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Thermodynamic characteristics of supramolecular complexes of aroma compounds with ordered structures of polysaccharides of corn starch and its cryotextures

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Supramolecular complexes of organic odorants (*n*-octanol and *n*-octyl acetate) with polysaccharides of corn starch, its cryotextures, and waxy corn starch cryotextures were studied by differential scanning microcalorimetry. It was shown that complexes are formed with amylose-containing starch and no complexes are formed with amylopectin starch. The melting enthalpies of the complexes were determined. It was shown that complexes of the odorants with native corn starch and its cryotextures have different thermodynamic characteristics.

Key words: corn cryotextures, native corn, waxy corn starch, supramolecular complexes, *n*-octanol, *n*-octyl acetate, differential scanning microcalorimetry.

Polysaccharides are widely distributed in nature; they are actively used in various branches of industry including food industry. The stability of the odor of foodstuffs is determined by the noncovalent binding of aroma-forming compounds to proteins and polysaccharides. Study of the properties and structures of polysaccharide associates with organic compounds fixed by noncovalent bonds is the subject of supramolecular chemistry.[1] Supramolecular associates (complexes) are formed spontaneously due to noncovalent interactions of different nature. These include van der Waals, electrostatic, and donor-acceptor interactions and hydrogen bonding.

Our study was concerned with polysaccharides of corn starch cryotextures. Starch is a composite material consisting of polysaccharides with linear (amylose) and branched (amylopectin) structures. The ratio of these two components depends on the type of raw material used to obtain starch. The structures and the properties of amylose complexes with organic molecules have scarcely been studied.[2] In addition to the linear form of amylose, aqueous media contain single-helix V-modification able to form inclusion complexes with lipids and other organic substances.[3,4]

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It was shown that[4] in the complexes of amylose with fenchone and indan, the ratio of the number of guest molecules to the number of glucose units in amylose is 1 : 6, while that for vitamin A acetate is 1 : 20.

A detailed study of the formation of complexes of synthetic amylose with sodium dodecyl sulfate and 4-*tert*-butylphenol in water showed that in the former case, the inclusion complex of amylose is shaped like a helix with six glucose units in a coil; upon inclusion of 4-*tert*-butylphenol, the amylose helix rearranges into coils containing seven or eight glucose units. The enthalpies of formation of complexes were calculated; it was shown that amylopectin, having amylose chains with polymerization numbers N_P = 15—20 at the branching points, is capable of forming complexes with organic compounds. A helical coil of amylose consists in this case of six glucose rings.[5]

Inclusion complexes formed by various types of starch with *n*-C_6—C_{10} alcohols and other organic compounds have been obtained.[6] It was found that the alkan-1-ol concentration in the complexes sharply decreases with lengthening of the alkyl chain in the alcohol molecule. The formation of inclusion complexes from starch gels with an amylose content of 55% with alcohols, diols, and acids has been studied by DSC. It was found that, depending on the structure of the compound, several types of complexes with different melting points are produced.[7]

We have started investigating the sorption of aroma-forming substances by corn starch cryotextures from aqueous solutions.[8—12] It was found by capillary gas chromatography that sorption of alcohols and alkyl acetates increases as the length of the alkyl radical in the molecule increases. In the case of *n*-octyl acetate and *n*-octanol, irreversible sorption is observed. Study by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy[13] demonstrated that the surface of the cryotexture with aroma-forming compounds has sections with a developed microrelief. The contents of *n*-octyl acetate and *n*-octanol in these parts is increased; they occur as complexes. The complexes change the structure of the surface of the cryotexture walls. It was of interest to estimate the stability of these complexes in the cryotexture—water system.

In this work, we studied the formation of *n*-octanol and *n*-octyl acetate complexes with polysaccharides of corn starch and their cryotextures.

Experimental

Samples of native corn starch with an amylose content of ~25% were prepared at the All-Russia Institute of Corn Products. After delipiding by extraction in the Soxhlet apparatus with a 3 : 1 isopropanol—heptane mixture for 5 h, the native starch (NS) contained ~0.1% lipids. Samples of the native starch from waxy corn (WS) mainly contained amylopectin and no more than 4% amylose.

Cryotextures of native corn starch (CNS) and of waxy corn starch (CWS) were prepared from 3% starch sols.[8] The samples prepared for calorimetric studies were 1% aqueous dispersions of native starch and 1.2% dispersions of cryotextures obtained from starch sols either containing or not containing odorants (*n*-octyl acetate and *n*-octanol). Calorimetric studies of dispersions of cryotextures and native starch were carried out on a DASM-4 differential scanning microcalorimeter (Scientific and Industrial Concern Biopribor, Pushchino) using water as the reference sample in the temperature range of 283—400 K, a manometer pressure of 2.5 atm, and programmed heating at a rate of 2 K min^{-1}. A 0.5-cm^3 stainless-steel cell was hermetically closed with a rubber ring, which allowed maintaining pressure and preventing water from evaporation. Thermodynamic parameters of thermal destruction of the ordered structures of polysaccharides determined under these conditions did not depend on the programmed heating rate or on aggregation effects.[14] In each experiment, the heat capacity scale was calibrated by passing the electric current through the cell. The averaged enthalpies of the complexes were calculated per mole of the glucose unit (gu) (162 Da) based on five independent measurements. Deconvolution of peaks characterizing the endothermal transitions was performed using the PEAK FIT program (Gandel Scientific Software). The applicability of this program for deconvolution of endothermal transitions in starch was demonstrated in previous studies.[15,16]

Results and Discussion

Native corn starch. Figure 1 presents the DSC thermogram of a 1% aqueous dispersion of delipided native corn starch. The main low-temperature peak at 341 K, corresponding to the melting enthalpy of 3 kJ per mole of glucose units, characterizes melting of a crystalline lamella* formed by A and B chains of amylopectin and stabilized by water molecules.[17—19] This value of melting enthalpy points to the presence of a hydrogen-bonded supramolecular complex of polysaccharides with water molecules. The second complex is not clearly defined; it has a melting point of 357 K and ΔH = 0.16 kJ per mole of glucose units; most likely, it is an amylose—lipid inclusion complex of the host—guest type (see Fig. 1, *a*, curve *1*). The amylose macromolecules are known to occur in the simple-helix conformation in these complexes.[17] It was shown by additional experiments that the solvent we used to remove lipids (isopropanol—heptane, 3 : 1) has no influence on the thermodynamic parameters of melting of the crystalline lamella with T = 341 K but decreases the enthalpy of melting of the amylose—lipid complex. This means that the solvent we use does not delipid completely the native starch. The introduction of octanol or octyl acetate into the native starch—water system does not change the thermodynamic characteristics of the low-temperature major complex, whereas the temperature and the enthalpy of the high-temperature complex somewhat increase and, simultaneously, the asymmetry of the corresponding peak increases. Evidently, the high-temperature endothermal

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* Crystalline lamella is an ensemble of crystallites arranged on the polymer backbone normal to the principal axis of the starch grain.

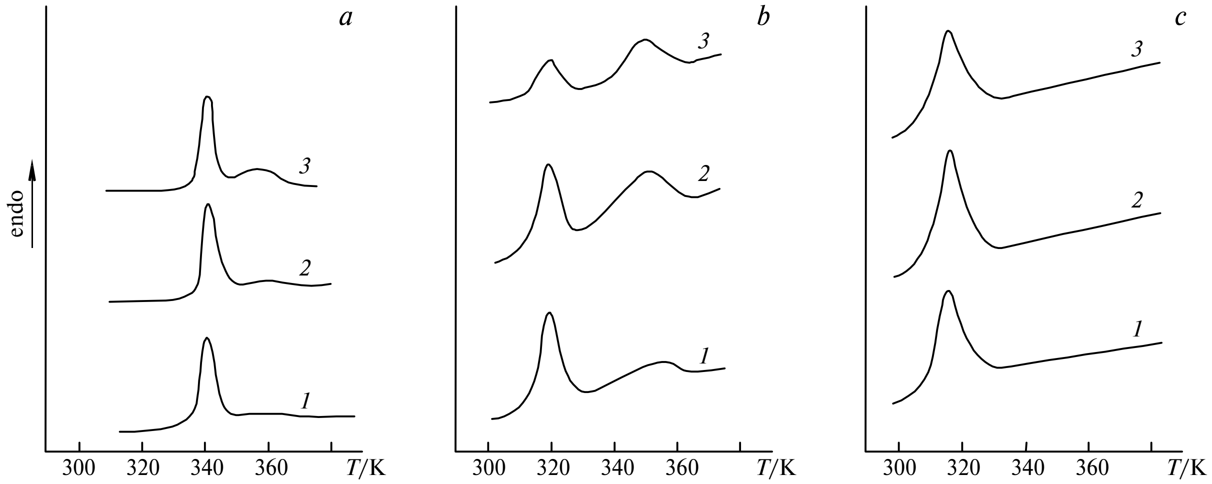

Fig. 1. Melting thermograms of supramolecular complexes: (*a*) native corn starch (*1*), complex with *n*-octyl acetate (*2*) and with *n*-octanol (*3*); (*b*) corn starch cryotextures (*1*), cryotexture with *n*-octyl acetate (*2*) and with *n*-octanol (*3*); (*c*) waxy corn starch cryotextures (*1*), cryotexture with *n*-octyl acetate (*2*) and *n*-octanol (*3*).

transition observed in the thermogram, which is especially typical of the starch—octanol system (see Fig. 1, *a*, curve *3*), reflects melting of two types of structures, namely, amylose-lipid and amylose-octanol (or octyl acetate) complexes. The possibility of the formation of amylose-octanol complexes is confirmed by the fact that the molecules of synthetic amylose with a degree of polymerization of more than nine can form inclusion complexes in which the amylose macromolecules occur in the simple-helix conformation.[5,17,20] Deconvolution of the high-temperature peak made it possible to resolve and characterize a third high-temperature complex with a melting point of 363 K and $\Delta H = 0.22$ kJ per mole of glucose units, which was formed by starch with octyl acetate and octanol (see Table 1). The low melting enthalpy of this complex points to the absence of hydrogen bonds. The complexes with odorants melt at higher temperature (363 K) than the amylose—lipid complex. This means that complexes with adsorbents show higher thermal stability than amylose—lipid complexes.

Table 1. Thermodynamic characteristics of melting of the supramolecular complexes (T/K and ΔH/kJ per mole of glucose units) of polysaccharides of native corn starch (NS), its cryotextures (CNS) and cryotextures of waxy corn starch (CWS) with *n*-octyl acetate (OcAc), *n*-octanol (OcOH), and their mixture determined by DSC

Sample	T_1	ΔH_1	T_2	ΔH_2	T_3	ΔH_3
NS	341	3.00	357	0.16	—	—
NS + OcAc	341	3.00	357*	0.38	363*	0.22*
NS + OcOH	341	3.00	357*	0.07	363*	0.21*
NS + OcAC + OcOH	341	3.00	355	0.40	—	—
CNS	317	1.10	360	0.40	—	—
CNS + OcAc	318	0.60	341*	0.18	352*	0.44*
CNS + OcOH	318	0.42	348*	0.22	352*	0.40*
CWS	315	1.48	—	—	—	—
CWS + OcAc	315	1.27	—	—	—	—
CWS + OcAc + OcOH	316	1.09	—	—	—	—

* The T and ΔH values were calculated after deconvolution of the high-temperature peak.

Corn starch cryotextures. The complexes of polysaccharides formed in cryotextures prepared from sols of native starch differ sharply from the complexes found in the native starch itself. Indeed, the melting point of the low-temperature complex is by 24 K lower than that of the complex formed in the native starch, and the melting enthalpy is 3 times smaller (see Fig. 1, *b*, Table 1). Since this complex was detected in all three cryotexture samples (see Fig. 1, *b*, curves *1—3*), it can be interpreted as a complex of polysaccharides with water, although it seems to be less hydrated than the complex with native starch. The second high-temperature complex with a melting point of 360 K is, apparently, an amylose complex with lipids. The addition of an odorant to the sol prior to cryotexturing gives rise to broad high-temperature peaks (see Fig. 1, *b*, curves *2* and *3*) indicating a change in the melting point. Deconvolution of these peaks (see Table 1) shows that the high-temperature peaks corresponding to the temperature T_3 are present in both samples, while the peaks with T_2 are probably due to supramolecular associates of amylose with lipids. The complexes with T equal to 352 K are formed in cryotextures of CNS with octyl acetate and with octanol. It was found by gas chromatography that interaction of odorants with starch polysaccharides is mainly hydrophobic.[8—13] The noncovalent binding of polysaccharides with odorants is due to van der Waals interactions with the hydrophobic *n*-octyl group of odorants. The complexes of NS and CNS polysaccharides with odorants differ in melting points, which is due to the differences in the structures of the complexes formed by polysaccharides of native starch and its cryotextures.

Waxy corn starch cryotextures. The waxy corn starch consists mainly of amylopectin polysaccharides. One supramolecular complex of amylopectin formed, apparently, with water molecules is found in its cryotextures (see Fig. 1, *c*, curves *1—3*). The addition of an odorant (6.5% of the weight of the initial starch) results only in a decrease in the melting enthalpy of the complex, which is likely to attest to a decrease in the number of noncovalent bonds in it caused by the decrease in the degree of hydration. In the presence of an odorant, the complex is a sort of "loosened". No additional complexes of CWS polysaccharides with odorants can be found. Thus, amylopectin polysaccharides in the cryotextures of amylopectin-containing waxy corn starch do not form complexes with odorants. Apparently, the supramolecular complexes of odorants with starch cryotextures involve only amylose.

Thus, the studies carried out by differential scanning microcalorimetry provide the first characterization of supramolecular complexes of odorants with the polysaccharides of starch cryotextures and demonstrate that they differ in enthalpies and melting points from the complexes of odorants with native starch polysaccharides. The cryotextures of waxy corn starch containing no amylose do not form complexes with odorants.

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