Sorption of aliphatic alcohols from aqueous solutions by starch cryotextures

M. B. Terenina, T. A. Misharina, and R. V. Golovnya*

*N. M. Emanuel' Institute of Biochemical Physics, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 137 4101*

Capillary GLC was applied to study the sorption of *n*-butanol, *n*-hexanol, *n*-octanol, and linalool from aqueous solutions by corn starch cryotextures. The concentrations of alcohols in aqueous solutions were varied from 0.5 to 15 mmol L^{-1}. The sorption of alcohols by cryotextures formed of sols containing these alcohols and the coefficients of their distribution depend on the initial concentration and structure of the alcohols. *n*-Butanol is not sorbed by the corn starch cryotextures over the range of 0.5—80 mmol L^{-1}. The sorption of other alcohols increases with increasing length of the alkyl substituent and the concentration of the alcohol. The highest sorption capacity of the cryotexture (88%) was observed for *n*-octanol. The sorption of linalool decreases due to the double bonds and branching in its molecules.

Key words: corn starch cryotextures, sorption, aliphatic alcohols, aqueous solutions, capillary gas chromatography.

Templation of synthetic and natural polymers with low-molecular substances due to covalent or noncovalent binding with polymer increases its sorption ability in organic solvents after the removal of the substance (template).[1] Organic compounds that form cavities with certain structures and sizes in polymers are used as templates. For example, templation of soluble starch by dye (Methylene Blue) followed by covalent cross-linking of the polymer gave[2] a modified starch with a high concentration of binding sites and a high sorption activity. Noncovalent binding of low-molecular organic compounds by polysaccharides is insufficiently studied.

Binding by polysaccharides of organic compounds, including aroma substances, occurs mainly due to noncovalent electrostatic interaction and hydrogen bonds.[3,4] Alcohols, aliphatic acids, their derivatives, and some carbonyl compounds form inclusion complexes in polysaccharide sols.[5—11] The interaction of low-molecular substances with polysaccharides in sols depends on the biopolymer structure and the nature of functional groups of the odorant. Determination of quantitative parameters of the sorption activity of polysaccharides is impeded because of difficulties that appear during separation of sorbed and nonsorbed compounds.

It is known that water-insoluble cryotextures can be obtained from starch sols (with retention of their food properties) by freezing.[12] An additional noncovalent binding of polysaccharide molecules in cryotextures that appears during freezing results in the formation of the elastic sponge texture. This cryosponge can easily be separated from an aqueous phase containing nonsorbed substances, which allows the process of odorant binding to be monitored at the quantitative level.

The sorption of the essential rosemary oil components containing various classes of organic compounds by corn starch cryotexture in aqueous solutions has previously been studied.[13] It has been shown that the cryosponge sorbs terpene hydrocarbons from aqueous solutions almost quantitatively due to the hydrophobic interactions. A lower degree of sorption is observed for compounds capable of forming hydrogen bonds with OH groups of starch polysaccharides.

In this work, we studied the influence of the structure and concentration of aliphatic alcohols on their sorption by corn starch cryotextures formed of sols in the presence of alcohols.

Experimental

Delipidized corn starch (Russia) containing 25—27% amylose was used. The corn starch sol was obtained by heating of a 3% suspension (600 mL) of the starch in distilled water to 90 °C with vigorous stirring. The sol was cooled to room temperature and placed in polypropylene tubes with caps. Freshly distilled *n*-butanol, *n*-hexanol, *n*-octanol, or linalool was added to the sol with vigorous shaking, and the concentration of the alcohol was varied from 0.5 to 15 mmol L^{-1}, or in the case of *n*-butanol, from 0.5 to 80 mmol L^{-1}. The levels of alcohol concentrations corresponded to the contents of odorants in natural food products.

Samples of sols with additives of alcohols were kept for 3 h at +5 °C and for 24 h at −18 °C, thawed out, and kept for 16 h at −20 °C to establish a constant concentration of the

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substance in the solution. Then the cryosponge that formed was separated from the aqueous phase from which 10-mL samples were taken. A 20% ether solution (from 2 to 30 μL) of *n*-heptanol used as the internal standard was added to the samples. The amount of the nonsorbed alcohol in the solutions obtained was determined by capillary GLC.

Alcohols were determined in samples of aqueous fractions by GLC on a Biokhrom capillary chromatograph with a flame-ionization detector. The temperature of the detector and injector was 200 °C; a silica fused capillary column (25 m× 0.32 mm, layer thickness d_f = 0.2 μm), (Chrompack, Holland), with CP-Wax 58CB was used. Analysis was carried out in an isothermal regime at 100 °C. The split of the carrier gas (helium) flow at the inlet of the column was 1 : 50. The volume of the sample injected was 2 μL. Each sample was analyzed 5—6 times. The concentration of the alcohol nonsorbed by the cryosponge and remaining in the aqueous phase was calculated by the ratio of surface areas of the peaks of the substance and standard.

The degree of sorption (%) was calculated for the quantitative estimation of binding of the substance by the cryosponge as the ratio of the amount of the alcohol sorbed on the sponge to the amount of the alcohol in the starting solution.

To prepare reference samples of aqueous solutions of the compounds studied, 40 mL of distilled water was placed in polypropylene tubes, and alcohol was added in amounts corresponding to the average concentration of the alcohol of the given series. Reference samples were kept at the corresponding temperatures for the same time as the working samples. The results of GLC analysis of reference solutions were used for quantitative determination of the fraction of nonsorbed alcohols in aqueous solutions above cryosponges.

The error of determination of the concentration of the nonsorbed portion of substances, including errors of GLC analysis, was 3—7%. Each experiment was repeated 2—5 times.

To reveal the reversibility of the sorption process, distilled water was added to the cryosponge after separation of the aqueous phase to a total weight of 40 g. The system obtained was kept at –20 °C for 16 h, and the amount of desorbed alcohol was determined by GC. The desorption process was repeated 2 times.

Results and Discussion

Saturated aliphatic alcohols $C_nH_{2n+1}OH$ with a carbon chain length n = 4, 6, and 8 and linalool, tertiary alcohol with a branched carbon skeleton and two double bonds, were chosen for the study.

The diagram illustrating a change in the degree of sorption of alcohol at its different concentrations in the starting sol taken for the sponge formation is presented in Fig. 1. *n*-Butanol in concentrations of 0.5—15 mmol L^{-1} and 80 mmol L^{-1} is not sorbed by the cryosponge formed from an aqueous solution of the sol with *n*-butanol. As can be seen in Fig. 1, binding of *n*-hexanol with the cryosponge begins only at a concentration of 4 mmol L^{-1}. As the concentration increases, its sorption increases, reaching 20% at a concentration of 10 mmol L^{-1}.

n-Octanol is bound with the cryosponge to the highest extent. At concentrations of 0.5—1 mmol L^{-1}, the degree of its sorption by the cryosponge is 85—88%.

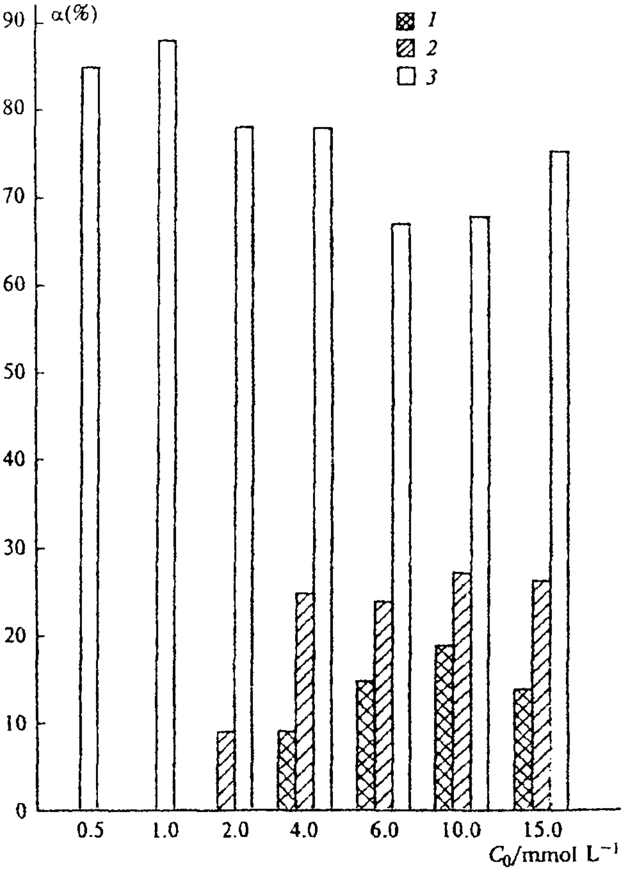

Fig. 1. Dependence of the degree of sorption of alcohols (α) by the corn starch cryosponge on their initial concentrations (C_0) in an aqueous solution of sol: *1*, *n*-hexanol; *2*, linalool; and *3*, *n*-octanol.

Unlike *n*-hexanol, the degree of sorption of *n*-octanol at first somewhat decreases as its concentration increases, reaching 69% (5 mmol L^{-1}) and remaining almost unchanged with a further increase in the alcohol content. The average degree of sorption is 67%, which is threefold higher than the maximum sorption of *n*-hexanol observed at a concentration of 10 mmol L^{-1}.

As can be seen in Fig. 1, at concentrations of 0.5—1 mmol L^{-1}, linalool is not sorbed by the corn starch cryosponge. Insignificant sorption is observed at concentrations of ~2 mmol L^{-1}. When the concentration changes from 2 to 4 mmol L^{-1}, the degree of alcohol sorption increases by more than 2 times. Further increase in the amount of linalool has almost no effect on the degree of sorption, which is ~25%. The degree of sorption of linalool is 2.5 times lower than that of octanol and comparable with that of hexanol.

The results of calculations of the amount of each of the alcohols sorbed on the cryosponge at different concentrations of the starting solutions are presented in Table 1. It is seen that an increase in the concentrations of alcohols results in an increase in their amounts in the

Table 1. Dependence of the amount of alcohol sorbed on the cryosponge (m) on its concentration in the starting solution (C_0)*

C_0/mmol L^{-1}	m/g(100 g of dry starch)$^{-1}$		
	n-Hexanol	n-Octanol	Linalool
0.5	0	0.17	0
1	0	0.42	0
2	0	1.08	0.08
4	0.13	1.42	0.50
5	0.26	1.50	—
6	0.33	2.33	0.67
10	0.67	3.00	1.33
15	0.76	4.92	1.67

* The relative error is 7%.

cryosponge, and the influence of the alcohol structure is also observed. For example, an increase in the concentrations of alcohols in the sol from 4 to 15 mmol L^{-1}, *i.e.*, by 3.75 times, results in an almost sixfold increase in the amount of n-hexanol sorbed, and that of linalool increases by only 3 times. Despite the fact that the degrees of sorption of n-hexanol and linalool are comparable at the same concentrations of the starting solutions, the amount of linalool sorbed is 2 times higher. n-Octanol is sorbed to the greatest extent, its amount reaching 4.92 g per 100 g of starch.

Linalool, whose molecular weight is the highest and solubility in water is the lowest among the alcohols studied, is sorbed much better than n-hexanol and worse than n-octanol. Branching and double bonds affect the sorption. The capabilities of formation of inclusion complexes of acids having the same alkyl chain length but differing by the presence of double bonds have previously[11] been compared. It has been found that oleic acid with one double bond is retained considerably better, and linoleic acid with two double bonds in the molecule exhibits the lowest retention. Probably, the presence of double bonds and branching results in a decrease in the sorption of linalool.

Thus, of the four alcohols studied, n-octanol is sorbed by the cryosponge to the highest extent and n-butanol is not sorbed at all. The capability of binding of the alcohols studied by the cryosponge changes in the order: n-octanol > linalool > n-hexanol. Therefore, as the chain length of saturated alcohol increases, the degree of its sorption by the corn starch cryosponge increases. This behavior distinguishes substantially corn starch cryotexturates in the capability of noncovalent binding of alcohols from sols of starches that form inclusion complexes. In studying inclusion complexes of aliphatic alcohols C_4—C_{14} with sols of various starches, it has been shown[6,10] that the yield of the complex decreases as the alkyl chain length in the alcohol increases. In this case, a situation opposite to the sorption of alcohols by cryotextures is observed. A decrease in the capability of complex formation with an increase in the length of the alkyl radical has been observed for inclusion complexes of free aliphatic acids with sols of polysaccharides and starches.[11] It can be assumed that beginning from the initial stage (sol), aliphatic alcohols template starch polymers, *i.e.*, polymer chains are arranged around alcohol molecules to form "cavities," which are additionally fixed at the cryotexturing stage by noncovalent bonds. An increase in the degree of binding of alcohols with an increase in the alkyl chain length indicates a predominantly hydrophobic character of the interaction with the corn starch cryotexturate. The possibility of "incapsulation" of alcohol microdroplets concentrated on freezing also cannot be ruled out.

Our data on sorption reversibility indicate that the processes of binding of alcohols by the cryosponge are complex. For example, it has been found that all alcohols studied are desorbed incompletely: n-hexanol is desorbed by 80%, whereas n-octanol and linalool, by 15 and 18%, respectively, *i.e.*, a considerable portion of these alcohols is irreversibly bound by the cryosponge.

Application of scanning electron microscopy has shown[14] that the structures of the pure cryosponge and cryosponge with sorbed n-octanol differ. A uniform undeveloped surface relief is observed for the pure cryosponge. The addition of n-octanol changes the surface of the cryosponge wall. The starch cryotexture formed with 1 mmol L^{-1} of octanol has uniformly arranged regions with strongly developed relief and fibrillar elements 0.5—1 μm in size. The results of the electron microscopic study of different cuts suggest that during the process of cryosponge formation from the sol, organic substances are sorbed both in the bulk and on the surface.

Thus, the data obtained suggest that the degree of binding of alcohols by the corn starch cryosponge increases as the length of the alkyl substituent increases. The presence of double bonds and branching results in a decrease in the degree of sorption of alcohol. Binding of alcohols by the cryosponge is a complex process including templation, formation of inclusion complexes with amylose, and sorption on the surface and in the bulk of the cryosponge.

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