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Study Of Physico-Chemical Properties Of Sodium Salt Carboxymethyl Starch

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Abstract:In this work, samples of sodium salt of carboxymethyl starch (Na-KMK) were synthesized by chemical modification of corn starch in the solid phase. X-ray studies of the structure of the synthesized polymers were carried out. The rheological properties of aqueous solutions of synthesized Na-KMK were studied by rotational viscometry. It was found that an increase in the degree of substitution of Na-KMK leads to a decrease in the viscosity of its solutions.

Keywords:starch, sodium salt of carboxymethylstarch, degree of substitution, X-ray diffraction patterns, polymer solution, rotational viscometry, viscosity, shear stress.

1. INTRODUCTION

Water-soluble starch derivatives, especially the sodium salt of carboxymethyl starch (Na-KMK), are widely used in various industries. In particular, this polymer is used in large volumes as a component of drilling fluids in the oil and gas industry, for flotation concentration of rocks in the mining and chemical industry, as a thickener in the paper and textile industries, as a stabilizer for aqueous solutions, suspensions and emulsions, etc. etc. [1-3]. As can be seen from the above examples, Na-KMK is mainly used in the form of aqueous solutions, the rheological properties of which play an important role in the development of technological processes. Therefore, the purpose of this work is to study the physicochemical properties of aqueous solutions of Na-KMK with various degrees of substitution (DS) using the method of rotational viscometry.

2. ЭКСПЕРИМЕНТАЛЬНАЯ ЧАСТЬ

The synthesis of Na-CMC was carried out by carboxymethylation of corn starch with sodium salt of monochloroacetic acid (Na-MCAA) in the presence of NaOH by the solid-phase method [4]. The SD of the Na-CMC samples was determined by the method [5] by applying the equations:

$$СЗ = \frac{162 * \mathrm{n_{COOH}}}{\mathrm{m_{ds}} - 58 * \mathrm{n_{COOH}}};$$

$$\mathrm{m_{ds}} = \frac{(1 - \mathrm{W_{вода}})}{100} * \mathrm{m_s};$$

$$n_{COOH} = (V_b - V) * C_{HCI} * 4;$$

where: 162 - molar mass of one glucoside chain (in g / mol);n_{COOH}- the number of COOH groups (in moles);m_{ds} -weight of carboxymethylated sample (in g); 58 - the number at which the molecular weight of the glycoside chain increases when one carboxymethyl group is

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attached to it;m_c - starch sample weight (in g), $W_{вода}$(%) - water content; V_b - ovolume of HCl consumed for titration of the control sample (in ml); V - volume of HCl consumed for titration of the sample (in ml), C_{HCl} - concentration of HCl used for titration (in mol / l), 4 is a number indicating the ratio of the total volume of the solution (100 ml) and the volume taken for titration (25 ml).

PX-ray studies of polymer samples were carried out on an X-ray diffractometer "Panalytical Empyrean" (Netherlands) equipped with a Cu tube (Kα1= 1,5406 Ǻ). The measurements were carried out at room temperature in the range of angles 2θ, in the range from 0 ° to 90 ° in a step-by-step scanning mode with a step of 0.013 degrees and a signal accumulation time at a point of 5 s.

Rheological studies were carried out on a rotational viscometer "Rheotest-2" type RV (Germany) using a cell system of coaxial cylinders S / S2 in a wide range of velocity gradient (γ)and temperature (T)by method [6].

Effective viscosity$\eta_{эфф.}$solution was calculated by the expression:

$$\eta_{эфф.} = \sigma/\gamma = z\alpha/\gamma$$

where:σ- shear stress, Pa.c;z= 0,58 –cell constant; α – meter reading measured at different valuesγ, c^{-1}.

3. RESULTS OBTAINED AND THEIR DISCUSSION

The synthesis of Na-KMK samples was carried out in a special mixer equipped with paired Z-shaped blades rotating in different directions around the horizontal axis and providing high friction of the mixture. When mixing the components into the mixer, a dosed amount of solvent was injected: water, methyl, ethyl or isopropyl alcohol (no more than 10-15% of the mass of the dry mixture), which ensured a better course of the reaction. The purification of Na-KMK from impurities was carried out by precipitation of an aqueous solution of the polymer in ethyl alcohol. By varying the ratio of the starting components, the reaction time and the type of solvent used, Na-KMK samples with degrees of substitution from 0.10 to 0.95 were obtained. It was found that the addition of small amounts of organic alcohols increases the DS of Na-KMK samples, from which it follows that alcohols have a catalytic effect on the starch carboxymethylation reaction. This effect increases in the series: ethanolанmethanol□isopropanol.

As is known, the rheological behavior of polymers is determined by many factors, one of which is the structure of the polymer. Therefore, in this work, using X-ray phase analysis, we studied the structures of Na-KMK samples.

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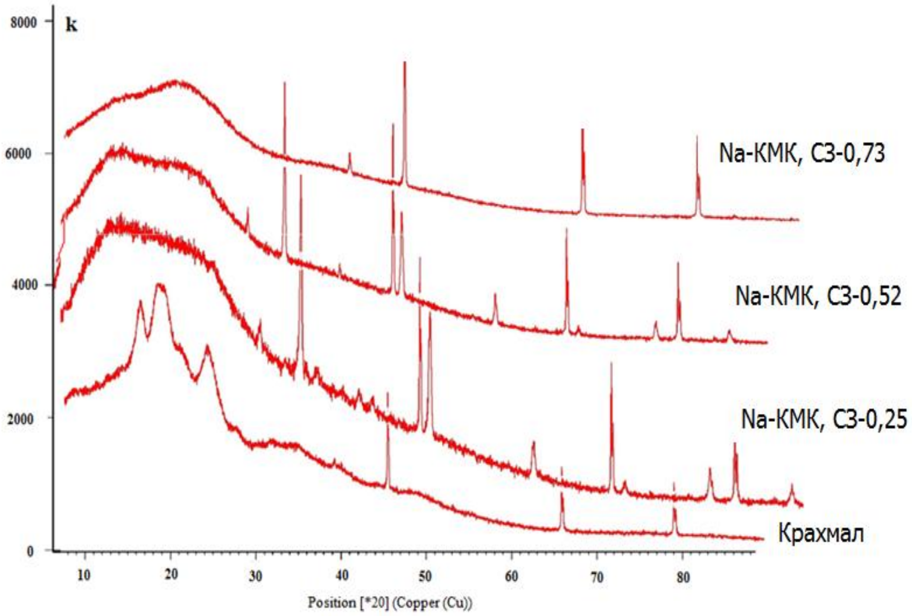

Fig.[1.] Diffraction patterns of starch and Na-KMK samples with different DS values.

As can be seen from Fig. 1, the diffractogram of native starch clearly shows peaks in the regions of 16, 19, and 24 °, corresponding to the crystalline regions of this polymer. And in the diffraction patterns of the Na-KMK samples, these peaks are smoothed. In this case, in the diffractogram of Na-KMK with СЗ = 0.95, the peaks are completely absent, which indicates the amorphous structure of this polymer.

Rheological experiments were carried out in the rangeγ = 0,5 – 150 $c^{-1}$by generating a shear flow of 10% Na-KMK aqueous solutions at 25 ° C, 40 ° C and 55 ° C. On the basis of the data obtained, rheograms were constructed. An example for a Na-KMK solution with СЗ = 0.73 is shown in Fig. 2.

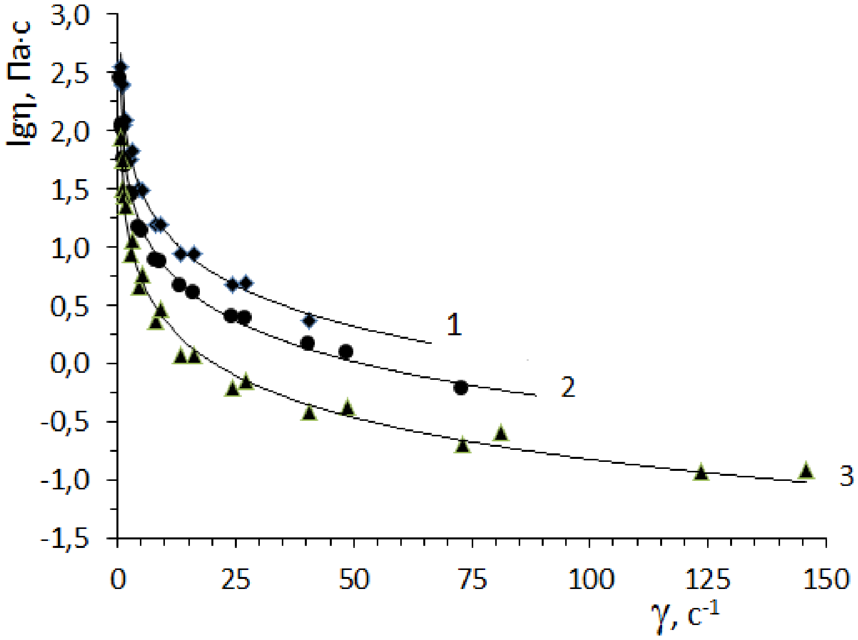

Fig. [2.] Dependence of the logarithm of effective viscosity(*ln*□$_{эфф.}$) from speed gradient (γ) for 10% aqueous solutions of Na-KMK (СЗ = 0.73) at different temperatures: 1 - 25^{o}C, 2 - 40^{o}C; 3 - 55^{o}C.

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It can be seen from Fig. 2 that the dependence curves have a form characteristic of non-Newtonian liquids. This behavior of solutions is due to a deformation change in the conformation of Na-KMK molecules in the flow. The shift of the curves to the region of low viscosity values indicates a weakening of intermolecular friction in the shear flow with increasing temperature.

If we extrapolate*γ*→0 in rheograms, then the condition*ln*□$_{эфф}$ = *ln*□□□from here□$_{эфф}$ = □□□At the same time□□□characterizes the viscosity of the solution in the absence of flow, i.e. the coefficient of internal friction, manifested by the offset of the thermal movements of the components of the liquid. In this case, the parameter□can be considered as the "dynamic" viscosity of the solution.

Parameter values□were determined for 10% aqueous solutions of Na-KMK samples with SZ 0.25; 0.52 and 0.73. Comparative graphs of the dependence of the dynamic viscosity of Na-KMK solutions on temperature are shown in Fig. 3.

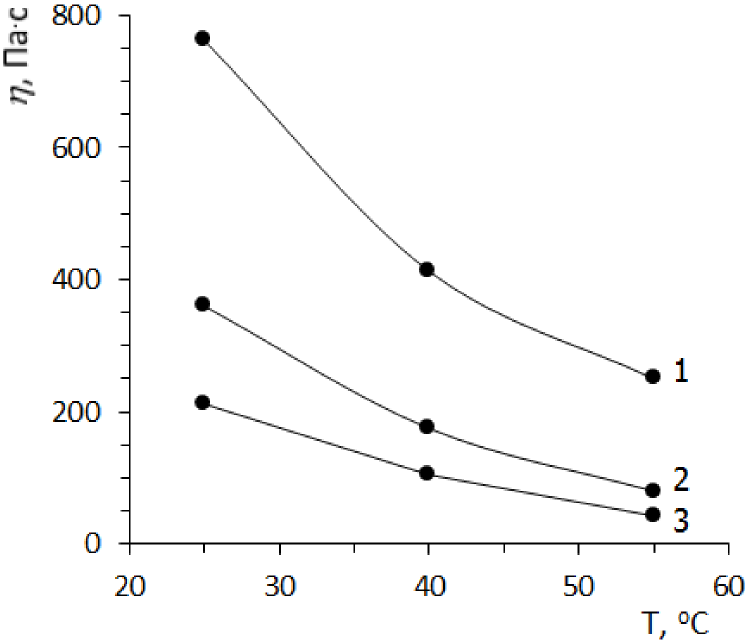

Fig.[3.] Dependences of the dynamic viscosity of 10% aqueous solutions of Na-KMK samples on temperature (*T*). 1, 2, 3 - SD of Na-KMK samples, respectively equal to 0.25; 0.52 and 0.73.

As can be seen from Fig. 3, in all cases the viscosity of Na-KMK solutions decreases with an increase in the SZ value of the Na-KMK macromolecules. This is due to the fact that with an increase in the SZ of the polymer, intermolecular interactions decrease. This phenomenon leads to amorphization of the polymer structure, which is confirmed by X-ray structural analysis. In this case, it is also possible to destroy the helical structure of amylose and amylopectin macromolecules, which are part of the starch. A decrease in the viscosity of solutions with increasing temperature can be explained by an increase in the thermodynamic flexibility of macromolecules.

Thus, the results obtained in the study of the rheological properties of Na-KMK solutions show that these solutions exhibit a non-Newtonian nature of flow in a shear flow, and an increase in the polymer SZ and temperature is accompanied by a decrease in their viscosity.

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