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STUDY OF THE PARTIAL O-ALKYLATION OF COTTON CELLULOSE

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The O-alkylation of cotton cellulose with monochloroacetic acid has been studied. A change in the sequence of addition of the components to the reaction mixture enables the course of the reaction to be regulated and weakly substituted fibrous carboxymethylcellulose with valuable physicochemical and medicobiological properties to be obtained.

The O-alkylation of cotton cellulose with monochloroacetic acid (MCAA) or its Na salt takes place with the formation of Na carboxymethylcellulose (CMC). This reaction has been well studied, and by its use several types of CMC differing by their degrees of substitution (DSs), degrees of polymerization (DPs) [1-4], and solubilities have been obtained. The production of CMC includes the alkaline treatment of the initial cellulose followed by its O-alkylation with MCAA. Samples of CMC with DSs of 0.5-1.2 and DPs of 250-1000, which are readily soluble in water, are of practical interest.

In this paper we give the results of investigations of the properties of CMCs obtained from cotton cellulose by changing the sequence of addition of the reactants in O-alkylation.

The industrial method of obtaining CMCs consists in the treatment of wood cellulose with an aqueous [5] or aqueous-alcoholic [6] solution of alkali under conditions permitting a uniformly swollen cellulose with the maximum content of sorbed alkali to be obtained. The cellulose is then subjected to O-alkylation with MCAA in heterogeneous [7] or suspension [8] media. The uniformity of distribution of the substituents is determined by the degree of swelling of the initial cellulose and by the reaction conditions. Samples of CMC obtained by the traditional method with DSs of 0.5-1.2 are almost completely soluble in water.

The method of O-alkylation that we have developed consists in the preliminary impregnation of the cellulose with a 5-10% solution of MCAA in isopropyl alcohol at 15-20°C. Under these conditions the cellulose scarcely swells and does not enter into the O-alkylation reaction with the MCAA. The etherification of cotton cellulose impregnated with the MCAA solution and pressed out to a sixfold weight was conducted in 40-50% aqueous solutions of NaOH at 20-90°C.

With a rise in the temperature, the rate of etherification of cotton cellulose increases. Etherification apparently takes place at the surface of the elementary fibers without affecting their internal structure, which is responsible for their low DSs and their insolubility in water.

The product obtained in 35-45 sec at 75-87°C by the method developed scarcely dissolves in water.

We have studied the physicochemical properties of samples of O-alkylated cotton cellulose obtained by the traditional and by the proposed methods. It was established by x-radiography that the degree of crystallinity of the CMC samples obtained by the traditional method was considerably lower. This was due to the fact that the cellulose swollen in the solution of alkali swells still more during the O-alkylation process, with a rearrangement of its structural elements. This facilitates the access of the alkylating agent to the crystalline parts of the cotton fiber, and a rise in the DS takes place.

In x-radiograms of CMC with DS values close to those obtained by the proposed method, the transition from structure I to II was less pronounced. The diffractograms were similar to those of samples of cotton cellulose treated with dilute solutions of alkali.

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TABLE 1. Change in the Relative Optical Densities of the Bands of OH Groups of Samples of CMC with a DS of 0.16 as % of the Initial Values after an Exchange Reaction with D_2O

Sample	Frequency, cm^{-1}			
	3200	3360	3455	3490
Obtained by the traditional method	91.3	82.2	78.1	81.4
Obtained by the proposed method	97.6	89.8	86.2	91.4

TABLE 2. Influence of the Method of Carboxymethylation and the DS on the Physicochemical Properties of Samples of CMC

Sample	DS	Solubility in		Moisture absorption, %	Capillarity, cm
		H_2O	6% NaOH		
Medical absorbent cotton	0	–	–	340	0.6
Obtained by the traditional method	0.10	3.4	78.2	1640	3.1
	0.16	9.8	84.9	1790	3.6
	0.20	22.1	96.4	1420	3.0
Obtained by the method developed	0.10	–	24.0	2320	5.2
	0.16	–	34.5	2500	5.6
	0.21	6.2	41.2	2250	4.9

The IR spectroscopy of the products of the deuterium-exchange reaction of the weakly substituted CMC showed that the samples obtained by the traditional method were more accessible for deuterium exchange than samples with similar DSs but obtained by the proposed method (Table 1).

Thus, IR-spectroscopic and x-radiographic investigations have unambiguously confirmed a difference in the structures of CMCs with the same DS but obtained by the different methods [9].

It can be seen from Table 1 that the samples obtained by the proposed method had the highest values of the relative optical density (ROD) of the bands of OH groups.

The investigations showed that the samples obtained by the traditional method had a water solubility of 9.8%, while those obtained by the proposed method and having a similar DS were insoluble in water and their sanitary-chemical indices corresponded to those of medical absorbent cotton.

The water absorption and capillarity of the weakly substituted samples of CMC obtained by the different methods were compared with medical absorbent cotton (Table 2).

Samples of weakly substituted CMC obtained by the method developed and having a DS of 0.16 were practically insoluble in water and their water-absorbing properties and capillarity were considerably higher than those of medical absorbent cotton. Samples of CMC with a similar DS but obtained by the traditional method also had high capillarity and water absorption but they were partially soluble in water, which prevented their use in the production of cellulosic materials for medical and hygienic purposes.

Thus, the method for the partial carboxymethylation of cotton cellulose fibers that has been developed permits the production of highly hydrophobic fibrous cellulose materials that may find use in medical practice as tamponage and highly hydrophobic dressing materials and also as articles for hygienic purposes.

EXPERIMENTAL

IR spectra were taken on a Specord 75IR spectrometer. Tablets were prepared by molding ground samples with KBr [12].

X-ray studies were made on a Dron-3M diffractometer with monochromatized CuK_α radiation by reflection at a voltage of 25 kV and a current of 13 mA. The samples were prepared in the form of tablets from ground preparations.

ROD values were calculated as described by Karlivan [13].

The carboxymethylation of cotton cellulose by the traditional method was conducted by the preliminary alkaline treatment of medical absorbent cotton and gauze (5 g) with a 30% aqueous solution of NaOH in IPA at 20±2°C for 60 min, followed by O-alkylation with an 8% solution of MCAA in IPA at 55°C for 90 min.

Carboxymethylation by the proposed method was conducted by the preliminary impregnation of medical absorbent cotton (5 g) with an 8% solution of MCAA in IPA at 20 ± 2°C, followed by etherification in a 40% aqueous solution of NaOH at 87°C for 45 sec.

The O-alkylation reaction was stopped by immersing the samples in cold water and then neutralizing them with a solution of acetic acid.

The degree of substitution of the partially carboxymethylated cotton cellulose fibers was determined by a standard method [10, 11].

The deuteration of the samples for IR spectroscopy was carried out by the procedure of [12].

The moisture absorption of the highly hydrophobic cellulosic material was determined by weighing a sample of it (3 g, with an accuracy of 0.0002) which was then immersed in a beaker of distilled water (volume of water 100 ml, temperature 23±2°C) and after 0.5 h was reweighed on an analytical balance.

Moisture absorption was calculated from the formula:

$$W = \frac{m_1 - m_2}{m_2} \cdot 100\%,$$

where W is the moisture absorption, %; m_1 is the weight of the sample with absorbed water, g; and m_2 is the weight of the dry sample, g.

To determine the capillarity of the highly hydrophilic cellulosic material, a strip 30 mm wide, 100 mm long and not less than 5 mm thick was prepared, the end of which was lowered so that it just touched the surface of an aqueous solution of Basic Violet K with a concentration of 0.01% of which 100 ml had been poured into a Petri dish and was kept like that for 10 sec. The height of rise of the liquid was determined after 0.5 h.

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