Features of the formation of hydrogen bonds in solutions of polysaccharides during their use in various industrial processes.

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ABSTRACT

Study the role of water in stabilizing the ordered structure of biological macromolecules using X-ray, rheology, NMR and infrared spectroscopy. It was found that in a certain range of temperatures observed change in the nature of intermolecular interactions in polysaccharide macromolecule. Such macromolecular conformational reactions occur through an orderly transition from the (form spiral) structure in which the macromolecule has a "surface" and "interior", the branching structure (coil form), in which the "interior" spirals is open to contact with the dispersion medium. As a result, substantially changing characteristics of the colloidal solution. With increasing temperature change the ratio of free energies spiraling chaotic and static states. Difference free energies between ordered and diverse structure in the aquatic environment depends on several factors but primarily is a change of free energy during the opening of "internal domain" spirals outward. Decisive role in these processes plays water, which affects the conformational transitions in macromolecules and serves as a reservoir of free energy.

Key words: native and heat-treated at different temperatures starches; ordered structure; water molecules.

INTRODUCTION

Development of new processes and multicomponent formulations that stabilize quality and biological value of food is a priority for modern scientific research. Reliable knowledge of solution properties of polysaccharides and their application in modern food technology to create a wide range of quality products and emulsion gel nature.

Aqueous solutions of polysaccharides rapidly structuring, because they are characterized by high viscosity, strength, elasticity, durable stability. The mechanism of polysaccharide gel colloidal food system depends on temperature, concentration of polysaccharides in the mixture, its own characteristics and features of basic raw materials. Behavior of solutions of polysaccharides depends strongly on the state of water in biopolymers, since it plays an important role in the formation of ordered structures of macromolecules.

Natural polymers, unlike synthetic, characterized partially ordered structure that forms in the course of their occurrence in nature and growth. This behavior of biological macromolecules is due, above all, the structure of their chiral molecules and formation of hydrogen bonds with water molecules. Latest perform the role at the origin defines the structure of spiral structures.

MATERIALS & METHODS

For the experiments, prepared 10\% suspension of native potato starch (36\% amylose) in distilled water and endured their 30 minutes in a thermostat at 20-90\(^{\circ}\)C. The specimens were dried at room temperature and powder.

Rheological behavior of starch suspensions heated at different temperatures, was studied on the «Reotest-2 (Germany) at room temperature. For X-ray powder diffractograms were obtained with a "Dron-2" (Russia). IR spectrum were recorded on Vector - 22 (Bruker Optics GmbH). \(^1\)H and \(^{13}\)C CP/MAS NMR were recorded on Avance - 400 (Bruker Optics GmbH).

RESULTS & DISCUSSION

Change of viscosity with temperature (Fig. 1) due to the increase of the energy necessary to acquire macromolecules of starch with increasing temperature to overcome the barrier and hopping into a new position.
The sharp increase of viscosity occurs in a narrow temperature range 50-80°C. Further temperature increase leads to the forces of interaction between dispersed particles are weakened and the viscosity decreases markedly.

Parallel to these measurements samples of starch suspensions were studied by X-ray, whose results are shown in Figure 2. In the native starch find out the presence of wide and narrow lines reflex, which indicates the existence of crystal structure in the tested substance. According to modern views [1,2], the substance is characterized by partially ordered structure, i.e. stimulated structures observed in the direction of only one or two axes in Cartesian coordinate system, while in other areas there is no orderly. Such ordered structures occur in case of natural substances, macromolecules which are able to rotate the plane of polarization of light rays and form a double helix. We can assume that the existence and stability of such structures due to the structural effect of water molecules that are in the middle of the double helix and form intramolecular hydrogen bonds with molecules of polysaccharides.

The IR spectrum of starch (Fig. 3) exhibit broad absorption bands of stretching vibrations of hydroxyl groups in the 3000 -3700 cm⁻¹, as well as a number of bands in the low-frequency region from 2000 to 400 cm⁻¹ relating to the vibrations of other bonds.

Comparison of IR spectrum of starch samples treated at different temperatures, shows that with increasing temperature, the band of stretching vibrations of OH groups significantly narrower and shifted to higher wavelengths. This suggests that thermal processing of starch reduced the proportion of structurally bound water molecules.

Thermal conversion of quasi-crystalline structure of starch molecules clearly defined on X-ray diffraction (Fig. 2), due to the redistribution in the form of participation of donor atoms. Durable bonding between water molecules inside the spiral structure of the macromolecule responsible for additional stability crystal hydrate.

In the ¹H NMR spectrum of air-dried samples treated at different temperatures, there is a broad and narrow absorption bands of the protons of the polysaccharide and water (Fig. 4). A broad band refers to the protons of hydrocarbon fragments and water molecules which are firmly fixed in the space of a solid matrix. Half-width of starch molecules is about 4 kHz, and the crystal water of 80 kHz. In a narrow line half-width of 1 Hz contribute to the protons of mobile water, which may be in different states of starch: an adsorption-related, water in the capillaries and free.

Ratio of integrated intensities of the narrow and broad NMR lines can be used to estimate the proportion of water molecules tightly bound in the structure of the crystalline hydrate the polysaccharide and in motion. Comparing the parameters of the experimental spectrum of starch samples gives information about the number of crystallization water in the structure of polysaccharides at their treatment 20°C - 1.4, 70°C - 1.23 and 90°C-1.08. Parallel to this, according to the thermal analysis, reduced the total amount of water in starch from 15% for the initial sample to 9% heat-treated at 90°C. These data clearly indicate the destruction of a partially ordered structure of starch when it is heated above 60°C with the division of water phase and the polymer.

These findings are confirmed by the analysis of the spectrum of ¹H and ¹³C CP/MAS NMR study of aqueous solutions of polysaccharides. Thus, the proton NMR spectrum of solutions of the native starch (Fig. 5) there is almost one intense absorption line in = 5 ppm, whereas in the spectra of solutions of heat-treated at 90°C of starch along with the signal of water are clearly distinguished signals of polysaccharide units. This indicates that the free movements of individual units of the polymer after the conversion of its quasi-crystalline structure under the influence of temperature.

Fig. 6 shows ¹³C NMR spectrum of solutions of native and heat-treated at 90°C starch. As in the proton spectra during heat treatment of the spectra become more resolved, that is also associated with increasing mobility of the hydrocarbon parts of the polymer after its destruction. Here, clearly visible absorption bands of individual types of carbon nuclei of the polysaccharide units.

CONCLUSION

The obtained results allow to explain the sol-gel phase transitions in solutions of polysaccharides, a substantial increase of sorption capacity of these molecules to the surface of solutions of mineral adsorbents with increasing temperature in the process of cleaning liquid foods (juice, alcohol and soft drinks), retrogradation mechanism of biological molecules [3].

REFERENCES

Figure 1.

![Graph showing viscosity vs. temperature](image)

**Figure 1.** Viscosity as a function of temperature for starches.

**Figure 2.** X-ray diffraction patterns of native (1) and treated at different temperatures (2) 60; (3) 70; (4) 80; (5) 90°C potato starches.
Figure 3. IR spectrum of native (A) and heat-treated at 90°C (B) starches.
Figure 4. Characteristic spectrum $^1$H NMR of air-dried sample potato starch.

Figure 5. $^1$H NMR spectrum of solutions of native (1) and heat-treated at 90°C (2) starches.
Figure 6. $^{13}$C NMR spectrum of solutions of native (1) and heat-treated at 90$^\circ$C (2) starches.