

# Synthesis of Carboxymethyl Cellulose from Powder and Microcrystalline Cellulose in Isopropyl Alcohol and Ethanol Medium

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## ABSTRACT

Synthesis conditions of different substituted water-soluble carboxymethyl cellulose (CMC) based on microcrystalline and powder cellulose in isopropyl alcohol and ethanol medium are studied. Samples of water-soluble CMC with a degree of substitution of 0.38-0.40 based on microcrystalline and powdered cellulose were obtained. Also, by the one stage carboxymethylation of cellulose samples were obtained CMC samples with high degree of substitution.

**KEYWORDS:** microcrystalline cellulose, powder cellulose, carboxymethyl cellulose, etherification, degree of substitution, ethanol, isopropyl alcohol.

## 1. INTRODUCTION

Carboxymethyl cellulose (CMC) is the product of the interaction of alkaline cellulose with monochloroacetic acid or its sodium salt [1-5].

Obtaining of CMC from cellulose involves two stages of chemical reactions [6-7]. The first stage is the alkaline treatment of cellulose and the second stage is the reaction of carboxymethylation of alkaline cellulose with an alkylating reagent.

Depending on the type of raw cellulose, production technology, CMC is produced on an industrial scale, characterized by the degree of substitution (DS) and the degree of polymerization (DP). Currently produced CMC has above DS = 0.6 and DP = 400 [8].

Depending on the number of carboxymethyl groups, CMC grades are subdivided into low ( $\geq 0.5$ ), medium (0.55–0.85) and highly substituted ( $\leq 0.9$ ) grades. CMC samples with a degree of substitution greater than 0.9 are called polyanionic cellulose [9-11]. Traditional CMC acquires the ability to dissolve in water at a degree of substitution above DS = 0.5.

We have studied the possibilities of obtaining low- and highly substituted water-soluble samples of CMC based on microcrystalline cellulose (MCC) and powder cellulose (PC) by the suspension method.

This method allows to obtain products with a high degree of substitution and a uniform distribution of carboxymethyl groups along the cellulose macromolecule, which leads to an improvement in the physicochemical and operational properties of CMC.

## 2. Materials and methods

### 2.1. Material

Materials MCC (degree of crystallinity of 83%, degree of polymerization 280, particle size of 100 microns) and PC

(degree of crystallinity of 22%, degree of polymerization 420, particle size of 100 microns) were collected from the production part of Institute of Polymer Chemistry and Physics, Uzbekistan. Chemicals used during the study were sodium hydroxide (Tianye Chemicals, China), monochloroacetic acid (Azko Nobel Industrial Chemicals B.V., The Netherlands), ethanol (China), etc. All chemicals used were of reagent grade and used without further purification.

### 2.2. Synthesis of carboxymethyl cellulose

10 g of the cellulose-containing feedstock is treated with 60 ml of ethyl alcohol and dispersed for 15 minutes. With stirring, 40% NaOH solution is added. The alkaline treatment process is carried out for 90 minutes at a temperature of 16°C. Then a solution of monochloroacetic acid (MCA) dissolved in 60 ml of ethyl alcohol is added by vigorous stirring for 15 minutes at 16°C. After that, the temperature of the reaction mixture rises to 55°C and the esterification reaction is carried out for 3 hours. The product is filtered off on a glass filter and washed with aqueous ethanol. The product is dried at 60-70°C to a certain humidity.

### 2.3. Characterization

#### 2.3.1. Measurement of CMC yield

CMC yield was measured based on a dry weight basis. The net weight of dried CMC was divided by the weight of cellulose to get the yield value [12], as follow:

$$\text{CMC yield (\%)} = \frac{\text{Weight of prepared CMC (g)}}{\text{Weight of dried cellulose (g)}} \times 100 \quad (1)$$

#### 2.3.2. Determination of degree of substitution

To determine the degree of substitution, 0.5 g of dried sodium CMC was ashed gently between 45°C and 55°C for 24 h, and then dissolved in 100 mL of distilled water. 20 mL of this solution was titrated with 0.1 N sulphuric acid using methyl red as an indicator. After the first end point, the solution was boiled and titrated to a sharp end point. The carboxymethyl content was calculated from the degree of substitution [13], as follow:

$$\text{DS} = \frac{(0.162 \times B)}{(1 - 0.08 \times B)} \quad (2)$$

$$B = \frac{(0.1 \times b)}{G} \quad (3)$$

where, b is the volume (in mL) of 0.1 N sulphuric acid and G is the mass of pure CMC in grams.

### 2.3.3. Moisture content and ash content

Moisture content was determined at 105°C after 2 h in an oven. [14]. Also, the amount of ash was estimated by igniting the sample, at 58-60°C, in a muffle furnace [15].

### 2.3.4. CMC content

Exactly 1.5 g of CMC was added to 100 mL of 80% aqueous methanol solution. This mixture was stirred, kept for 10 min and filtered. The cake was washed with 100 mL of fresh 80% aqueous methanol and dried to obtain pure CMC [16]. The CMC content was calculated as follows:

$$\text{CMC content (\%)} = \frac{W}{W_0} \times 100 \quad (4)$$

where  $W_0$  (g) is the weight of sample before washing and  $W$  (g) is the weight of washed sample.

### 2.3.5. Determination of solubility

The solubility technique of Na-CMC is based on the dissolution of the sample in water, followed by filtration of this solution through filter funnels.

The filtering funnels are dried to constant weight for 2 hours at a temperature of 105°C, followed by cooling in a desiccator to room temperature.

700 g of Na-CMC solution are prepared with a mass fraction of 0.1% in terms of an absolutely dry technical product.

Dissolution is carried out for at least 2 hours with stirring with a propeller-type stirrer.

The resulting solution settles for 1.0-1.5 hours to settle insoluble particles and is filtered through a filter funnel on a water-jet pump, while the precipitate is quantitatively transferred to the filter. The filter residue is washed with 150-200 ml of distilled water with stirring with a glass rod, then washed with 10 ml of ethyl alcohol, and then dried to constant weight ( $m_2$ ) at a temperature of 105°C.

The solubility of Na-CMC in water ( $X_i$ ) in percent is calculated by the formula:

$$X_i = \frac{(m_1 - m_2)}{m_1} \cdot 100 \quad (5)$$

where  $m_1$  is the mass of the Na-CMC sample in terms of absolutely dry matter, g;

$m_2$  - mass of filter cake, dried to constant weight, g.

### 2.3.6. Infrared spectroscopic analysis

Infrared spectra of Na-CMC samples are recorded on a SPECORD IR-75 instrument in the range of 4000  $\text{cm}^{-1}$  - 400  $\text{cm}^{-1}$ .

## 3. Results and discussions

The esterification of MCC and PC was carried out according to the known suspension technology [17, 18] in ethanol. To do this, 20 ml of ethanol is added to 10 g of MCC or PC with vigorous stirring for 20 minutes, followed by the inclusion of 30 ml of a 40% aqueous solution of sodium hydroxide. Then 25 ml of ethyl alcohol containing 11.0 g of dissolved MCC was gradually added to the mixture, and stirred for 3 hours at 70 °C. The reaction product is filtered off, washed with ethyl alcohol and dried to constant weight at a temperature of 80°C.

The results of suspension carboxymethylation of samples of cellulose-containing raw materials of different nature and

dispersion under the same conditions are presented in table 1.

**Table 1: Physicochemical characteristics of CMC samples obtained from CC, PC and MCC**

Raw celluloses	DS of CMC	Solubility in water, %	CMC content, %	pH of 1 % solution
Cotton cellulose	0,65	97,0	53,0	9,6
MCC	0,70	100	73,0	8,9
PC	0,78	100	78,0	8,5

As can be seen from table 1, with the suspension method of obtaining such quality indicators of CMC as DS, solubility in water and the content of the main substance in the samples is quite high.

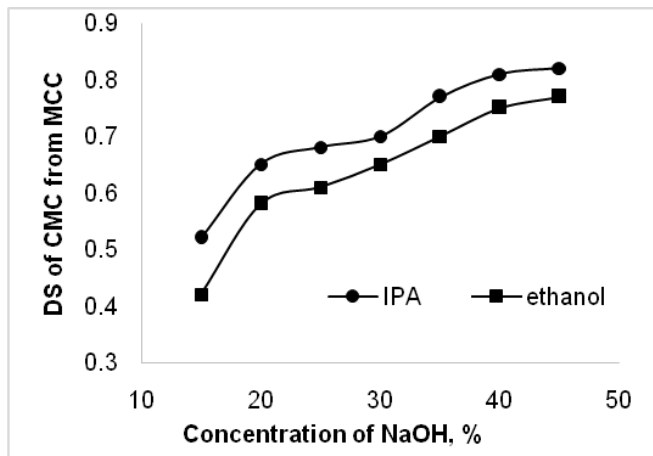
The high DS value of CMC obtained by the suspension method is explained by the low water content in the reaction medium, as a result of which the rate of side reaction of hydrolysis of MCC is significantly reduced in the aqueous organic medium, and as a result, the useful coefficient of the flow of the esterifying agent increases. And the high value of the solubility index of CMC samples is apparently explained by the high DS CMC values, in particular, its compositional homogeneity and low DP values.

The absence in Uzbekistan of the production of organic solvents, such as isopropyl alcohol (IPA), benzene, toluene and others, hinders the development of suspension technology for the production of CMC. Suspension technology of special grades of CMC can be mastered in the republic using technical grades of ethyl alcohol.

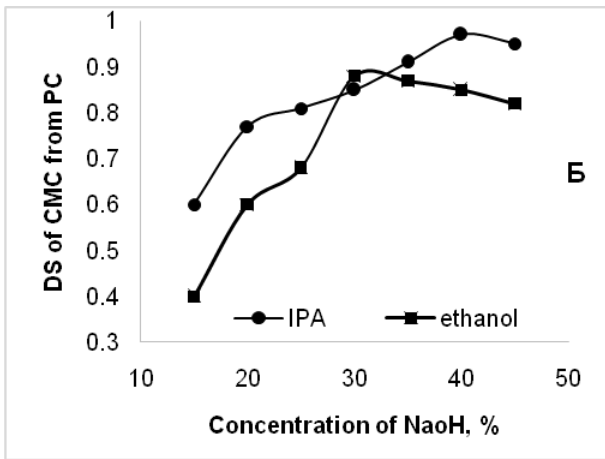
At present, the industrial production of IPA has not been mastered in the republic. Thus, local ethyl alcohol can be used in the production of CMC in a slurry manner.

We studied the effect of the carboxymethylation reaction of MCC and PC on the physicochemical parameters of the obtained CMC samples and determined the optimal conditions for the preparation of highly substituted CMC samples from the MCC and PC in the suspension method in isopropyl and ethyl alcohol.

Comparative studies of the alkaline treatment of MCC and PC at various concentrations of sodium hydroxide in the medium of IPA and ethanol were carried out.



**Fig. 1: Dependence of DS of CMC from MCC on alkali concentration**

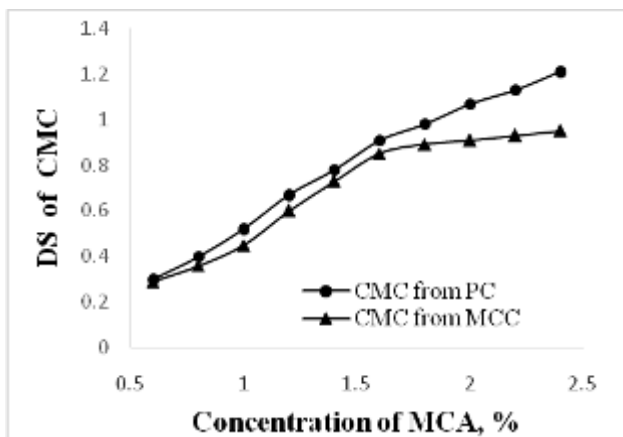


**Fig. 2: Dependence of DS of CMC from PC on alkali concentration**

Fig. 1 and 2 shows comparative data on the treatment of MCC and PC with alkali solutions of various concentrations in the environment of solvents of IPA and ethanol. With an increase in the concentration of sodium hydroxide solution up to 40% for MCC treatment and 30% for PC, the DS of CMC increases to 0.82-0.94 in the IPA medium and 0.75-0.88 in the ethanol medium, respectively.

The use of organic solvents in the process of carboxymethylation of cellulose-containing raw materials plays an important role, in particular, in increasing the availability of chemicals due to their low polarity than water, on the one hand. On the other hand, a decrease in the amount of water in the reaction medium, correspondingly reducing the rate of a side reaction of hydrolysis of MCA [19]. The polarity of the solvents increases in the order of IPA-ethanol-water. The higher the polarity, the lower the reaction efficiency [20]. With MCC carboxymethylation, the maximum DS values are reached at an alkali concentration of 40%, and in the case of esterification of an amorphous PC, a 30% sodium hydroxide solution is required. This fact is explained by the fact that the MCC has a highly ordered crystalline structure, and its crystallinity is 83% in the ratio of the crystallinity of the PC 22%. Therefore, for the penetration of the alkylating agent into the crystal structure of MCC, more concentrated alkali solutions are required than in the case of PC.

High values of DS of CMC from MCC and PC were achieved using 40% and 30% NaOH solutions. With a further increase in the concentration of alkali solution, a decrease in the DS of CMC values occurred. This is apparently due to the formation of sodium glycolate, which is known as a by-product in the synthesis of CMC [21].

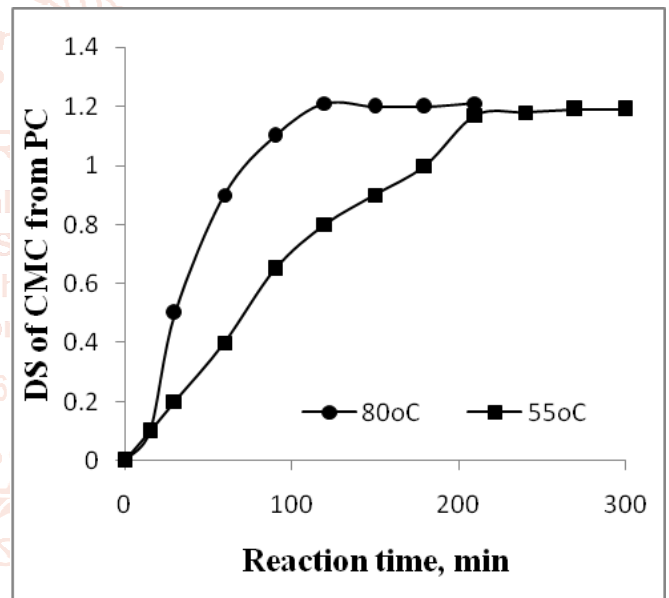


**Fig. 3: Dependence of DS of CMC on the consumption of an alkylating agent**

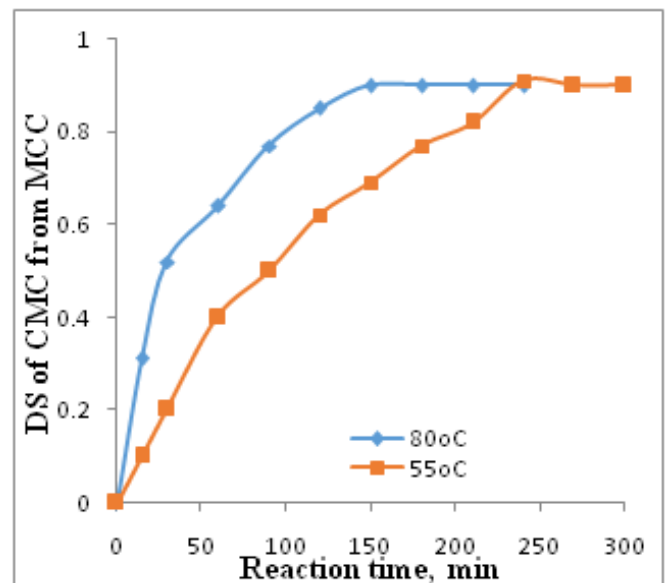
Figure 3 shows the results of the carboxymethylation reaction of alkaline samples of MCC and PC, which were obtained by treating them with 30 and 40% sodium hydroxide solutions, followed by etherification with various concentrations of alkylating agents. It can be seen that with an increase in the consumption of MCC to 2.2-2.4 relative to the elementary element of the feedstock, the SZ of the CMC samples when using the PC reaches 1.2. Under the same conditions of carboxymethylation, MCC in ethanol with vigorous stirring, DS CMC reached 0.89.

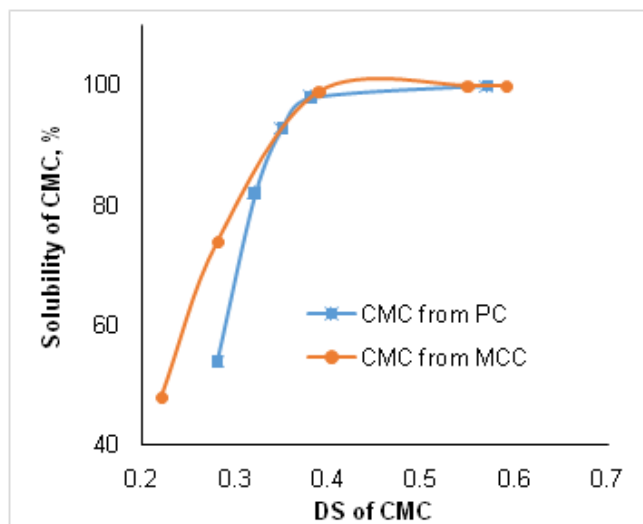
The dependence of the duration of the esterification reaction on the DS of CMC at a temperature of 55°C and 80°C was also investigated (Fig. 4.).

With an increase in the duration of the carboxymethylation reaction, the DS of CMC increases, approaching the maximum. With an increase in temperature from 55°C to 80°C, the reaction time sharply decreases. The high reactivity and low molecular weight of MCC and PC allow their alkylation to be carried out at small liquid modules, using reagents more efficiently for a short time and under significantly mild conditions. In addition, the high reactivity of the PC and MCC makes it possible to obtain their derivatives in colloidal form [22].



**Fig. 4: Change DS of CMC from PC on duration of reaction**





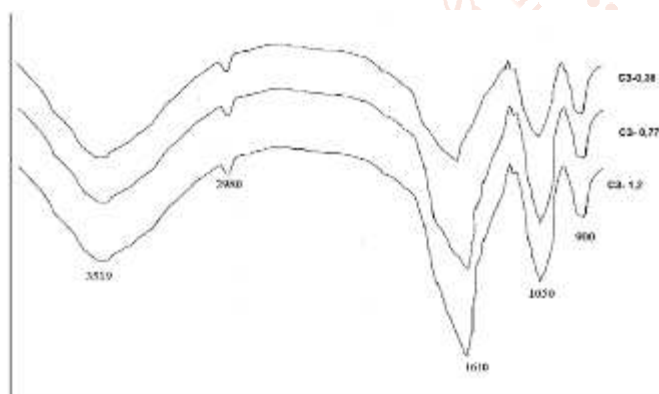
**Fig. 5: Solubility of CMC samples with a change in their DS**

Depending on the DS and DP, CMC is soluble in water, aqueous solutions of alkalis and practically insoluble in organic solvents. It is known that the complete solubility of Na-CMC is ensured with its  $DS \geq 0.60$  in water and  $DS \geq 0.45$  in aqueous solutions of alkalis [23].

The solubility of CMC samples from MCC and PC from their DS was studied.

As can be seen from Figure 6, the solubility of CMC samples obtained from MCC and PC reaches high values at low DS values. Starting from  $DS=0.35$ , CMC samples are completely soluble in water, which can be explained by the low values of the initial samples and the uniform distribution of substituents along the cellulose macromolecule.

The IR spectrum of CMC samples (Fig.6) shows that the carboxymethyl and hydroxyl groups of the polymer are in the absorption band of 1618, 1426, and 1300  $cm^{-1}$ , respectively.



**Fig. 6: IR spectra of CMC samples**

The IR spectrum of CMC samples shows that the carboxymethyl and hydroxyl groups of the polymer are in the absorption band of 1618, 1426, and 1300  $cm^{-1}$ , respectively. According to the presented data, the absorption bands at a wavelength of 1620 and 1423  $cm^{-1}$  correspond to two carboxyl and methyl functional groups of CMC [24]. Additional absorption bands at 2152 and 2376  $cm^{-1}$  may be associated with the presence of their by-products in CMC — a reaction or a combined bond of CMC with water [25]. Obviously, the wide absorption band at 3432  $cm^{-1}$  and 2909  $cm^{-1}$  is characterized with asymmetric vibrations of the hydroxyl ( $-OH$ ) and methylene ( $C-H$ ) groups, respectively.

These types of bonds have a light terminal hydrogen atom. Oscillations of this kind of bonds in the molecule are experienced only by a slight effect from the rest of the molecule. It can be argued that a set of energetically unequal hydrogen bonds is realized in such compounds [26,27]. Strong vibrations at 1610  $cm^{-1}$  confirmed the presence of the carbonyl group of the carboxymethyl anion ( $-C=O$ ). The absence of a wide band in the region of 2500-2800  $cm^{-1}$  and the high value of the position of the stretching vibration band of the carboxyl group indicate that the carboxyl groups are not at a high level, and they do not form hydrogen bonds with each other. Absorption bands of about 1423 and 1325  $cm^{-1}$  belong to the  $-CH_2$  group and the hydroxyl group ( $-OH$ ), respectively. Absorption in the region of 1140-1065  $cm^{-1}$  refers to vibrations of CO groups. With an increase DS of CMC SC, the intensity of the bands decreases, characterizing the planar deformation vibrations of hydroxyl groups. A band appears characterizing the vibrations of C-O-C of the simple ether bond. [28.29].

#### 4. Conclusion

As a result of the studies, low and high substituted CMC samples based on MCC and PC were obtained and characterized. Maximum of solubility of low substituted CMC was reached at  $DS=0.38$  by consumption of MCA

It is known that obtaining highly substituted CMC i.e. polyanionic cellulose (PAC) is carried out by multi-stage carboxymethylation of the feedstock, which leads to an increase in the cost of the final product due to an increase in chemical reagents and energy consumption. It is shown that the use of PCs as a starting material in one-stage carboxymethylation makes it possible to obtain PAC samples, which are a valuable reagent for the oil and gas industry, in the production of drilling and other solutions in oil and gas production.

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