IOP Conf. Series: Materials Science and Engineering **123** (2016) 012004 doi:10.1088/1757-899X/123/1/012004

# Electrochemical synthesis of cellulose mesylate

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**Abstract**. The article deal with the possibility anode modification of cellulose to form its ester – mesylate by voltametric measurement method and preparative electrosynthesis on a platinum electrode in the system cellulose – dimethyl sulfoxide - methanesulfonic

## 1. Introduction

Oxidation of cellulose in which there is no the polymer degradation leads to a modifying to form various functional groups [1]. The oxidation products of cellulose are used for different application in medicine and pharmacy [2-4]. Mesylates are the esters, which are formed at interaction of the functional hydroxyl groups of cellulose with methylsulfogroups. It is also known that the mesylates by used in organic synthesis for the protection of hydroxyl groups [5]. Previously, the authors [6,7] proposed the electrochemical modification of cellulose in copper - ammonia solution (reagent of Schweitzer - $[Cu(NH_3)_4](OH)_2$). The paper [8] in a wide range of positive potentials studied electrochemical modification of another representative of sugar-starch polysaccharides. Cellulose is difficult to dissolve in organic solvents. Selection of the solvent and supporting electrolyte aqueous solution is a difficult task. Found that aqueous solutions of dimethyl sulfoxide (DMSO) is well dissolved cellulose [9].The authors of [10-11] it was stated that DMSO is oxidized to methanesulfonic in this field potentials.

In this paper, the possibility of formation of mesylates by means of anode modification of cellulose by dissolving in dimethyl sulfoxide (DMSO) is shown.

## 2. Formulation of the problem and method of solution

### *2.1. Subject of investigation*

Anode modifying processes of cellulose pulp in the system –dimethyl sulfoxide- methanesulfonic acid are studied using a potentiostatic methods and preparative electrolysis. Potentiostatic measurements were carried out using a potentiostat IPC – Pro MF.

### *2.2. Materials and reagents*

All measurements were performed on a platinum electrode. We used the following reagents: DMSO (chemically pure), 75% solution of methanesulfonic acid (BASF), a cellulose - ashless filter of the brand FILTRAK and bi distilled water.

*2.3. Preparative methods of electrosynthesis*

Preparative electrolysis was carried out in a diaphragm electrolyze with anode and cathode separation cationiteof membrane brand МК-40. All measurements were performed at room temperature. As a source of direct current with adjustable voltage by used TYPE: TR-9252. Anodic current density was set at a preparative electrosynthesis according to the oxidation potentials of cellulose in stationary conditions.

The anode compartment of the electrolytic cell was filled with 50 ml of DMSO solution containing $CH_3SO_3H$ (0.4 M) and dissolved of cellulose (0.75 g/ml), the cathode compartment was billed solution water solution. Electrolysis was carried out at a temperature 40- 60□C in current of 4 hours at a current density of 5.15 mA/cm$^2$. After electrolysis, the anolyte became viscous without discoloring.

*2.4. Methods of chemical analysis*

Purification of the final product - a modified of cellulose, prepared by electrochemically, was carried out as follows: an electrolyte - methanesulfonic acid was is neutralized with aqueous ammonia solution, water and DMSO were distilled off the solvent by vacuum distillation, samples were thoroughly washed with water bidistilled water and supported on the slide glass and dried in an oven at 75$^o$C for 1 hour.

Products of electrooxidation were analyzed by infrared (IR) and quantitative X-ray spectral fluorescence spectrometry (XRF) spectrometer for IR «Nicolet 6700» the company «Thermo Nicolet» USA and «Shimadzu EDX-800 HS».

The qualitative and quantitative elemental analysis by X-ray fluorescence spectrometry «ShimadzuEDX-800 HS» was carried out in the following conditions: voltage 50 kV for the range from the titanium to uranium, 15 кВ for a range from the sodium to scandium time set 100 seconds, calculation of concentrations - by the method of fundamental parameters of the software to the spectrometer using a standard database and processing of the X-ray fluorescence spectra of the program DXP-700E (Version 1.00 Rel.017).

## 3. Results and Discussion

*3.1. The results of IR analysis*

The presence of methylsulfogroups in the product electrochemically modified of cellulose is found by IR spectroscopy. Terms of: The number of scans 32, resolution - 4 reciprocal centimeters (identification of the material). Absorption spectra taken with the prefix of frustrated total internal reflection (FTIR) in the range of wave numbers 4000 – 640 cm$^{-1}$ and in the transmission mode in the wavenumber range 4000 - 400 cm $^{-1}$ was recorded. The obtained spectra are interpreted in terms of a separate absorption maxima, and was directly compared with the spectra library standards using the program «Omnic».

The resulting product was identified as a modified cellulose mesylate (methanesulfonic acid ester of cellulose) having a gross formula $[C_6H_7O_2(OH)_{3-X}(SO_3CH_3)_3]_n$ of the following structure (Fig. 1).

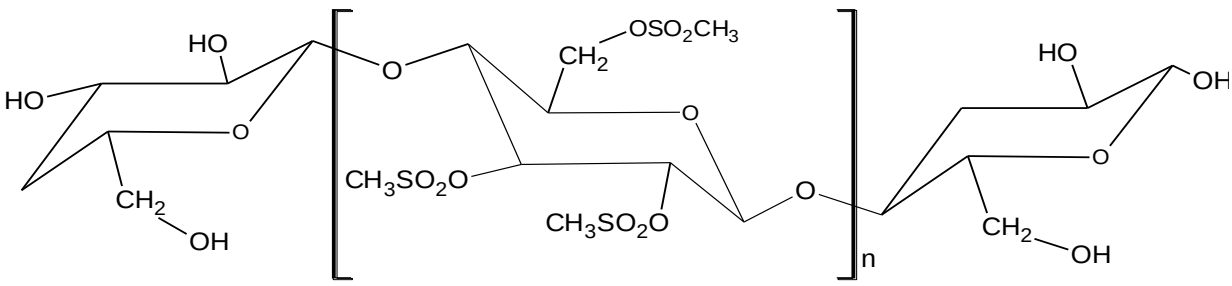


**Figure 1.** The structural formula of cellulose mesylate

The values of characteristic absorption bands of the functional groups are shown in table1.

**Table 1.** Values of the characteristic absorption bands of functional groups of the product electrochemically modified of cellulose

| The region of absorption, $cm^{-1}$ | Characteristic groups |
|---|---|
| 1480-1450 | $CH_2$– |
| 1280-1230 | $R–SO_2–R^1$ |
| 1100-1050 | S=O; R–S(O) –OH |
| 850-800 | S–O |
| 600-580 | C–S |

*3.2. The results of EDX -analysis*

The presence of sulfur atoms in the methylsulfogroups in the resulting product of the modified pulp was found by energy dispersive analysis (EDX).

EDX-analysis of data mesylate of indicate shows the presence of of sulfur atoms - 84.1% oxygen - and 13.1% carbon - 2.8%. From the results of obtained by X-ray fluorescence analysis, it is seen that the ratio of sulfur to carbon in the resulting product is 40: 1, which are close to the theoretical values calculated for the molecular level mesylate of cellulose. Such coincidence is observed when complete substitution residues methylsulfogroups three hydroxyl groups of of cellulose monomer.

Figures 2-3 are images structural changes of cellulose (before and after electrolysis) obtained by the scanning electron microscope ACPEX PSEM Express.

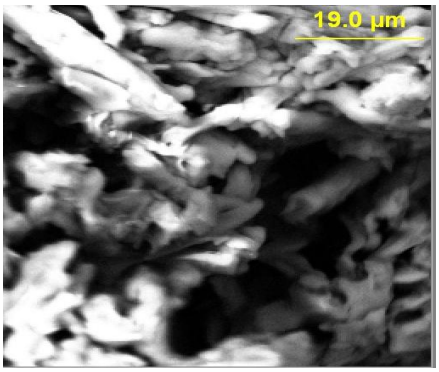


**Figure 2.** Image of scanning electron microscopy the surface of cellulose before electrolysis

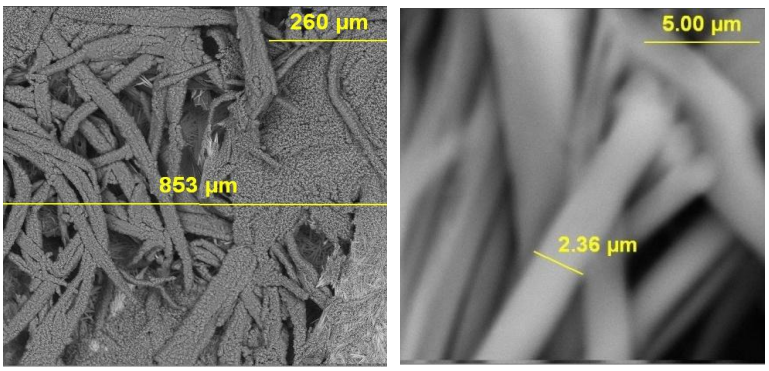


**Figure 3.** Image of scanning electron microscopy cellulose surface after electrolysis.

## 4. Conclusion

His found that by electrochemical the oxidation cellulose dissolved in dimethyl sulfoxide on the background of the electrolyte methanesulphonic acid is to modification to form esters - mesylate.

**Acknowledgements**

The work was supported by the Russian Foundation for Assistance to small innovative enterprises in the scientific and technical field (FASIE) grant № 3326GU1/2014.

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