

## Sulphating of Powder Cellulose that Was Obtained by the Catalytic Destruction Method by Titanium Tetrachloride

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### Abstract

Sulphated derivatives have been synthesized around powder cellulose (PC) that was obtained by a procedure of catalytic destruction by titanium tetrachloride. PC involvement in sulphating reaction has been studied as a function of the obtaining conditions. It has been found that sulphates of PC show variable physicochemical properties depending on the obtaining methods.

### INTRODUCTION

One of the basic directions in modification of cellulose is the development of methods to obtain its powder forms through structural change of biopolymer. A rather new method to produce powder cellulose (PC) is treatment of fibrous cellulose with Lewis acids [1] that is accompanied by structural reorganization of the initial biopolymer and, as consequence, by change in its functional composition. Study of further chemical transformations of these PC is of both scientific and practical interest. In case of the former, this is a study of the mechanism of reactions; in the latter case, this is an investigation of synthesis methods for tailor-made multifunctional cellulose materials. Further modification of these PC constitutes a promising direction to produce anionic cellulose derivatives with variable biological activity [2].

### EXPERIMENTAL

#### *Analytical methods*

Content of carbonyl groups in cellulose preparations was determined by a condensation method with hydroxylamine [3]. The content of carboxylic groups in PC was determined by

means of an ion-exchange method with the use of calcium acetate [3]; the sulphur content analysed with an EA 1110 CE Instruments. A degree of replacement (DR) with respect to sulphate groups ( $DR_s$ ) was determined by the formula  $DR_s = 162\omega_s / (3200 - \omega_s \cdot 103)$ , where  $\omega_s$  is the sulphur content, %.

The IR Fourier transmission spectra were measured by an Oriel MIR 8000 spectrometer (in KBr tablets).

X-ray diffraction analysis has been performed in DRON-3 diffractometer.

Degree of polymerisation ( $DP_{av}$ ) of the specimens was determined from viscosity of the solutions in cadoxene in Ostwald viscometer with the capillary diameter of 0.82 mm [4]. Reduced viscosity of water solutions of sodium salt of cellulose sulphate Na-CS was measured on an Ubbelohde viscometer (0.56 mm capillary diameter) at a temperature of 30 °C.

#### *Starting materials*

We used bleached sulphate cellulose from deciduous species that was produced by Mondi Syktyvkar Pulp and Paper Mill ( $DP_{av} = 520$ ) and cotton microcrystalline cellulose that was produced by Polieks JSC (Biysk, Russia) ( $DP_{av} = 230$ ). Mineral compounds were removed

by treatment with 1 M HCl solution, then water was poured into to reach a neutral reaction of the medium, and the product was dehydrated with acetone.

#### Preparing for powder celluloses

1. Hydrolysis of cellulose was performed in water solution of peroxymonosulphuric acid (1 % solution of  $H_2O_2$  in 10 % solution of  $H_2SO_4$ ). The reaction was conducted at the boiling temperature of the mixture over the course of 2 h and thereupon, the samples were washed out on a filter by distilled water to reach the neutral reaction of washing waters, applied to prepare inclusion complex with acetone and dried in the air at ambient temperature.

2. A weighted specimen (1.65 g) of cellulose that was dried at 105 °C was placed in a conical flask and covered with 100 cm<sup>3</sup> of freshly prepared titanium tetrachloride solution (0.1 mass %) in phenoxin or hexane [5]. A commercial  $TiCl_4$  of "ch." (pure) grade was used that was refined by simple distillation [6]. The reaction conducted in the medium of anhydrous organic solvents at their boiling temperature. Then the reaction mixture was brought onto a glass filter, the solution was filtered off, and the residue of the catalyst was washed by the same solvent, applied to prepare inclusion complex with ethanol and dried.

#### Sulphating of powder cellulose

The procedure [7] with certain modifications was used. A PC sample (1 g, 6.17 mmol) that has been dried up to constant mass at 103 °C was suspended in pyridine at 0 °C. Sulphuric chlorohydrin (3 mol per anhydroglucose unit) was brought dropwise in the reaction mixture with cooling and intensive stirring. After thermostatic standing over the course of 1 h at 90 °C, the reaction was continued over the course of 2 h at 80 °C. The product was filtered off on a glass filter, washed out with 20 cm<sup>3</sup> of acetone, and dissolved in 50 cm<sup>3</sup> of 4 % NaOH solution. The produced mixture of Na-CS was precipitated with 100 cm<sup>3</sup> of ethanol, refined from inorganic salts by washing with water-ethanol mixture and dried in vacuo.

#### RESULTS AND DISCUSSION

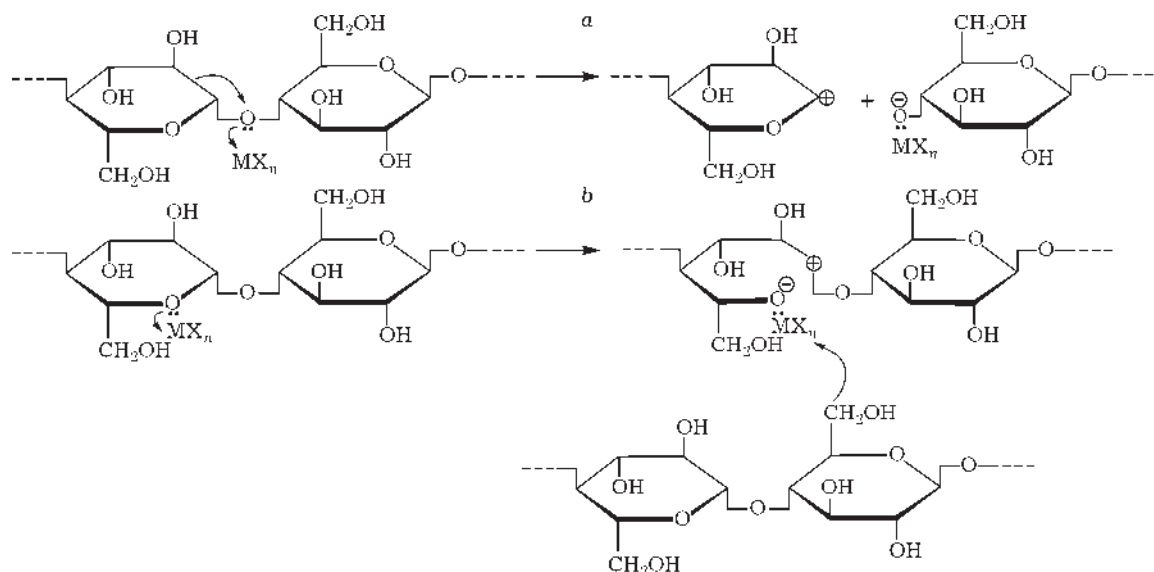
Procedures of acid hydrolysis are typically used in industry and laboratory practice to obtain PC, whereby the content of PC functional groups remains at the level of the initial biopolymer. Process of acid hydrolysis is followed by structural reorganization of cellulose: its accessible amorphous regions are disrupted, which is accompanied by a decrease of  $DP_{av}$  magnitude (Table 1, PC samples 1, 2) and by

TABLE 1  
Characteristics of powder celluloses

Specimen	Destruction method	Time, min	$DP_{av}$	Content of, %	
				carbonyl groups	carboxylic groups
PC 1	Hydrolysis by HCl	120	230	0.08	0.11
PC 2	Hydrolysis by $H_2SO_3$	120	240	0.05	0.15
PC 3	$TiCl_4-C_6H_{14}$	5	350	0.10	0.28
PC 4	$TiCl_4-C_6H_{14}$	15	280	0.13	0.44
PC 5	$TiCl_4-C_6H_{14}$	60	130	0.18	0.82
PC 6	$TiCl_4-CCl_4$	5	322	0.21	—
PC 7	$TiCl_4-CCl_4$	15	145	0.29	—
PC 8	$TiCl_4-CCl_4$	60	220	0.25	—
PC 9*	$TiCl_4-CCl_4$	60	230	0.28	—
Initial cellulose	—	0	540	0.02	0.22

Note. The specimen PC 1 was obtained from cotton cellulose; the remaining ones, from sulphate deciduous cellulose.

\* Additional thermal treatment (1 h, 100 °C).



Scheme 1. Mechanism of destruction (a) and "cross-linking" (b) of cellulose in the presence of a Lewis acid.

an increase in crystalline component of the cellulose material [8].

Treatment of cellulose with Lewis acids in the medium of aprotic solvents leads to a decrease of  $DP_{av}$  of a cellulose material and to its chemical modification. After washing out of organic solvent and a reaction of the modified cellulose with water, an increase in its content of carbonyl and carboxylic groups occurs (see Table 1).

It is known [8] that PC derivatives show the properties that are similar to properties of derivatives of fibrous cellulose preparations of a higher molecular mass.

The Scheme 1 gives a possible mechanism of destruction of a cellulose fragment ( $MX_n$ ) on exposure of Lewis acids. Particle  $MX_n$  is coordinated by way of unpaired electrons with hemiacetal (glycosidic or cyclic) oxygen atoms with the formation of donor-acceptor bonds by

way of unpaired electrons of oxygen atoms and vacant orbitals of central atoms of  $MX_n$ , which leads to weakening of C-O bond [9]. The destruction of cellulose occurs by two competing mechanisms. The major one of them is disclosed on the Scheme 1, a. In parallel with this, the formation of opened pyranose parts (see Scheme 1, b) or the formation of functional groups occurs. By virtue of the fact that polymeric macromolecules are arranged in fibres, the formation of free radicals leads to "cross-linking" of the next macromolecules or to the emergence of new acetal bonds that are distinct from  $\beta$ -1-4. The formation of acetal bonds following the 1-6 pattern is energetically more favourable as compared with alternative types of bonds.

Coordination of metal catalyst by functional groups of a polymer is a heterogeneous reaction. Meanwhile, the polymer links significant amounts of polyvalent metal, which gives rise to "inter-linked" cross-linked structures. Shown in Fig. 1 is a process of  $Ti^{4+}$  accumulation in PC samples.

A content of titanium in the form of a peroxide complex in the samples that were destructurized under the effect of  $TiCl_4$  and then washed out by hexane was determined by a

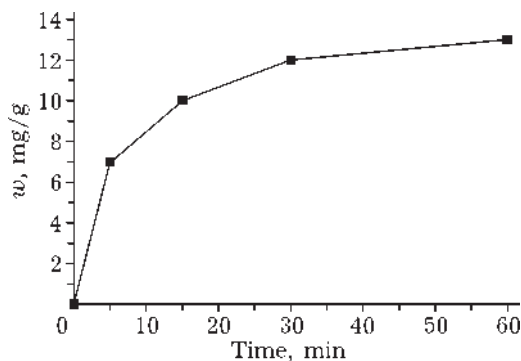
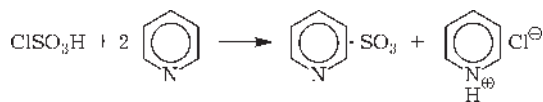


Fig. 1. Accumulation of  $Ti^{4+}$  ( $w$ ) in cellulose samples. Concentration of Lewis acid is 1.0 %.



Scheme 2. Formation of  $SO_3$ -pyridine complex.

TABLE 2  
Results of sulphating of powder celluloses

Specimen	DR <sub>s</sub>	Yield, %	Reduced viscosity ( $\eta_{red}$ ), cm <sup>3</sup> /g*	
			Water	1 % NaCl solution
PC 1	0.74	85	203.5	46.8
PC 2	0.95	87	219.1	44.2
PC 3	1.53	71	412.4	61.3
PC 4	1.57	—	insoluble	insoluble
PC 5	1.49	82	»	»
PC 6	1.42	75	441.1	78.0
PC 7	1.21	83	insoluble	insoluble
PC 8	1.76	88	»	»
PC 9	0.03	94	»	»

\* It was determined at the concentration of polymer in the solution that was equal to 1 %.

photocolorimetric method [10]. With this end in view, an element to be determined that implanted in a cellulose matrix was transferred into solution of 10 % sulphuric acid in the form of a soluble salt of titanium (IV) sulphate. A decrease of PC brightness serves as the direct result of metal introduced in the structure of cellulose [5].

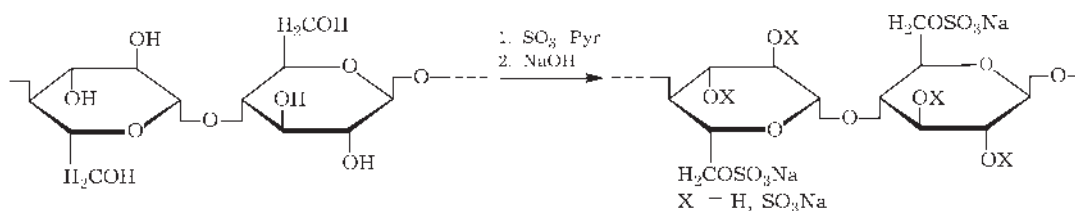
Sulphating of cellulose by sulphuric chlorohydrin in pyridine occurs through the formation of SO<sub>3</sub>-pyridine complex (Scheme 2).

As a rule, sulphating yields sulphated preparations of cellulose and other natural polysaccharides with 1–4 bond with a high degree of replacement [11]. It is reported [7, 12] that both primary and secondary hydroxyl groups of a constitutional repeating unit of cellulose (Scheme 3) react with SO<sub>3</sub> pyridine complex.

Presented in Table 2 are results of PC sulphating. All the preparations show high reactivity in sulphating reaction. PC sample No. 9 that has been obtained by catalytic destruction of initial cellulose and dried at elevated temperature without removal of the rests of a reaction mixture is distinguished by a reduced de-

gree of replacement with respect to sulphate groups. In addition, the sample colour has changed after the given procedure. Thermal final drying of this sample leads to a deeper destruction and to structural modification of cellulose, which manifests itself as a decrease of its DP [5].

PC sulphating is a heterogeneous reaction. In this case, the reactivity of cellulose is controlled by the availability of its reaction centres and depends in many respects on its supermolecular structure. Structural inhomogeneity of PC and the sulphated preparations was estimated through X-ray diffraction technique. This work used the PC samples, wherein a significant fraction of crystalline part was preserved after their catalytic treatment. The results arrived at bear witness to appreciable distinctions in supermolecular structure of samples. Treatment of cellulose with Lewis acids leads to destruction of the crystallites (Fig. 2). Samples of cotton microcrystalline cellulose (PC 1) are characterized by a high degree of crystallinity (Fig. 3, curve 1), and their sulphating leads also to destruction of their crystal structure (see Fig. 3, curve 2).



Scheme 3. Sulphating of cellulose by sulphuric chlorohydrin.

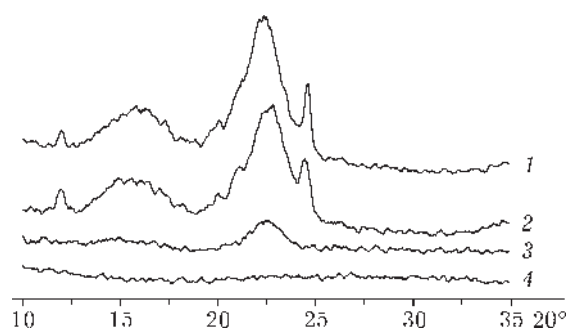


Fig. 2. Roentgenograms of deciduous bleached cellulose (1), PC 4 (2), powder cellulose that was modified in the presence of  $\text{TiCl}_4$  at the concentration of Lewis acid of 0.5 % (3), and of sulphate PC 4 ( $\text{DR}_s = 1.57$ ) (4).

It appears that higher  $\text{DR}_s$  values that have been reached on sulphating of samples PC 3–8 are caused by the predominance of amorphous permolecular structure in these samples.

Introduction of sulphate groups in PC is confirmed by the emergence of the absorption bands that are typical for  $\text{R-OSO}_3^-$  functional group in IR spectra (Fig. 4).

Preparations Na-CS are dissolvable in water even at  $\text{DR}_s = 0.3$  [13].  $\text{DR}_s$  with respect to sulphate groups for the majority of the sulphated samples may amount from 1 to 1.7. Intensive action of Lewis acids leads to changes in the functional composition of cellulose and its structure (a build-up of its amorphous part, "cross-linking" of the material by acetal bonds and the formation of steady metal-carbohydrate complexes).

Sulphated samples PC 4, 5, and 7–9 (see Table 2) are practically indissoluble in water, and they form viscous gels (PC 4 and 7) or slightly swelling deposits (PC 5 and 8). The samples that have been subjected to a less inten-

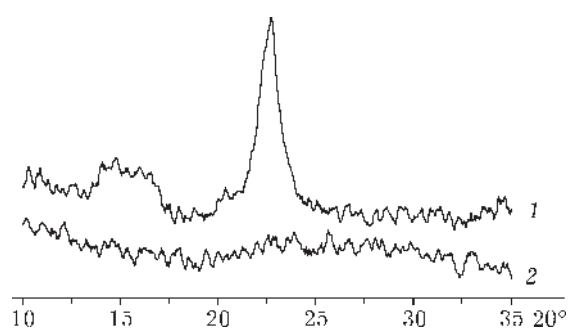


Fig. 3. Roentgenograms of samples of initial (1) and sulphated PC 1 ( $\text{DR}_s = 1.28$ ) (2).

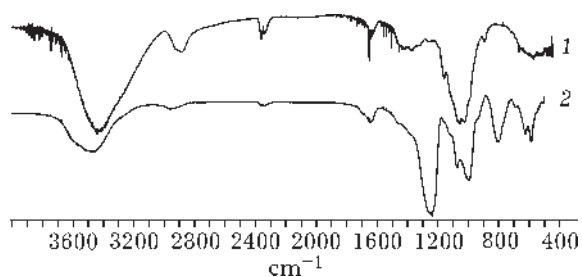


Fig. 4. IR Fourier spectra of samples: 1 - PC 5:  $1161 \text{ cm}^{-1}$  ( $\nu_{\text{COC}}$ ),  $2884 \text{ cm}^{-1}$  ( $\nu_{\text{CH}}$ ),  $3443 \text{ cm}^{-1}$  ( $\nu_{\text{OH}}$ ); 2 - sulphated PC 5:  $1237 \text{ cm}^{-1}$  ( $\nu_{\text{SO}_2}$ ),  $804 \text{ cm}^{-1}$  ( $\nu_{\text{SO}}$ ).

sive treatment by Lewis acids (PC 3 and 6), as well as those obtained by "classical" acid hydrolysis (PC 1 and 2), are readily soluble in water.

Rheological behaviour of water solutions of samples PC 3 and 6 is close to that for sulphated samples PC 1 and 2. Synthesized preparations of Na-CS are characterized by a distinct electroviscous effect in the region of low concentrations. They are also typified by a deviation from the linear relation  $\eta_{\text{sp}}/c = f(c)$  that is caused by a polyelectrolyte nature of the sulphated ethers of cellulose (Fig. 5), which gives

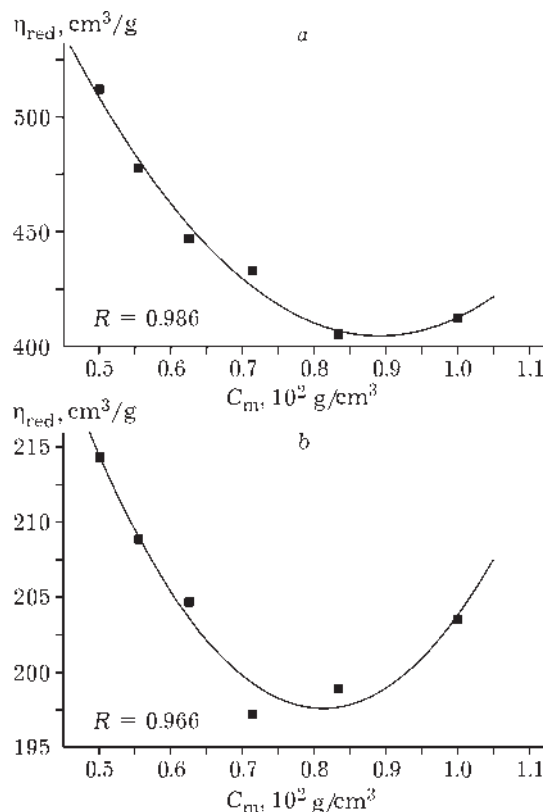


Fig. 5. Concentration dependence of reduced viscosity of sulphated PCs (water): a - PC 3; b - PC 1.

rise to extreme values in the region of concentrations of  $(0.7-1.0) \cdot 10^2 \text{ g/cm}^3$ . With an increased number of ionised groups, electroviscous effects manifest themselves to a greater extent.

In the presence of extraneous electrolyte (1 % NaCl solution), electroviscous effects are also observed, which is in good agreement with the data that have been received for PC 1 and 2 (see Table 2). Values of reduced viscosity for the samples PC 3 and 6 are considerably higher when compared to samples PC 1 and 2. This is brought about by higher molecular weights and  $DR_s$  of the initial preparations and apparently by a more uniform distribution of sulphate groups along the cellulose macromolecule.

Preparations of PC, which were synthesized by the procedure of catalytic destruction by Lewis acids, and their sulphates may be of significant interest to prepare anionic and multifunctional cellulose derivatives. Characteristics of these derivatives (DP, solubility, functional composition, etc.) can be assigned even at the stage of PC obtaining by varying parameters of the destruction process.

## CONCLUSION

1. For the first time we have synthesized sulphates of powder cellulose materials that have been produced by the procedure of catalytic destruction by titanium tetrachloride.

2. A method of synthesis of PC sulphates with high degrees of replacement has been put forward.

3. The solubility of the sulphated preparations depends on the intensity of catalytic treatment of cellulose.

4. Rheological behaviour of sulphated water-soluble PCs that have been obtained in aprotic solvents coincides with those for PCs that have been obtained by the "classical" hydrolysis method.

## REFERENCES

- 1 R. I. Sarybaeva, T. V. Vasilkova, V. A. Afanasiev, *Izv. AN KirgSSR*, 2 (1979) 42.
- 2 A. Chaidedgumjorn, H. Toyoda, E. Rhan, *Carbohydrate Res.*, 337 (2002) 925.
- 3 Z. I. Kuznetsova, *Metody issledovaniya tsellyulozy*, in V. P. Karlivan (Ed.), Zinatne, Riga, 1981.
- 4 L. S. Bolotnikova, S. N. Danilov, T. I. Samsonova, *Zh. Prikl. Khim.*, 1 (1966) 176.
- 5 S. V. Frolova, V. A. Demin, *Ibid.*, 81 (2008) 152.
- 6 Yu. V. Karyakin, I. I. Angelov, *Chistye khimicheskiye veshchestva*, Khimiya, Moscow, 1974.
- 7 M. Gohes, P. Mischnick, *Carbohydrate Res.*, 309 (1998) 109.
- 8 *Cellulose and Cellulose Derivatives*, in N. Bikales and L. Segal (Eds.), Wiley, NY, 1971.
- 9 R. I. Sarybaeva, A. S. Sultankulova et al., *Cellulose Chem. and Technol.*, 24 (1991) 199.
- 10 W. T. Elwell and D. F. Wood, *Analysis of the New Metals, Titanium, Zirconium, Hafnium, Niobium, Tantalum, Tungsten and Their Alloys*, Pergamon, Oxford, 1966.
- 11 S.-I. Nishimura, H. Kaia, K. Shinada, *Carbohydrate Res.*, 306 (1998) 427.
- 12 T. Groth, W. Wagenknecht, *Biomaterials*, 22 (2001) 2719.
- 13 G. I. Petropavlovskiy, *Gidrofilnye chastichno zameshchennyye efiry tsellyulozy i ikh modifikatsiya putem khimicheskogo sshivaniya*, Nauka, Leningrad, 1988.