

STRUCTURE AND RHEOLOGICAL PROPERTIES OF WATER SOLUTIONS OF SODIUM CARBOXYMETHYL STARCH OBTAINED IN SOLID PHASE

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ABSTRACT

Synthesis of the sodium salt of carboxymethyl starch was carried out by modification of corn starch in the solid phase. It was determined that moistening of the reaction mixture by small quantities of water, alcohols, and their water solutions caused a considerable increase in the degree of substitution of obtained products. By varying the ratio of the initial reagents and nature of solvent for moistening of reaction mixture samples of the sodium salt of carboxymethyl starch with the degree of substitution from 0.12 to 0.95 have from obtained. It was shown that the degree of substitution in obtaining product depended not only on the ratio of initial reagents but also on the nature of the used solvent. The morphology and structure of samples of the sodium salt of carboxymethyl starch have been investigated. By method of rotational, viscometry rheological properties of water solutions of the sodium salt of carboxymethyl starch was investigated and it was determined that with increasing degree of substitution dynamical viscosity of their solutions has increased.

Keywords: Corn Starch, Sodium Salt of Carboxymethyl Starch, Degree of Substitution, Morphology, X-Ray Diffraction, Rotational Viscometry.

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INTRODUCTION

Starch is a biological natural product and is not dangerous for the environment which has increased its attractiveness for obtaining different materials on its base.¹⁻⁵ The presence of its structure of different reactive functional groups which can be modified also has starch perspective natural polymers on a base of which different derivatives have been synthesized.⁶⁻⁹ One of the important ways to modify starch is to obtain its base water-soluble derivatives because starch itself does not dissolve in water, which has restricted its practical use. The sodium salt of carboxymethyl starch (Na-CMS) can be attributed to the most used water-soluble derivatives of starch because it has been used as a component of the boring solution in oil gas-extractive industry, for flotation enrichment mining rocks in mining-chemical production, as stabilizers of water solution emissions and so on.¹⁰⁻¹³ As shown from the above-cited date, Na-CMS has been used as water solution rheological properties of which have an important role in the elaboration of different technological processes. The aim of this investigation is carboxymethylation of corn starch in the solid phase by using mixtures of periodic action and investigating the rheological properties of water solutions of obtained samples of Na-CMS.

EXPERIMENTAL

Materials

For modification, corn starch (Uzbekistan) extracted from local types of corn has been used. NaOH and sodium salt mono chloroacetic acid (Na-MCAA) were used in the work of mark “chemical-pure” (Chimreactive, Russian).

General Procedure

Synthesis of Na-CMS was carried out by carboxymethylation of corn starch by Na-MCAA in the presence of NaOH in the solid phase. The modification was carried out in a mechanical mixer of periodic

action equipped with paired Z-shaped blades rotating in different directions around the horizontal axis and providing high friction of the reaction mixture (Fig.-1).

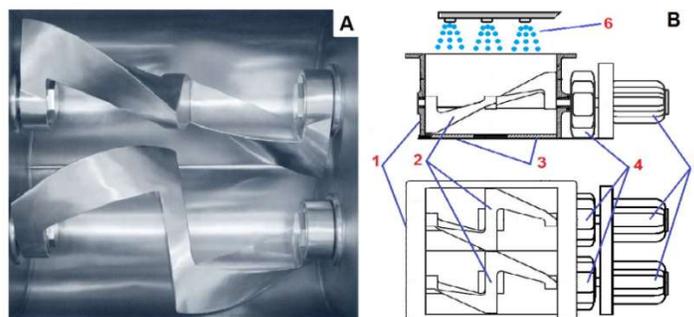


Fig.-1: Photography of Inner Appearance Of Bunker (A) and Scheme (B) of Two Screw Mixer Used for Starch Carboxymethylation: 1-Bunker; 2-Z-Figurative Blades; 3-Unlocked Folds; 4- Rotors; 5- Electric Motors; 6- Equipment for Injection of Solvent in Reaction Mixture.

A synthesis of Na-CMS load of initial components in the bunker has been carried out in the following order: starch, then pounded NaOH by three portions with interval 2-3 min, and then Na-MCAA also by three portions with interval 2-3 min. Simultaneously, their mixing and solvent injection was carried out. At injection of solvent in the reaction mixture in the bunker, it is necessary to watch for its consistency because it is inadmissible of stickiness-formation. Carboxymethylation of starch was carried out at a temperature of 25-28°C. Purification of Na-CMS from impurities was carried out by precipitation of its water solution in ethanol. Before the determination of DS of samples of Na-CMS, they were purified by triple re-precipitation.

Method of Investigation

The DS of the Na-CMS samples was determined according to the method described in the works.^{14,15} SEM-analysis were carried out on the microscope EVO MA10 (Carle Zeiss, Germany), equipped with an INCA Energy microanalyzer (Oxford Instruments, Great Britain). X-ray structural analysis of Na-CMS samples was carried out on a diffractometer «Panalytical Empyrean» (The Netherlands) equipped with Cu-tube ($K\alpha_1=1.5406\text{\AA}$). Measurements were carried out at room temperature in an interval of 20 in the range of corners 0-90° in the regime of step-by-step scanning with a step of 0.013° and duration of signal accumulation in point 5 s. Rheological investigations of water solutions of Na-CMS have been carried out on rotational viscosimetry «Rheotest-2» of type RV (Germany) with using of the system of the cell of coaxial cylinders S/S2 in a wide range of rate gradient ($\dot{\gamma}$) and temperature (T) by the method.¹⁶ Effective viscosity η_{eff} of solutions was calculated by the equation:

$$\eta_{eff} = \sigma / \dot{\gamma} = z\alpha / \dot{\gamma}$$

Where: σ - shear stress, Pa·s; $z=0.58$ constant of cell; α – reading of device determined at different values of $\dot{\gamma}$, s⁻¹.

RESULTS AND DISCUSSION

Starch Carboxymethylation

Methods for obtaining Na-CMS can be divided into the so-called "solid phase", "aqueous" (carried out in aqueous media), and "suspension" (carried out in an organic solvent).^{17,18} At this, the DS of Na-CMS obtained in organically mediums is higher than products obtained in water solutions or solid phase.^{19,20} But from the technological point of view, the solid-phase method is preferable, since it is simpler in hardware design, economical since it does not require a large amount of solvent, and the resulting product is easy to dry. By this reason in this investigation to obtain Na-CMS, namely, the solid-phase method was used. Preliminary studies have shown that mixing the reagents in a completely dry state does not lead to the production of Na-CMS with a degree of substitution of more than 0.15, even for a long time (about 2 hours). By this reason, at mixing of reagents in a mixer for carrying out of the reaction of starch carboxymethylation injection of necessary quantities of different solvents (water, ethanol, and isopropanol, or their water solution with concentrations 20 and 80%) has been carried out. At this quantity

of injected solvents depends on their nature, quantities of water, and water solutions of alcohols were about 20% from the mass of reagents but dried alcohols – before 35% owing to their light evaporation. It was shown that using this method has allowed to increase DS of obtained samples of Na-CMS. In Fig.-2 changing of DS of samples Na-CMS in dependence on time of starch modification at using water and 80% solution of ethanol used for moistening of reaction, systems is presented.

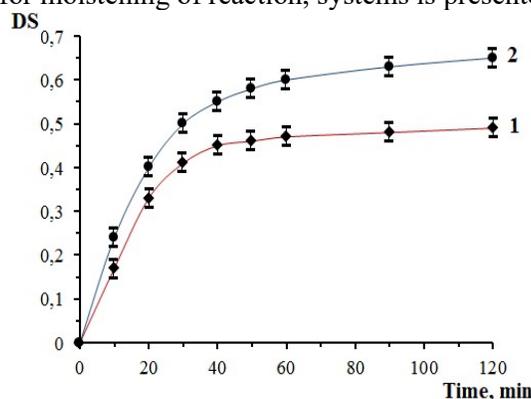


Fig.-2: Influence of Reaction Duration on DS of Obtained Samples Na-CMS in presence of 1-water; 2-80% solution of Ethanol. The Ratio of Reagents in Molar Fraction 1:1:1

From Fig.-2 it is shown that with an increase in the duration of carboxymethylation starch, the DS of forming Na-CMS also has increased. At using moistening 80% solution of ethanol DS of Na-CMS was higher than using water and also DS increased during 30 minutes and then didn't increase. And by this reason, at Na-CMS synthesis mixing of reagents in a reactor has carried at during 30 minutes. The influence of the mole ratio of reagents on the DS of obtaining Na-CMS has been investigated (Table-1) and it was shown that increasing NaOH and Na-MCAA quantity has caused its increase. In this calculation, the molecular mass of starch, and the molecular mass (162 g/mole) of anhydroglucose unit (AGU) from which starch has consisted were used.

Table-1: Influence of Molar Ratio of Reagents and Solvents on DS obtained Samples of Na-CMS (Duration of Modification 30 min. Temperature 25°C)

No.	The molar ratio of reagents, AGU: NaOH: Na-MCAA	Solvent using for moistening of the reaction mixture	DS of Na-CMS
1	1:0.5:0.5	water	0.21
2	1:1:1	water	0.42
3	1:1.25:1.25	water	0.54
4	1:1:1	ethanol (absolute)	0.32
5	1:1.25:1.25	ethanol (absolute)	0.47
6	1:1:1	20% solution of ethanol	0.64
7	1:1.25:1.25	20% solution of ethanol	0.72
8	1:1:1	80% solution of ethanol	0.74
9	1:1.25:1.25	80% solution of ethanol	0.81
10	1:1:1	isopropanol (absolute)	0.68
11	1:1.25:1.25	isopropanol (absolute)	0.91
12	1:1:1	20% solution of isopropanol	0.73
13	1:1.25:1.25	20% solution of isopropanol	0.81
14	1:1:1	80% solution of isopropanol	0.82
15	1:1.25:1.25	80% solution of isopropanol	0.95

As shown from table value of DS of forming Na-CMS has increased with increasing mole part of NaOH or Na-MCAA. DS is higher at using alcohols and their water solution in comparison with samples obtained at using water. Also, it was determined that at using alcohols for moistening of dry mass DS of forming products was lower in comparison with using their water solution. This has shown that alcohol has catalytically effect at starch carboxymethylation, which has been displayed in greater degree for isopropanol. These data have proved literature data by polysaccharides carboxymethylation^{21,22} where it

has been shown that at suspension method of Na-CMS obtained the DS of obtained samples was higher in comparison with samples obtained in water solutions. Investigation of solubility of obtained samples of Na-CMS in water has shown that samples with DS more than 0.15 have dissolved in water at room temperature. Samples of Na-CMS obtained using ethanol, isopropanol, and their 80% water solutions have dissolved easily and quickly in comparison with samples, obtained in presence of water. It was established that the nature of the solvent used as moistening the reaction mixture has influenced not only DS of obtained samples of Na-CMS but also their structure. For this reason, obtained samples of Na-CMS have been investigated by methods of XR- and SEM-analysis.

SEM Analysis

In Fig.-3 SEM-microphotographic images of starch and samples of Na-CMS obtained in presence of different solvents used for moistening the reaction mixture are presented.

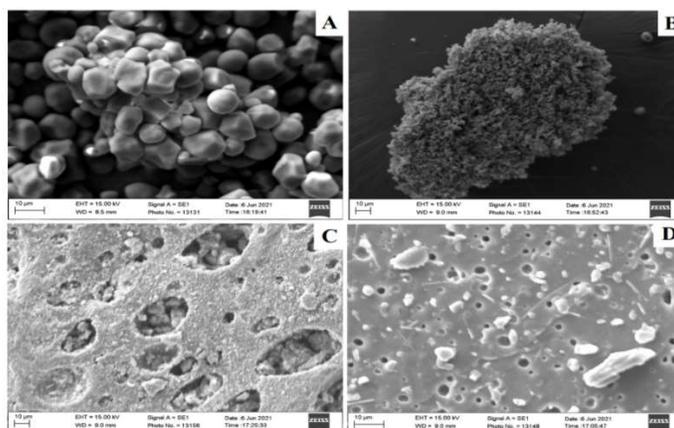


Fig.-3: Microphotography of Native Starch (A) and Samples of Na-CMS (B, C, D) Obtained by Modification: B- Obtained in Presence of 80% Isopropanol Solution (DS=0.82); C-Obtained in Presence of 80% Ethanol Solution (DS=0.81); D-Obtained in Presence of Water (DS=0.54)

As shown in Fig.-3 the microphotographic of Na-CMS obtained in different conditions differ from each other. The surface of the Na-CMS sample obtained using 80% solution of isopropanol has a small-porous structure (fig.-3, B), and the surface of the sample obtained using 80% water solution of ethanol has pores in low degree but they are larger (Fig.-3, C). The use of water for moistening the reaction mixture product has a more compact structure (Fig.-3, D). It is possible to maintain that the more porosity of Na-CMS samples the higher rate of its dissolution.

X-ray Analysis

Analysis of diffractograms of Na-CMS samples has shown that with increasing their DS smoothing of peaks corresponding to crystal parts was carried out.

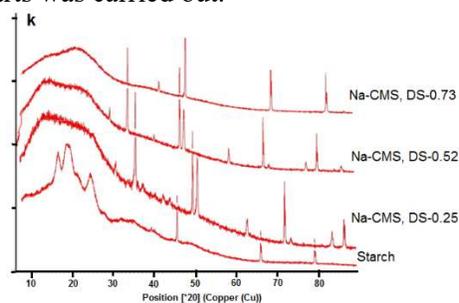


Fig.-4: Diffractograms of Starch and Samples of Na-CMS Having Different Values of DS

As shown for starch peaks in ranges 16, 19 on 24° have been observed corresponding to it is crystalline parts, and for Na-CMS samples smoothing of these peaks was observed. And care of Na-CMS with DS=0.95 these peaks completely are absent what has been witnessed about it is a completely amorphous structure. Investigations have shown that differences in diffractograms of Na-CMS samples have been

caused by their DS and the nature of solvents used for moistening of reaction mixture did not render marked influence.

Rheology

Rheological investigations have been carried out in a range of $\gamma=05-150$; by the generation of shear flow, 10% water solution of Na-CMS at 25, 40, and 55°C.

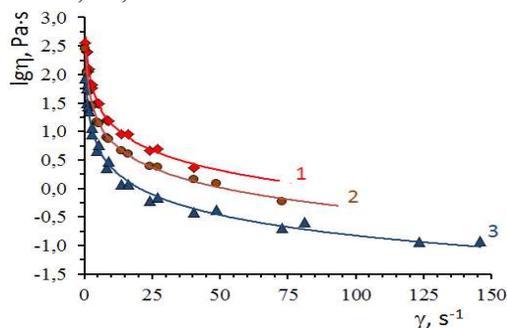


Fig.-5: Dependence of Logarithm Effective Viscosity ($\ln \eta_{eff}$) on Gradient of Rate (γ) for 10% Water Solutions of Na-CMS (DS=0.19) at Different Temperatures (°C): 1-25; 2-40, 3-55

In Fig.-5 rheograms of solution of Na-CMS with DS=0.73 are presented at different temperatures from which it is shown that they have an appearance characteristically for non-Newtonian liquids. Such behavior of solution has been caused by deformational changes of conformations of Na-CMS macromolecules in flow. Displacement of curves in a range of small values of viscosity has witnessed the weakening of intermolecular frictions in shear flow with temperature increasing. If we extrapolate $\gamma \rightarrow 0$ in rheograms, then the condition $\ln \eta_{eff} = \ln \eta$ is satisfied hence $\eta_{eff} = \eta$. Moreover, η characterizes the viscosity of the solution in the absence of flow, i.e. coefficient of internal friction, manifested by the offset of the thermal motion of the components of the liquid. In this case, the parameter η can be considered as the “dynamic” viscosity of the solution. The values of parameters η were determined for 10% water solutions of Na-CMS samples with DS 0.25; 0.52 and 0.73. Dependence of dynamical viscosity of Na-CMS solutions on temperature is presented in Fig.-6, from which it is shown that in all cases viscosity of Na-CMS solutions has decreased with increasing of DS in macromolecules of Na-CMS.

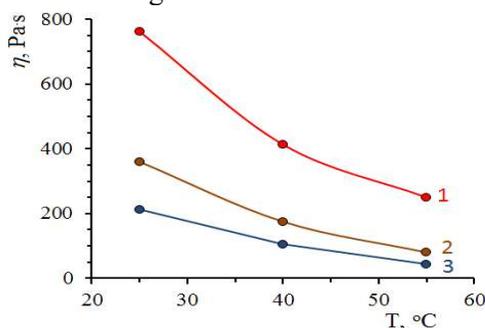


Fig.-6: Dependence of Dynamical Viscosity of 10% -Water Solutions of Na-CMS Samples on Temperature: 1, 2, 3- DS of Samples in 0.25; 0.52 and 0.73.

This is caused by the fact that with increasing of DS polymers, intermolecular interactions also increased. This fact caused amorphization of polymer structure which has been confirmed by XR-analysis of Na-CMS samples. In this case, it is also possible to destroy the helical structure of amylose and amylopectin macromolecules, which are part of the starch composition. Decreasing the viscosity of Na-CMS solutions will increase temperature can be explained by increasing of thermodynamic flexibility of macromolecules.

CONCLUSION

It was determined that chemical modification of corn starch in the solid phase and moistening of the reaction mixture by small quantities of solvents have caused an essential increase of DS obtained Na-CMS. It was also shown that alcohols have possessed a catalytic influence on this reaction. Moistening of

reaction mixtures by ethanol, isopropanol, and their water solutions also have an influence on the structure of obtaining product, which has caused its dissolution in water. Investigation of rheological properties of Na-CMS solutions has shown that they have revealed a non-Newtonian character of flowing in shear flow and this increase of polymer DS and temperature has caused decreasing in their viscosity.

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