CENTRAL ASIAN JOURNAL OF THEORETICAL AND APPLIED SCIENCES

Volume: 04 Issue: 06 | Jun 2023 ISSN: 2660-5317
https://cajotas.centralasianstudies.org

Synthesis of Low-Substituted Carboxymethylcellulose in Ethyl Alcohol Medium

Goyibnazarov I. Sh., Yuldoshov Sh. A., Sarimsakov A. A.
Institute of Polymer Chemistry and Physics of Academy of Sciences of the Republic Uzbekistan

Received 4th Apr 2023, Accepted 6th May 2023, Online 17th Jun 2023

Abstract: *The circumstances of carboxymethylation of cotton cellulose were investigated in this study when 0.2-1.0 mol of alkylating agent was utilized per elementary unit in ethanol medium. At the same time, the influence of the reaction conditions (alkali concentration, alkali treatment conditions, monochloro acetic acid (MCA) consumption, carboxymethylation duration, etc.) on product qualities was investigated.*

Keywords: *sodium carboxymethylcellulose, partially substituted, ethyl alcohol, carboxymethylation, reaction efficiency.*

1. Introduction. Sodium carboxymethylcellulose (Na-CMC) use the extensive is due to its ability to dissolve in water and aqueous solutions of alkalis. Partially substituted Na-CMC preparations does not widely used, they cannot be used in medicine and for the production of hydrophilic fibers for medical purposes [1].

Currently, medium and highly substituted grades of Na-CMC is use mainly on an industrial scale [2-4].

Currently, there has been an increase in study on the manufacture of Na-CMC in organic solvents such as isopropyl alcohol, ethanol, benzene, toluene, and others, which aids in the manufacturing of similar substituted products [5].

In some works, it is proposed to obtain Na-CMC by treating cellulose with an aqueous solution of NaOH in an ethanol medium with the addition of monochloro acetic acid or its sodium salt [6].

Na-CMC can also be synthesized via the solid phase approach or by treating cellulose with an aqueous solution of NaOH in an ethanol medium, followed by alkylation with an aqueous solution of MCA [7,8].

To simplify the process of obtaining Na-CMC, it is proposed to treat cellulose with an alkali and an alkylating agent simultaneously, for example, cellulose in an ethanol medium is treated with a homogeneous solution of MCA and NaOH in aqueous alcohol, or cellulose in an aqueous medium is treated with MCA or Na-MCA in the presence of NaOH [8].

The procedures described above were utilized to obtain medium and highly substituted grades of Na-CMC for a variety of applications. The sampling properties of under substituted Na-CMC in organic solvents, on the other hand, have not been investigated.

The findings of a study on the reaction of partial carboxymethylation of cellulose in ethanol medium, as well as the effect of carboxymethylation settings on the physicochemical parameters of Na-CMC, are presented in this paper.

2 Materials and method

2.1 Materials and raw materials

As research objects, polymerization degree (DP) 1000-2600 (MEDIKOT LLC), sodium hydroxide (Kimyo Farm Invest LLC), monochloro acetic acid (Azko Nobel), and ethyl alcohol (ALFAMEDIKA LLC) were utilized.

2.2 Carboxymethylation of cotton cellulose in the ethanol

Alkaline treatment of cellulose was carried out with 30% aqueous sodium hydroxide solution at a temperature of 20℃ during 60 minutes. Carboxymethylation was carried out with a solution of MCA in ethanol, where in serial experiments the temperature and duration of alkylation were changed, the concentration of MCA

2.3. Determination of quality indicators of CMC

2.3.1 Degree of substitution determination of Na-CMC

The approach is based on the precipitation of Na-CMC with copper (II) sulfate in the form of a copper salt and the iodometric measurement of copper in Cu-CMC [21].

To determine DS, 1.5 g of Na-CMC mixed with 20 ml 94% of ethanol solution and dissolved in 100 ml of distilled water. After 25 ml of 0.05 M copper (II) sulfate solution, ammonia solution is added and the pH reduced to 4.0-4.1. The resultant precipitate is washed, filtered, and dried to consistent weight. Then 3-4 mL 94% of ethanol solution, to the dried Cu-CMC sample, 100 mL of distilled water and 8 mL 5% of ammonia solution added. Following that, 6.0 M acetic acid added to the previously obtained solution until the color changes from blue to light green, at which point 5 mL of acetic acid and 15 g of KI are added and titrated after 10 minutes with 0.1 M solution of sodium thiosulfate.

The degree of substitution ("γ") is calculated according to the equation:

$$\gamma = \frac{162 \cdot X_1}{31.77 - (0.888 \cdot X_1)} \cdot 100 \quad (1)$$

Where, 162 is the molar mass of the elementary unit of cellulose macromolecule, g/mol; 0.888 is the increase in the molar mass of the polymer unit when one $Cu(CH_2COO)_2$ group is introduced into it, g; 31.77 - molar mass of copper equivalent in the reaction with carboxymethyl cellulose, g. The mass fraction of copper in the copper salt of CMC (X_1, %) is calculated according to the following equation:

$$X_1 = \frac{V \cdot 0.006357}{M \cdot 100} \quad (2)$$

where V is the volume of sodium thiosulfate used for titration, mL; M is the mass of the copper salt of CMC; 0.006357 the mass of copper corresponding to 1 ml of 1 M $Na_2S_2O_3$ solution, g.

Results and discussion

To investigate the influence of MCA concentration on the carboxymethylation processes of cotton cellulose in ethanol medium, different concentrations of MCA (0.2-1.0 mol per elementary unit) were added to alkaline cellulose. The outcomes are depicted in Fig 1.

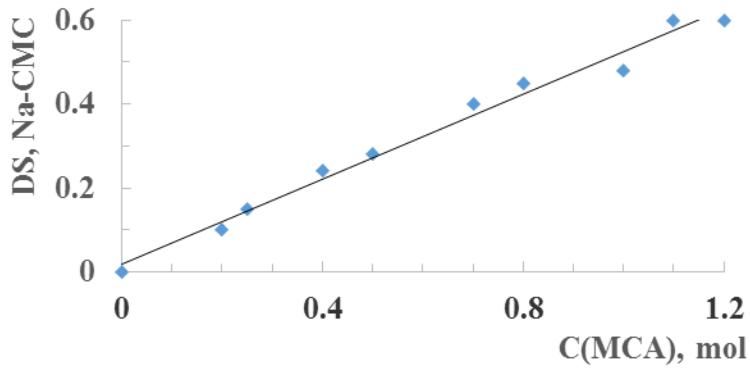

Figure 1. Dependence of DS Na-CMC on MCA concentration *(DP_{org}=1000, $\tau_{alkali\ treat}$=60 min, $t_{alkali\ treat}$=25±1℃=25±10S, t_{alkyl}=120 min, t_{alkyl}=55±1℃, bath module 1:10)*

According to the findings presented, an increase in MCA concentration leads to an increase in Na-CMC DS. The efficiency of employing MCA is 55-58% when 0.2-0.7 mol of MCA is added. And it reduce to 42-51% when 1.0 and 1.0 mol of MCA are added. This appears to be due to the difficulty of replacing the next carboxymethyl group on the already partially substituted glucopyranose ring due to electrostatic repulsion of similar charged groups, as well as the partial decomposition of excess MCA in an alkaline environment.

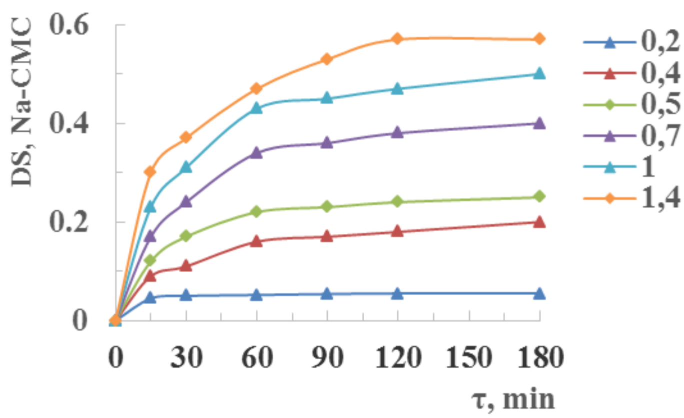

Figure 2. Dependence of DS Na-CMC on MCA concentration

(DS_{org}=1000, $\tau_{alkali\ treat}$=60 min, $t_{alkali\ treat}$=25±10S, t_{alkyl}=120 min, t_{alkyl}=55±1℃, bath module 1:10)

Figure 2 illustrate that the DS of Na-CMC increase rapidly at the start of the alkylation reaction. The sample DS grow rapidly in the first 60 minutes, then increase steadily to its maximum value after 120 minutes and then remains unchanged.

A similar result persists at various alkylating agent concentrations (from 0.2 to 1.0 mol).

The results of studies on the influence of the temperature of the reaction of cellulose carboxymethylation in an ethanol medium show that an increase in the duration of the reaction increases the DS of the products (Fig. 3).

The direct proportional dependence of CZ Na-CMC on MCA concentration (up to 0.7 mol MCA concentration) maintains at all reaction temperatures. Increasing the temperature, however, from 45℃ to

55℃ does not change the DS of Na-CMC. It can be seen that increasing the temperature above 45℃ leads to an increase in the decomposition rate of MCA. Therefore, the efficiency of using MCA decrease.

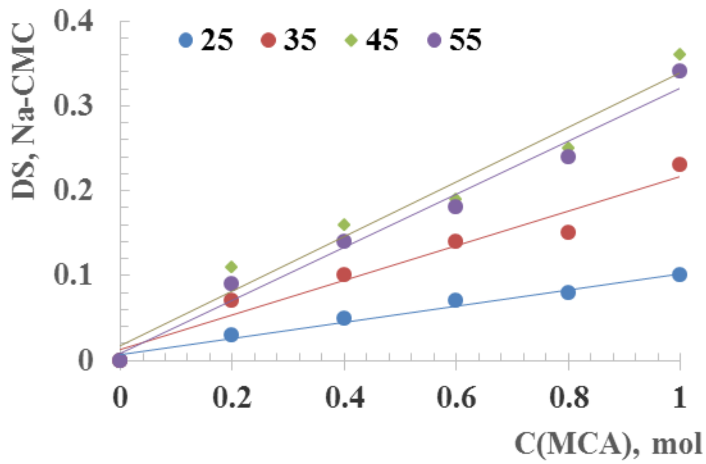

Figure 3. Carboxymethylation of cotton cellulose (DP=1000) in the ethanol medium depending on MCA concentration and reaction temperature

Using the Arrhenius equation, we calculated the rate of the carboxymethylation reaction at various temperatures and MCA concentrations, and we investigated the rate of the carboxymethylation reaction's relationship on MCA concentration and reaction temperature.

Table 1 shows the effect of MCA content and reaction temperature on the rate of carboxymethylation of cotton cellulose in the environment.

C_{MCA}, mol	The rate of carboxymethylation,$v*10^{-6}$ mol/l*sec			
	25^0C	35^0C	45^0C	55^0C
0,2	2,65	4,66	8	10
0,3	9	16	27	31
0,4	26	41	66	60
0,7	58	116	203	208

As seen in the table, increasing the concentration of MCA as well as the temperature increases the rate of the carboxymethylation reaction.

Conclusion

As a consequence of the study, low-displacement samples of Na-CMC with a DS of 0.1-0.5 were obtained when 0.2-1.0 mol of alkylating agent was spent per elementary unit of cellulose. The rate of carboxymethylation reaction was also investigated at various MCA flow rates and temperatures. The data acquired allow for the reduction of Na-CMC costs by enhancing quality parameters and minimizing alkylating agent consumption.

List of used literature

1. Rachtanapun P., Rattanapanone N. Synthesis and characterization of carboxymethyl cellulose powder and films from Mimosa pigra // Journal of Applied Polymer Science. 2011. vol. 122(5). pp. 3218-3226. https://doi.org/10.1002/app.34316.
2. Sarymsakov A.A. Medium- and low-substituted CMC: production, properties and application. Tashkent: Fan. 2005. pp. 5-14

3. Yuldoshov Sh.A., Shukurov A.I., Sarymsakov A.A., Rashidova S.Sh., "Preparation of carboxymethyl cellulose solutions by freezing-thawing" // Universum: Chemistry and Biology. 2016. vol. 23(5). pp. 1-9
4. Yuldoshov Sh.A., Sarymsakov A.A., Rashidova S.Sh., "Investigating of synthesizing possibility of low viscosity carboxymethyl cellulose based on microcrystalline cellulose". Institute of Plant Chemistry named after acad. S. Yu. Yunusov UzAS, Tashkent, 2015. March 12. pp. 191.
5. Liu Y.H., Wu M.Z., , Cui L., D. P. Synthesis of carboxymethylpotato starch and comparison of optimal reaction conditions from dif-ferent sources // Polymers for Advanced Technologies. 2008. Vol. 19(9). pp. 1185–1192. http://dx.doi.org/10.1002/Pat.1102.
6. Yuldoshov Sh.A., Goyipnazarov I.Sh., Nishonova S.R., Sarymsakov A.A., Karabaeva B.S., Azizova M.A. Synthesis of carboxymethyl cellulose from powder and microcrystalline cellulose in isopropyl alcohol and ethanol medium // International Journal of Trend in Scientific Research and Development. 2021. Pp. 56-61.
7. Yuldoshov Sh.A., Yunusov Kh.E., Sarymsakov A.A. Goyipnazarov I.Sh Synthesis and characterization of sodium-carboxymethylcellulose from cotton, powder, microcrystalline and Nanocellulose // Polymer Engineering & Science, 2022. 62(3), 677-686. https://doi.org/10.1002/pen.25874.
8. Adinugraha M.P., Marseno D.W., & Haryadi. Synthesis and charac-terization of sodium carboxymethylcellulose from cavendish banana pseudostem // Carbohydrate Polymers. 2005. Vol. 62(2). pp. 164–169. http://dx.doi.org/10.1016/j.carbpol.2005.07.019.