed in the UV spectra (see Fig. 2, *b*) of cellulose solutions after hydrolysis in 10 and 15 *M* MSA. Such a shift can be caused by the formation of a mesylate ester due to the interaction of the OH group of the cellobiose molecule with MSA molecules.

It should be noted that, due to limited spectral range of the UV-3600 spectrometer (200—1400 nm), UV spectroscopy failed to detect the presence of chromophore C=C-groups formed as a result of cellulose dehydration and causing the appearance of a brown color in a 15 *M* solution of MSA since absorption of these chromophore groups is observed only in the vacuum UV region (190—165 nm).

The presence of C=C chromophore groups in the products after dissolution of cellulose in 10 and 15 *M* MSA solutions was detected by Raman and IR spectroscopy (Fig. 3 and 4). Raman spectra were obtained both for the initial 10 and 15 *M* MSA solutions and in the presence of 1 g L^{-1} of cellulose. It should be noted that strong fluorescence of the MSA molecule is observed in the vibration ranges of 350—1550 and 2400—3450 cm^{-1}. Moreover, the fluorescence in the presence of cellulose modification products increases with an increase in MSA concentration from 10 to 15 mol L^{-1}. Apparently, this can be associated with the presence of ether (mesyl) groups. The interpretation of the obtained experimental data is given below.

The Raman spectrum of a 10 *M* MSA solution contains the following vibrations (cm^{-1}): 50—250 (O—H, C—S—O); 340 (C—S—O); 550 (ν C—S); 780 (O=S=O); 965 (δ O=S=O); 1045 (S=O); 1420 (C—S=O); 2940 (CH_2); 3025 (C—H). The difference between the Raman spectra of 10 and 15 *M* solutions is that in a 15 *M* solution of MSA, vibrations of additional groups appear, namely, 505 (C—S), 900 (ν_1 $S(O)_2—O—S(O)_2$), 985 (ν_2 $S(O)_2—O—S(O)_2$), 1345 (S—O—S), 2670 (ν_2 CH_2), 2820 (ν_2 C—H), and 2945 (ν_1 CH_2), 3030 (ν_1 C—H).

The presence of C=C bonds in cellulose subjected to chemical treatment in a 10 *M* MSA solution was not detected by the Raman method. However, in the Raman spectrum of cellulose in a 15 *M* MSA solution the appearance of bands corresponding to allene (—C=C=C—)-groups is observed in the region of 1010—1080 cm^{-1}, while vibrations of methanesulfonic acid anhydride groups are absent. The presence of allene groups in this solution was also confirmed by IR spectroscopy (see Fig. 4, *b*).

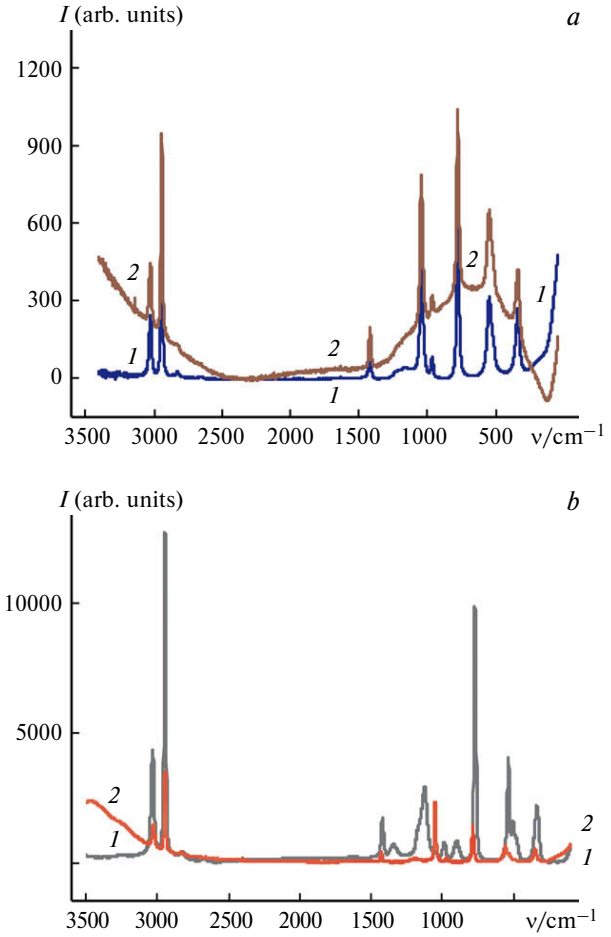


Fig. 3. Raman spectra of 10 (*a*) and 15 *M* (*b*) initial MSA solutions (*1*) and hydrolysis producsts (10 g L^{-1}) in MSA (*2*). Excitation source is solid-state laser (532 nm).

Figure 4 shows the IR spectra of cellulose modification products in 10 and 15 *M* MSA solutions. It is known from reference materials on the analysis of the IR spectra of cellulose[41,42] that these spectra are generally characterized by the presence of absorption bands of three different hydroxyl groups contained in each glucoside ring. From the analysis of the IR spectra of the purified and isolated solid products (see Fig. 4), it follows that the functional groups after acid hydrolysis of cellulose in MSA solutions do not change. At the same time (see Fig. 4, *a*) the intensity of the peaks after cellulose hydrolysis increases in comparison with the starting material. This may be due to the fact that dissolution of cellulose in 10 and 15 *M* MSA solutions results in acid hydrolysis of cellulose to cellobiose. The latter, in turn, when heated to 110—120 °C, yields glucose.

The IR spectrum of the starting cellulose (KBr) contained the following vibrations (ν/cm^{-1}): 520 and 670 (δ, C—O—C, ring); 898 (ν, C—O—C, ring); 1110, 1054, 1030, 1170, and 1315 (νCO + νCCH + νC—O—C);

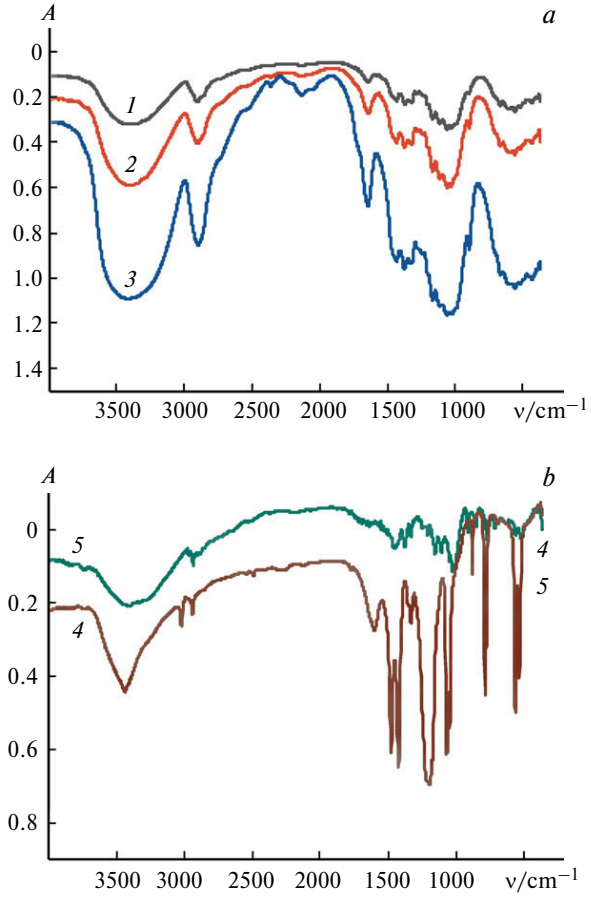


Fig. 4. FTIR spectra: *a*, initial cellulose (*1*) and solid products obtained as a result of its modification in MSA solutions: MCC (*2*); NCC (*3*); *b*, dehydrated cellobiose (*4*) and glucose (*5*).

(δ, OH); 1380 (δ, C—H); 1427—1450 (δ, CH_2); 1642 (ν, H_2O); 2870—2910 (ν, C—H); 3334—3274 (ν, OH); 3305—3405 (δ, OH).

In the IR spectrum of the obtained cellobiose (KBr) following vibrations were observed: (ν/cm^{-1}): 368, 540 and 565 (δ, C—O—C, ring); 502 и 943 (δ, CH_2); 692, 705, 790, 884 (νCO + νCCH + νC—O—C); 1050 and 1070 (ν, C=C=C); 1175,1200, 1220, and 1336 (ν, C—O, including νCOH/νCOC structure); 1470 and 1420 (C=C in cycle); 1604 (ν, H_2O); 2490 and 2545 (C=C); 2940 (ν, C—H); 3020 (ν, C=C); 3445 (ν, OH); 3740 (δ, OH).

In the IR spectrum of the obtained glucose (KBr) following vibrations were observed (ν/cm^{-1}): 368, 405, 420, 510, 526, 560 (δ, C—O—C, ring); 720, 770 (δCCO + δ CCH); 850, 915 (νCO + νCCH + νC—O—C); 1012, 1025, 1030 (νCO); 1050, 1110, 1155 (νCO + νC—C); 1210 and 1250 (δ CH + δ OH); 1330 (δCHO + δ CCH); 1375 and 1460 (δ CH_2 + δ CHO + δ CCH); 2880, 2900, 2935, and 2972 (ν_{as}C—H); 3396(ν_sC—H); 3410 (νOH); 3740 (δOH).

The possibility of cellulose ether formation in the process of its dissolution in concentrated MSA solutions is confirmed by the data of Raman and IR spectroscopy

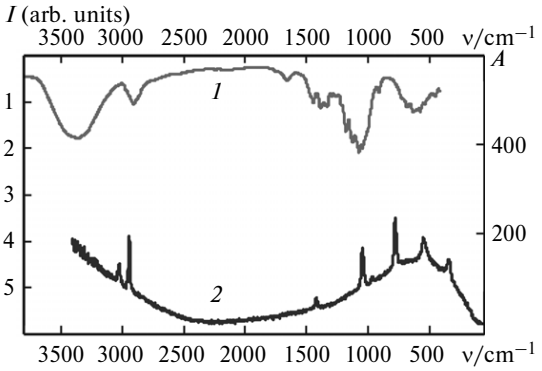


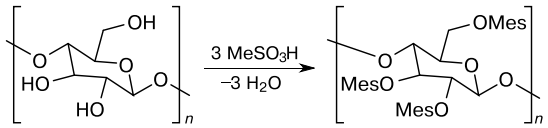
Fig. 5. FTIR spectrum (*1*) and Raman spectrum (*2*) of cellulose mesylate. Excitation source is solid-state laser (532 nm).

(Fig. 5). The presence of absorption bands of mesyl groups is observed in the IR spectrum of cellulose mesylate (KBr, cm^{-1}): 1280—1230 ($S(O)_2$); 1100—1050 (S=O, C—$S(O)_2$—OH). The Raman spectrum of cellulose mesylate contains functional groups of the MSA molecule (cm^{-1}): 50—250 (O—H and C—S—O); 340 (C—S—O); 550 (νC—S); 780 (O=S=O); 965 (δO=S=O); 1045 (S=O); 1420 (C—S=O).

At the same time, fluorescence of functional groups of the cellulose molecule is observed in the range of 10—2000 and 2400—3400 cm^{-1}. This may be due to the interaction of the OH group of the cellulose molecule with the MSA molecules to form cellulose mesylate.

We assume that the formation of cellulose mesylates occurs according to Scheme 2.

Scheme 2



Mes = $MeS(O)_2O^-$

Cellulose mesylates are a well-known class of organic compounds related to esters with the general formula $[C_6H_7O_2(OH)_{3-x}(SO_3CH_3)_3]_n$. These compounds are reactive, they undergo exchange reactions and nucleophilic substitution (S_N2). They are of interest primarily as a starting material for the synthesis of new classes of cellulose and carboxycellulose derivatives.[46]

Figure 6 shows images obtained using scanning electron microscope (SEM) of samples of the initial cellulose and its hydrolysis products. They indicate a change in the structure of cellulose fibers after their treatment in a 10 *M* solution of MSA.

As can be seen from Fig. 6, the dimensions of the fibers after hydrolysis of cellulose in a 10 *M* solution of MSA correspond to the values characteristic of microcrystalline (MCC) and nanocrystalline cellulose (NCC).

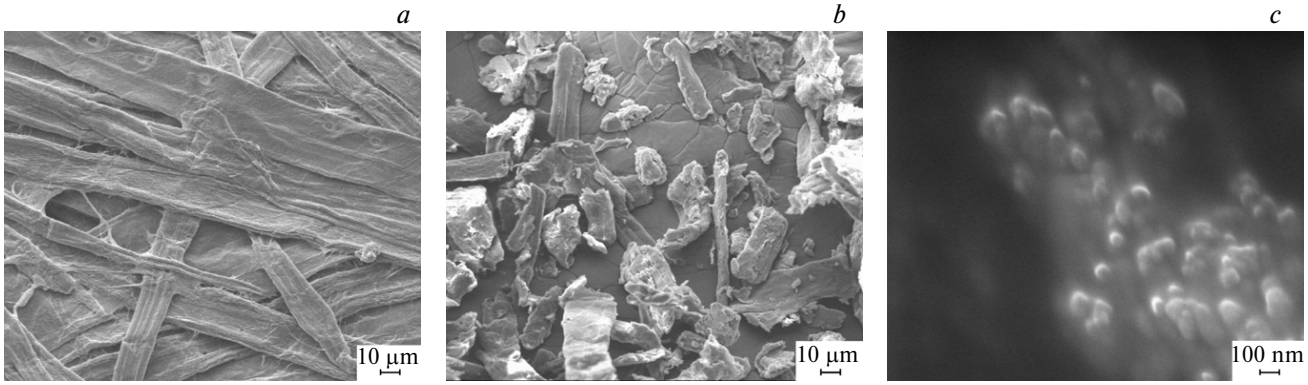


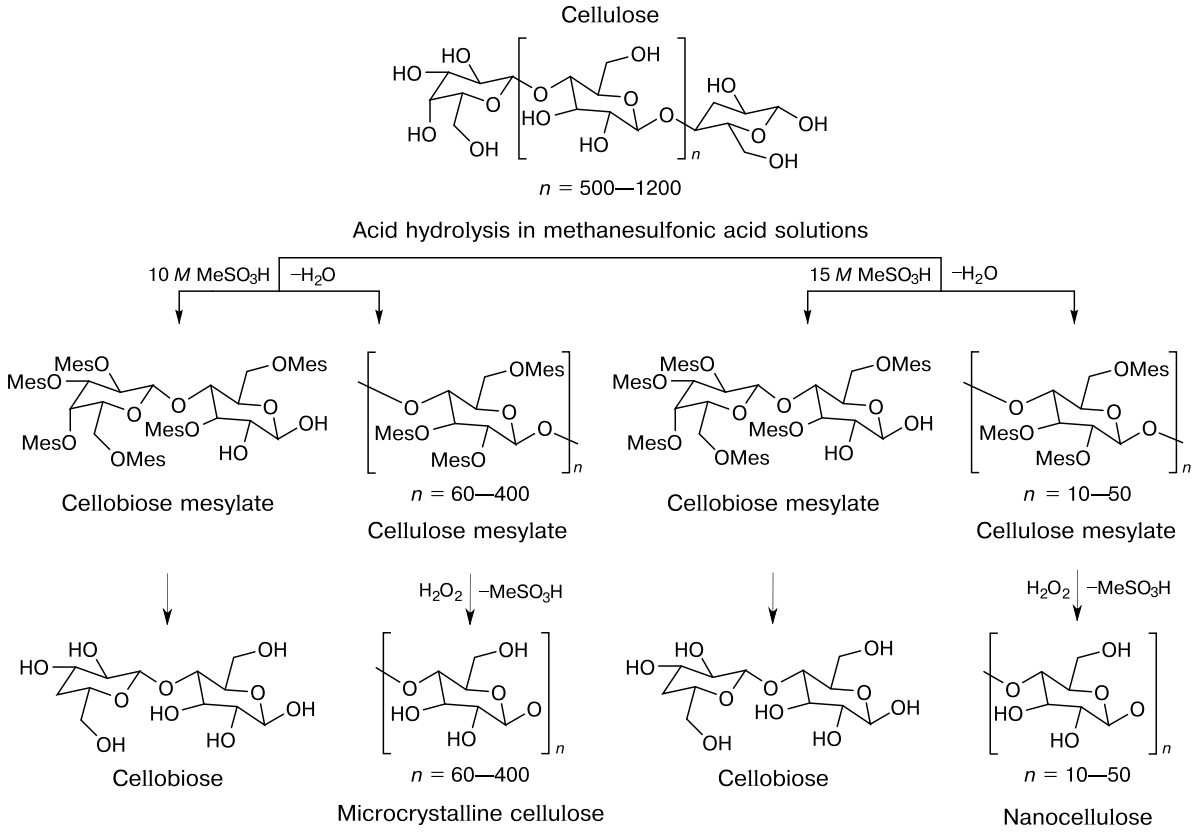
Fig. 6. SEM images of the original cellulose surface (*a*) and products of its hydrolysis in MSA solutions, namely, MCC (*b*) and NCC (*c*).

It is known from the literature[16,47–51] that hydrolysis of cellulose can occur in an acidic medium either in incomplete form, leading to the formation of MCC and NCC, or in complete form. Complete hydrolysis of cellulose yields glucose.[16,20] Samples of MCC and NCC obtained by biotechnological synthesis, are promising and demanded materials due to the possibility of improving some properties of the compositions (flexibility, strength, *etc.*).[47–50]

Scheme 3 shows the products of chemical modification of cellulose in concentrated MSA solutions.

Thus, using the methods of physicochemical analysis, we found that the dissolution of cellulose in 10 and 15 *M* methanesulfonic acid solution is accompanied by incomplete hydrolysis, the main products of which are glucose, cellobiose, microcrystalline and nanocrystalline cellulose. It was also found that the interaction of alcohol groups of cellulose with MSA leads to the forma-

Scheme 3



tion of esters, namely, cellulose mesylate, cellobiose and glucose.

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