Sorption of aliphatic alcohols, acetates, and their mixtures by corn starch cryotextures depending on concentrations of sorbates and starch in initial sols

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The sorption of a mixture of *n*-hexanol, *n*-octanol, and *n*-hexyl and *n*-octyl acetates from aqueous solutions by corn starch cryotextures was studied using capillary gas chromatography at different initial concentrations of the sorbates (1—25 mmol L^{-1}) and corn starch (2—6%). The amounts of compounds sorbed by cryotextures are proportional to the increase in their concentration in the initial sol and the length of the alkyl substituent. Linear equations describing the concentration dependence were proposed. The sorption of *n*-hexanol from a mixture of substances containing *n*-octanol increases as compared to that from the individual alcohol. It was shown that the degree of sorption of aroma by cryotextures was independent of the content of starch in the initial sol.

Key words: corn starch cryotextures, aliphatic acetates and alcohols, sorption, concentration dependence, capillary gas chromatography.

Noncovalent binding of low-molecular organic compounds by polysaccharides is poorly studied. It is known that binding of aroma substances by polysaccharides occurs mainly due to noncovalent electrostatic interactions and hydrogen bonds.[1,2] Alcohols, aliphatic acids, and their derivatives and some carbonyl compounds form insoluble inclusion complexes in sols of polysaccharides.[3—6]

We have previously[7—9] studied the sorption of aroma compounds (low-molecular organic compounds participating in the formation of odor of food products) by cryotextures formed of corn starch sol. It has been found that sorption of low-molecular organic compounds by corn starch cryotextures depends on the structure of the substances. For example, lower alcohols down to *n*-pentanol are not sorbed by the corn starch. As the alkyl chain length in alcohols (beginning from *n*-hexanol) and *n*-alkyl acetates increases, the degree of their sorption also increases, which indicates the hydrophobic character of interactions. At the same time, when studying the sorption of components of rosemary oil containing different classes of organic compounds from aqueous solutions by corn starch cryotextures, we established that the sorption of alcohols, in particular, linalool, from a mixture of substances is higher than that of individual compounds.[7,9] Probably, the presence of other substances affects the sorption properties of cryotextures.

The purpose of this work is to study the dependence of the sorption of aliphatic alcohols, acetates, and their mixtures by corn starch cryotextures on the concentration in the initial sol and the content of the starch and to reveal the competitive sorption of the substances under study from mixtures.

Experimental

Delipidized corn starch (Russia) containing 25—27% amylose was used. Corn starch sol was obtained by heating 2, 3, 4, or 6% suspension of starch in distilled water to 90 °C with vigorous stirring. The sol was cooled to –20 °C and placed in polypropylene tubes with caps (40 g in each tube). Freshly distilled *n*-hexanol, *n*-octanol, and *n*-hexyl and *n*-octyl acetates in amounts providing their concentrations from 1 to 25 mmol L^{-1} were added to sol under intense shaking.

Samples of sols with additives of organic substances were stored for 3 h at +5 °C and for 24 h at −18 °C. Then the samples were defreezed and kept (to establish equilibrium) for 16 h at –20 °C. The time of equilibration (an unchanged concentration of the substance in the solution) was predetermined by gas chromatography (GC) in the time interval from 3 to 30 h. The cryosponge obtained was separated from the aqueous phase, from which portions of 10 mL were taken. A 20% ether solution of *n*-heptyl acetate as the internal standard (1 to 10 mL) and diethyl ether (2 mL) were added to the taken aqueous solution. An unsorbed portion of alcohols and acetates was determined in the ether extracts by capillary GC.

Gas chromatographic analysis of organic substances in ether extracts was carried out on a Hewlett—Packard 5730 A capillary chromatograph with a flame-ionization detector. The temperature of the detector and injector was 250 °C. A fused silica capillary column with the SE-30 phase (50 m × 0.32 mm, d_f = 0.25 μm) was used. Analysis was carried out at 120 °C. The splitting of the carrier gas (He) flow was 1 : 50. The volume of the injected probe was 2 μL. Each sample was

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analyzed 5—6 times. The amount of alcohols and acetates unsorbed by the cryosponge and remaining in the aqueous phase was calculated from the ratio of peak areas of the substance and reference. The amount of sorbates on the cryosponge was determined as the difference between the amount of the substance in the initial solution and in the solution after separation of the cryosponge. This procedure made it possible to obtain quantitative data on sorption of organic substances with a high reproducibility. The error of determination of the concentration of the unsorbed portion of substances, including errors of GC analysis, was 5—9%. Each experiment was repeated 3—5 times. The sorption of *n*-hexyl and *n*-octyl acetates, *n*-hexanol, and *n*-octanol was calculated in mg per g of dry corn starch taken from the preparation of sol.

Results and Discussion

Low-molecular organic compounds were introduced to the corn starch sol, which was first exposed to +5 °C and then subjected to low-temperature treatment. During freezing, the starch sol forms a three-dimensional porous cryotexture (cryosponge), which after defreezing, easily separates an aqueous phases and retains its form and structure. Organic substances that are present in the initial sol are bound on the surface and in the bulk of cryosponge. The amount of sorbed substances was determined from their content in the aqueous phase separated from the cryosponge after equilibrium. The repeated treatment of the cryosponge with water showed that desorption of organic substances occurs unquantitatively, and up to 30% sorbed substances are bound irreversibly, *i.e.*, they are inaccessible for exchange with the aqueous phase. However, the process of noncovalent binding is well reproduced when the procedure presented in Experimental is fulfilled. Binding of low-molecular compounds by biopolymers plays an important role in various biological systems and in the chemistry and physiology of odor reception.

At the concentration of sorbates of 1 mmol L^{-1} (Table 1), no competitive sorption of acetates is observed, and the amount of *n*-hexyl and *n*-octyl acetates and *n*-octanol sorbed from a mixture of substances is almost the same as that from sorption of individual compounds. A different situation is observed for *n*-hexanol. Its sorption is almost unaffected by the presence of *n*-hexyl and *n*-octyl acetates (see Table 1, series I and V). The addition of *n*-octanol results in a twofold increase in the sorption of hexanol (series III and IV). From a mixture of four substances, *n*-hexanol is sorbed by the cryosponge 1.5 times more than from the individual alcohol (series VII). Thus, highly sorbed *n*-octanol increases, probably, the affinity of starch molecules for the low-molecular alcohol *n*-hexanol, which results in an increase in its sorption.

The dependences of the concentrations of sorbed substances *V* (degree of polymer filling, mmol per mol glucose) on the equilibrium concentration of the unbound ligand in an aqueous phase *L* (mmol L^{-1}) for systems with 3% starch sol and addition of individual alcohols and acetates and their mixtures are presented in Fig. 1. As can be seen in Fig. 1, *a*, the sorption of individual *n*-hexanol is lower than its sorption from the mixture of substances. The sorption isotherms are classical, and in both cases, saturation of sorption is observed. The sorption isotherms for *n*-octanol (Fig. 1, *b*) and *n*-hexyl and *n*-octyl acetates (Fig. 1, *c*, *d*) are different. At low concentrations, the distributions of substances between polysaccharide and an aqueous phase are close to those for the systems with individual sorbates and their mixtures. The distribution changes as the initial concentration of substances in sol increases. For example, individual sorbates are bound with the cryotextures to a greater extent than those from the mixture of substances, and their sorption isotherms have a complex S-like shape with an inflection point. Probably, in the case of individual octanol and acetates, polymolecular sorption on the surface occurs along with irreversible sorption in the bulk of cryosponge.[10]

Table 1. Influence of a mixture of substances on sorption of individual components by corn starch cryotexture obtained from 3% sol

Series	Compound	Sorption/mg g^{-1}	
		from mixture	individual
I	*n*-Hexanol	0.5	0.4
	n-Hexyl acetate	2.6	2.9
II	*n*-Octanol	4.0	4.1
	n-Octyl acetate	4.7	4.9
III	*n*-Hexanol	1.0	0.4
	n-Hexyl acetate	2.9	2.9
	n-Octanol	4.3	4.1
IV	*n*-Hexanol	0.9	0.4
	n-Octanol	4.2	4.1
	n-Octyl acetate	4.9	4.9
V	*n*-Hexanol	0.4	0.4
	n-Hexyl acetate	2.7	2.9
	n-Octyl acetate	4.9	4.9
VI	*n*-Hexyl acetate	2.6	2.9
	n-Octanol	4.0	4.1
	n-Octyl acetate	4.9	4.9
VII	*n*-Hexanol	0.6	0.4
	n-Hexyl acetate	2.8	2.9
	n-Octanol	4.2	4.1
	n-Octyl acetate	4.5	4.9

Note. The initial concentration of each compound in sol is 1 mmol L^{-1}.

To estimate the sorption of individual substances and those same substances from mixtures, we calculated the amount of sorbed compounds (mg per g starch) at different initial concentrations of substances in sol. The results obtained are presented in Fig. 2. Since the weight of the dried cryosponge obtained without addition of organic substances virtually does not differ from the weight of the

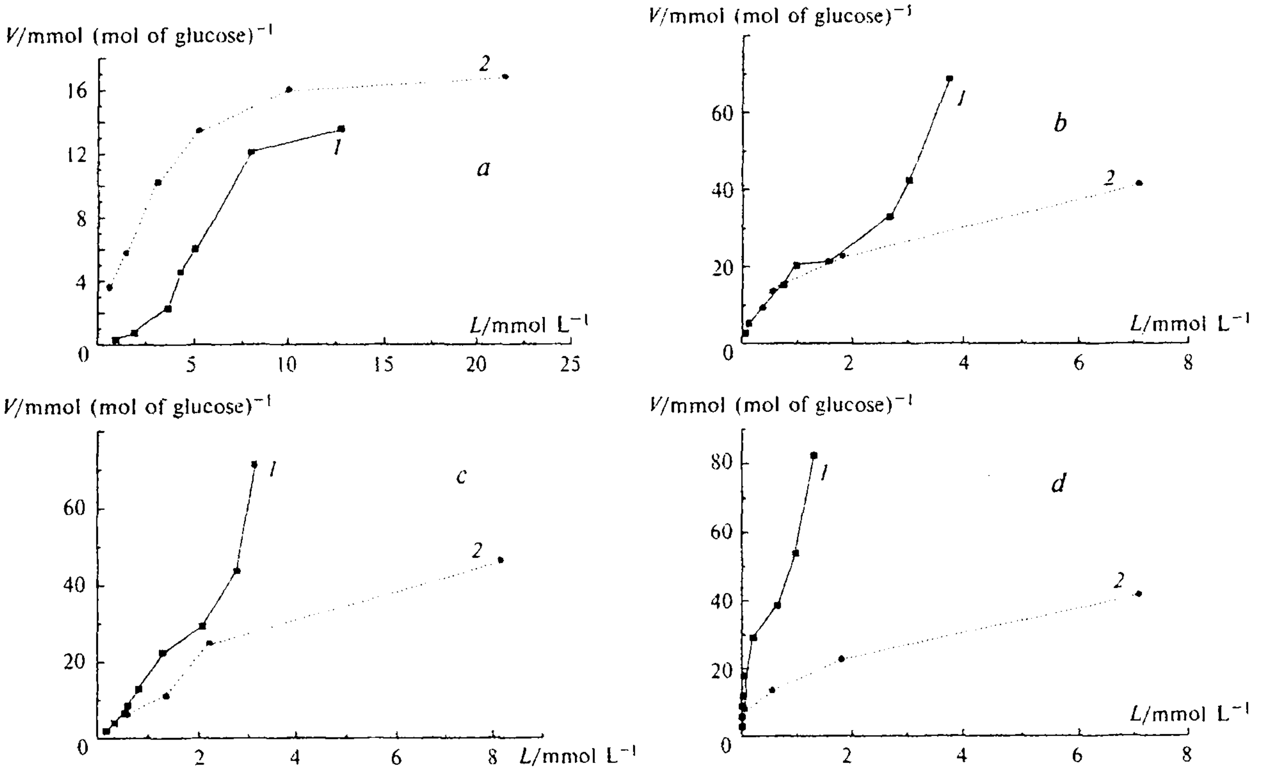

Fig. 1. Isotherms of sorption from individual compounds (*1*) and from their mixture (*2*) by corn starch cryotexture: *a*, *n*-hexanol; *b*, *n*-octanol; *c*, *n*-hexyl acetate; and *d*, *n*-octyl acetate.

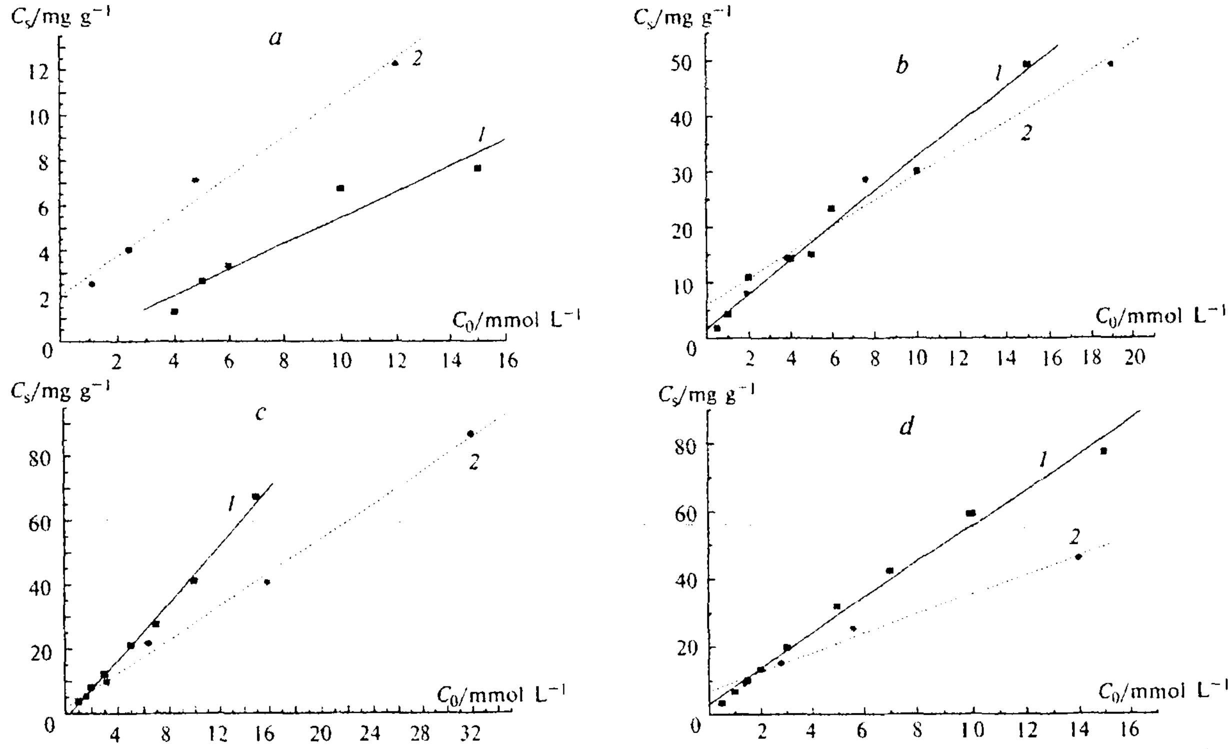

Fig. 2. Dependences of the amount of sorbed compound (C_s) on its initial concentration (C_0) in 3% sol of corn starch (*1*) and on the presence of three other components taken in the same concentration in sol (*2*): *a*, *n*-hexanol, R_1 = 0.955; R_2 = 0.990; SD_1 = 0.93; SD_2 = 0.73; *b*, *n*-octanol, R_1 = 0.990; R_2 = 0.985; SD_1 = 2.36; SD_2 = 3.83; *c*, *n*-hexyl acetate, R_1 = 0.998; R_2 = 0.998; SD_1 = 1.65; SD_2 = 2.64; and *d*, *n*-octyl acetate, R_1 = 0.995; R_2 = 0.993; SD_1 = 2.87; SD_2 = 2.20.

initial starch, the weight of starch used for the preparation of sol was used in calculations. As can be seen in Fig. 2, the amount of sorbed compounds increases with an increase in the concentration of substances introduced into the sol regardless of whether it was an individual compound or a mixture of four substances. The coefficients of linear equations were determined by computer processing. They allow one to estimate the amount of sorbed substances per g of starch taken for the preparation of the cryotexture with an error of 0.7—4 mg g^{-1} at any initial concentration (the correlation coefficient R varied from 0.955 to 0.998). The minimum concentration of sorbed substances was 0.5 mmol L^{-1}; therefore, the straight lines do not originate from the zero concentration. As the concentration of acetates in the initial sol increases, the sorption of individual substances exceeds their sorption from the mixture (see Fig. 2). For example, at a concentration of 15 mmol L^{-1}, the amount of sorbed individual hexyl acetate is 65 mg g^{-1}, and its sorption from the mixture with *n*-octyl acetate and alcohols is only 41 mg g^{-1}, which is 1.6-fold lower. At the same concentration, the sorption of individual octyl acetate is also 1.6 times higher than that from the mixture of substances. Alcohols differ substantially from acetates in the character of sorption. For example, the amount of *n*-octanol sorbed by the sponge depends weakly on whether it was an individual compound or a mixture of substances. At the initial concentration of 15 mmol L^{-1}, 48 mg g^{-1} of octanol are sorbed from its individual state or 41 mg g^{-1} are sorbed from the mixture. Individual *n*-hexanol is sorbed by the cryotexture only at a concentration of 2 mmol L^{-1}.[9] When the concentration increases, its sorption increases, as well as the sorption of other compounds under study. *n*-Hexanol is sorbed from a mixture of substances containing *n*-octanol at a lower concentration (0.5 mmol L^{-1}). The amount of hexanol sorbed is ~2 times higher than that for the sorption of individual compounds, although the total amount of sorbed *n*-hexanol is much lower than that of *n*-octanol. For example, at similar initial concentrations (15 mmol L^{-1}), only 8 mg g^{-1} of individual *n*-hexanol and 15 mg g^{-1} from the mixture are sorbed, whereas *n*-octanol at the same initial concentration is sorbed in the amount of 40—45 mg g^{-1}. Thus, the presence of other compounds affects the sorption of alcohols, which results, depending on the structure of the compounds, in an increase in their sorption or its decrease as compared to that of individual substances.

We studied the effect of the concentration of the corn starch in the initial sol on the amount of com-

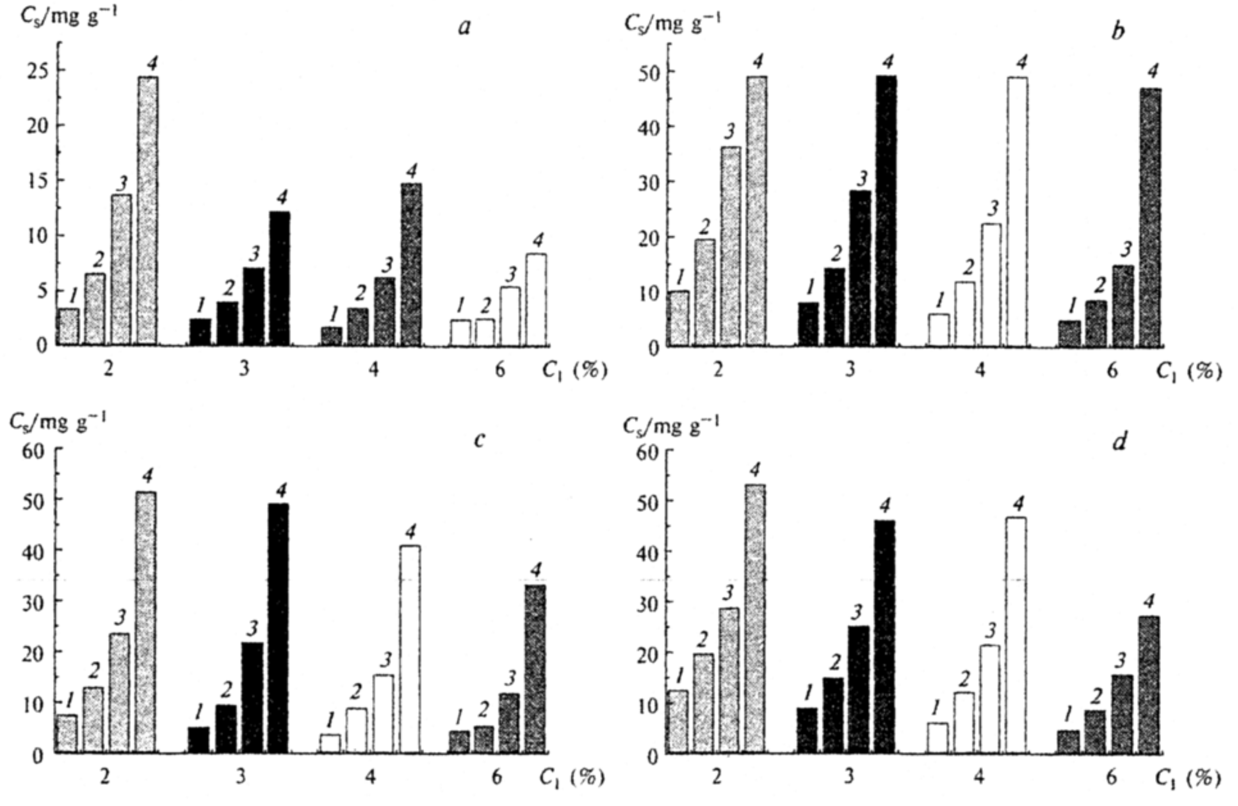

Fig. 3. Dependences of the amount of components sorbed by cryosponge from a mixture (C_s) on their initial concentration (C_0) in sol and on the amount of corn starch taken to prepare sol (C_1): *a*, *n*-hexanol; *b*, *n*-octanol; *c*, *n*-hexyl acetate; *d*, *n*-octyl acetate; C_0 = 1.2 (*1*), 2.5 (*2*), 5.0 (*3*), and 12 mmol L^{-1} (*4*).

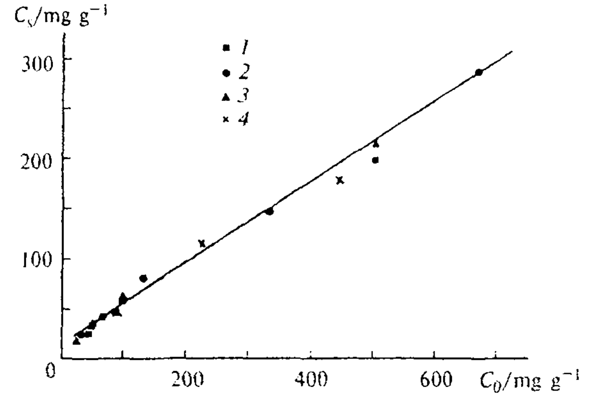

Fig. 4. Dependences of the total amount of compounds sorbed by cryosponge from a mixture (C_s) on the initial total concentration of all components (C_0) in sol containing 2 (*1*); 3 (*2*); 4 (*3*); and 6% corn starch (*4*).

pounds sorbed by the cryosponge from the mixture at different initial concentrations. The concentration of each of the volatiles in 2, 3, 4, or 6% sols was 1.2, 2.5, 5.0, and 12.0 mmol L^{-1}, respectively. The nature of the substances, their concentration, and the starch concentration in the initial aqueous sol affect the amount of sorbed compounds (Fig. 3). For all substances and all samples of cryosponges, the amount of sorbed compounds increases with an increase in their initial concentration. The influence of the amount of starch in the initial sol taken for the preparation of the cryotexture is unusual. As the starch content increases, the sorption of all compounds studied decreases, and these changes (insignificant for *n*-hexyl acetate and *n*-octanol) are more pronounced for *n*-octyl acetate and, most of all, for *n*-hexanol.

The calculation of the total concentration of substances sorbed by the cryosponges C_s (mg g^{-1}) for each mixture and comparison of it with the total concentration of compounds per g starch introduced into the 2—6% sol (C_0/mg g^{-1}) show that, regardless of the starch concentration in the sol, the sum of sorbed substances is the same for the same C_0 values (Fig. 4). When 1 g of the mixture of substances (per g starch) is introduced into a 6% sol, the sorption of organic substances by the cryotexture is 400 mg (g starch)$^{-1}$. Thus, 1 g of starch sorbs a mixture of organic compounds under study regardless of the initial starch concentration in the sol, but the sorption depends linearly on the concentration of the organic substances introduced (see Fig. 4). The fact that the amount of sorbed compounds is independent of the starch concentration indicates that binding of volatiles begins at the sol stage and continues during the formation of the cryostructure. It follows from this, that in sorption processes, the cryosponge surface is not, most likely, the determining factor, because the surface area and diffusion permeability of the cryosponges obtained from sols with different concentrations of starch differ substantially. This surprising fact indicates that noncovalent binding of sorbates occurs already in the initial sol before cryotexturation. Probably, the differences in sorption are mainly associated with change in the sorption activity of polymers under the effect of the sorbed substance. It is known that, depending on the sorbate nature, amylose molecules are capable of forming spirals (helices) with different diameters close to those of α-, β-, and γ-cyclodextrins.[11] Low-molecular organic substances can form inclusion complexes with spiral fragments of starch. It cannot be ruled out that amylose and amylopectin can form so-called "lacunas" that provide the most favorable interaction with the sorbate due to noncovalent bonds. During cryotexturation, lacunas and helices are "closed" due to the formation of additional noncovalent bonds between conformationally changed and unchanged polysaccharides of the initial sol, and then the sorption is irreversible. In our case, the number of binding sites in starch sols is higher than the number of molecules of odorants; therefore, the amount of compounds sorbed from the mixture in 1 g of starch is independent of the starch concentration in the initial sol.

The data obtained indicate that the sorption of low-molecular volatiles from the mixture differs from that of individual compounds. Some compounds, for example, *n*-octanol, are sorbed almost completely, and the sorption properties of starch increase with respect to other low-molecular alcohols (*n*-hexanol). Probably, *n*-octanol is the best sorbate that affects the conformation changes of polysaccharides. Its presence in the mixture increases the sorption of weakly sorbed *n*-hexanol. An insignificant decrease in the sorption of alkyl acetates from the mixture as compared to that of individual compounds indicates a weak competition in the series of acetates and alcohols for binding sites by starch cryotextures. These facts confirm that binding of organic substances occurs at the stage of sol formation and mainly depends on the structure of compounds sorbed. The main role of *n*-octanol, which increases the sorption of poorly sorbed *n*-hexanol, is, most likely, that *n*-octanol affects the conformation of polysaccharide, increasing its sorption capability with respect to alcohols. The cryosponge formation from sols with a low concentration of starch can be used for deodorization of aqueous solutions in food industry.

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