# Sorption of alkyl acetates from aqueous solutions by corn starch cryotextures

*T. A. Misharina,* N. I. Krikunova, 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) 135 5085*

Capillary gas chromatography was used to study noncovalent sorption of *n*-butyl, *n*-hexyl, and *n*-octyl acetates from aqueous solutions by corn starch cryotextures. In the concentration range of 0.5—15.0 mmol $L^{-1}$, about 38% *n*-butyl acetate, 70% *n*-hexyl acetate, and 98% *n*-octyl acetate are extracted from aqueous solutions. The sorption of the alkyl acetates depends on the alkyl chain length, indicating the hydrophobic character of their interaction with the corn starch cryotexture. No competitive sorption between acetates in the mixture was observed. Binding of alkyl acetates occurs during the cryosponge formation, due probably to the templation at the stage of starch sol, fixation in the cryosponge, and sorption on the surface of its walls.

**Key words:** corn starch cryotextures, *n*-alkyl acetates, noncovalent binding, aqueous solutions, capillary gas chromatography.

Studies of interactions of low-molecular aroma compounds with polymer macrocomponents of food products, in particular, polysaccharides, have recently evoked increasing interest. It is important to study polysaccharides, because native and modified starches and maltodextrins are widely used as inert supports in the production of dry forms of flavorings. The quality and stability of products and flavorings depends to a considerable extent on the strength of binding volatiles.

Aroma compounds can be bound by polysaccharides due to noncovalent interactions, mainly electrostatic and hydrogen bonds. The formation of inclusion complexes in amylose helix and amylopectin fragments in starch sols is possible.[1—5] These helix fragments are formed around molecules with functional groups capable of donor-acceptor interactions with OH groups of starch. Depending on the structure of an organic molecule, the helix fragments can contain from 6 to 8 glucose units.[5] Sorption depends on the structure of sorbates and type of functional groups,[1—3,6—8] moisture content in the system,[9] and nature and structure of polysaccharide.[10,11] To determine the quantitative parameters of sorption, a method of separation of sorbed and nonsorbed parts of aroma compounds should be developed.

It is known that freezing of an aqueous starch sol leads to the formation of a cryotexture, which can be easily and completely separated from the aqueous phase.[12] We have shown that the components of rosemary oil, which belong to different classes of compounds, show different degrees of sorption on corn starch cryotextures depending on their structures.[13]

In this work, we studied the effect of the structure and concentration of alkyl acetates on the degree of their sorption by corn starch cryotextures.

## Experimental

Delipidized corn starch with 25—27% amylose obtained from the Research Institute of Starch Products (Russian Agricultural Academy) was used. Corn starch sol was prepared by heating a 3% starch suspension (600 g) in distilled water to 90 °C with vigorous stirring. The sol cooled to room temperature was poured (in 40-g portions) into polypropylene tubes with caps. Freshly distilled *n*-butyl acetate, *n*-hexyl acetate, or *n*-octyl acetate was added to the sol with intense shaking in order to obtain colloidal solutions with the concentration of alkyl acetate from 0.5 to 15 mmol $L^{-1}$ (Table 1). Samples of sol containing two or three acetates introduced in different orders were prepared by the same procedure (Table 2). Natural food products contain alkyl acetates in the same concentrations.

Samples of sols with additives of alkyl acetates were kept at +5 °C for 3 h and then at −18 °C for 24 h. After freezing out and storage at room temperature for 16 h, the aqueous phase was separated from the cryosponge that was formed. The aqueous phase (38 mL) contained no amylose, which was confirmed by the negative reaction with iodine.

To determine the nonsorbed part of alkyl acetates, a 10-mL aliquot of the aqueous phase was taken, and an ethereal solution (10 mL) of *n*-heptyl acetate used as the internal standard was added.

Gas chromatographic analysis of samples of aqueous phases was carried out on a Pye-Unicam-104 chromatograph modified for work with capillary columns and a flame-ionization detector (temperature of the detector 200 °C, temperature of the evaporator 220 °C). A glass column with an OV-101/KF

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 1943—1945, October, 1998.

1066-5285/98/4710-1889 $20.00 © 1998 Plenum Publishing Corporation

**Table 1.** Sorption of *n*-butyl, *n*-hexyl, and *n*-octyl acetates by corn starch cryosponge

| Introduced in sol | | Found | Sorbed | Degree of |
|---|---|---|---|---|
| mmol $L^{-1}$ | μL $L^{-1}$ | /μL $L^{-1}$ | /μL L* | sorption (%) |
| | | *n*-Butyl acetate | | |
| 0.49 | 65 | 39.0 | 26.0 | 40 |
| 0.95 | 125 | 77.5 | 47.5 | 38 |
| 1.52 | 200 | 117.3 | 82.7 | 41 |
| 2.09 | 275 | 165.0 | 110.0 | 40 |
| 3.04 | 400 | 234.5 | 165.5 | 41 |
| 4.94 | 650 | 402.5 | 247.5 | 38 |
| 7.03 | 925 | 575.0 | 350.0 | 38 |
| 10.08 | 1325 | 762.5 | 562.5 | 42 |
| 15.02 | 1975 | 1137.5 | 837.5 | 42 |
| | | *n*-Hexyl acetate | | |
| 0.50 | 85 | 32.5 | 52.5 | 61 |
| 1.00 | 170 | 60.0 | 110.0 | 64 |
| 1.62 | 275 | 92.5 | 182.5 | 67 |
| 2.01 | 340 | 102.0 | 238.0 | 70 |
| 2.95 | 500 | 137.5 | 362.5 | 72 |
| 5.01 | 850 | 217.5 | 632.5 | 75 |
| 6.93 | 1175 | 350.0 | 825.0 | 71 |
| 10.03 | 1700 | 470.0 | 1230.0 | 72 |
| 15.04 | 2550 | 532.5 | 2017.5 | 79 |
| | | *n*-Octyl acetate | | |
| 0.50 | 100 | 2.5 | 97.5 | 97 |
| 1.01 | 200 | 3.0 | 197.0 | 98 |
| 1.51 | 300 | 3.5 | 296.5 | 99 |
| 2.02 | 400 | 5.0 | 395.0 | 99 |
| 3.03 | 600 | 10.5 | 589.5 | 98 |
| 5.04 | 1000 | 42.5 | 957.5 | 96 |
| 7.06 | 1400 | 127.5 | 1272.5 | 91 |
| 9.96 | 1975 | 192.5 | 1782.5 | 90 |
| 15.01 | 2975 | 260.0 | 2325.0 | 91 |

* Amount of acetate sorbed from 1 kg sol of 30 g cryotexture.

**Table 2.** Sorption of a mixture of alkyl acetates of corn starch cryosponge

| Order of introduction | Introduced into sol/μL $L^{-1}$ | Found /μL $L^{-1}$ | Degree of sorption (%) |
|---|---|---|---|
| 1) HxAc | 170 | 75.5 | 56 |
| 2) BuAc | 132 | 74.0 | 44 |
| 1) HxAc | 170 | 63.3 | 62 |
| 2) OcAc | 198 | 5.8 | 97 |
| 1) OcAc | 198 | 4.8 | 98 |
| 2) BuAc | 132 | 85.0 | 35 |
| 1) OcAc | 198 | 3.8 | 98 |
| 2) HxAc | 170 | 60.0 | 64 |
| 3) BuAc | 132 | 85.5 | 35 |
| 1) BuAc | 132 | 88.0 | 33 |
| 2) HxAc | 170 | 60.0 | 64 |
| 3) OcAc | 198 | 3.8 | 98 |
| 1) HxAc | 170 | 67.5 | 60 |
| 2) BuAc | 198 | 4.9 | 35 |
| 3) OcAc | 132 | 85.0 | 97 |
| 1) BuAc* | 132 | 90.0 | 32 |
| 2) HxAc* | 170 | 65.0 | 62 |
| 3) OcAc* | 198 | 5.0 | 97 |

* The preliminarily prepared mixture of acetates was introduced into the corn starch sol.

stationary phase was used (30 m × 0.3 mm), thickness of the phase layer 0.4 μm.[14] The temperature of the column was 90 °C for samples with *n*-butyl acetate and 120 °C for samples with *n*-hexyl and *n*-octyl acetates. Each sample was analyzed 5—6 times. The concentration of the nonsorbed part of alkyl acetates was calculated from the surface areas of peaks of the substance and standard. The degree of sorption was calculated from the change in the concentration of the starting solution and after separation of the cryosponge.

## Results and Discussion

The results of determination of the degree of sorption (in percentage) of *n*-alkyl acetates by the corn starch cryosponge at different concentrations of *n*-alkyl acetates (0.5—15 mmol $L^{-1}$) are presented in Table 1. The error of gas chromatographic determination of the nonsorbed part of *n*-alkyl acetates was from 4 to 13 rel.%, and reproducibility of the degree of sorption for different experiments varied from 5 to 7 rel.%. As follows from the data in Table 1, the fraction of bound *n*-butyl acetate depends slightly on its content in the starting sol and is equal, on the average, to 38%.

The sorption of *n*-hexyl acetate is higher than that of *n*-butyl acetate and equal, on the average, to 70% (see Table 1). When the concentration of *n*-hexyl acetate is 7 and 10 mmol $L^{-1}$, the degree of sorption decreases.

The sorption of *n*-octyl acetate by the cryosponge is different. At low concentrations, *n*-octyl acetate is bound to the corn starch cryosponge by 97—99%, and as the concentration increases, the degree of binding decreases to 90%. Thus, it is quite evident that the sorption of *n*-alkyl acetates by the corn starch cryosponge depends on the alkyl chain length: the longer the molecule, the higher the sorption.

Binding of alkyl acetates by biopolymers can occur both at the stage of their introduction into the starch sol and during the formation of the cryosponge. Different alkyl acetates have different effects on elasticity of the cryosponge and its structure. The differences in structures of cryosponge walls obtained without and with additives of alkyl acetates (1 mmol $L^{-1}$) were observed by electron microscopy.[15] The pure starch cryosponge without acetate additives is characterized by an undeveloped uniform relief of the surface. The cryosponge obtained with an additive of *n*-butyl acetate has the same surface. The surface of the walls of the starch cryosponge obtained with *n*-octyl acetate has a nonuniform structure. Regions (2—3 μm) with strongly developed relief distributed uniformly over the whole surface of the cryosponge walls were observed. Probably, the process of sorption of acetates by cryosponges formed from the sol containing aroma compounds differs from the formation of inclusion complexes in starch sols.[1] It is established that 1% aqueous starch sols form inclusion complexes with aliphatic alcohols, and their concentration in the complexes decreases as the alkyl chain in the alcohols increases.[1] By contrast, in the cryosponge—alkyl acetate—water systems studied, under equilibrium conditions, the concentration of alkyl acetates bound by the cryosponge obtained from the sol containing alkyl acetates increases with the length of the alkyl chain. As the alkyl chain length doubles (*n*-butyl acetate—*n*-octyl acetate), the degree of binding also increases almost twofold.

During the sorption of the mixture of two or three acetates, each taken in the concentration of ~1 mmol $L^{-1}$, they behave as individual compounds (see Table 2). Comparison of the data in Tables 1 and 2 with account of the error of determination shows that the degree of sorption of *n*-hexyl and *n*-octyl acetates is almost independent of the nature of other acetates and the order of their introduction into the starting sol. Thus, alkyl acetates exert no effect on each other during sorption on the corn starch cryotexture. This can be attributed to the variety of binding sites on the cryosponge, whereby binding occurs *via* several mechanisms: in particular, due to templation of starch polymeric molecules by acetates at the stage of sol aging (3 h, 5 °C), due to inclusion complexes formed during the formation of the cryosponge, and due to sorption on the surface of its walls.

Thus, the study of sorption of *n*-alkyl acetates from aqueous solutions by corn starch cryosponges shows that the degree of binding of *n*-alkyl acetates increases as the alkyl chain length increases. This indicates the hydrophobic character of their interaction with the corn starch cryotexture.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 97-03-33109a).

## References

1. F. Osman-Ismail and J. Solms, *Lebensm. Wiss. Technol.*, 1973, **6**, 147.
2. A. Voilley, C. Lawer, P. Dubois, and M. Fenillat, *J. Agric. Food Chem.*, 1990, **38**, 248.
3. M. A. Rutschmann and J. Solms, *Lebensm. Wiss. Technol.*, 1990, **23**, 80.
4. S. Kubik, O. Holler, A. Steinert, M. Tolksdorf, and G. Wulff, *Macromol. Symp.*, 1995, **99**, 93.
5. G. Wulff, *Angew. Chem. Int. Ed. Eng.*, 1995, **34**, 1812.
6. M. Z. Thank, P. Thibeaudeau, M. A. Thibaut, and A. Voilley, *Food Chem.*, 1992, **3**, 129.
7. T. G. Kieckbuch and C. J. King, *J. Agric. Food Chem.*, 1979, **27**, 504.
8. W. L. P. Bredie, D. S. Mottram, and G. G. Birch, in *Trends in Flavour Research*, Eds. H. Maarse and D. G. van der Heij, Elsevier, Amsterdam, 1994, 139.
9. S. Langourieux and J. Crouzet, *Food Sci. Technol.*, 1994, **27**, 544.
10. A. Voilley, V. Berhin, C. Charpentier, and D. Peyron, *Lebensm. Wiss. Technol.*, 1991, **24**, 469.
11. J. Solms and F. Osman-Ismail, *Can. Inst. Food Sci. Technol. J.*, 1973, **6**, A10.
12. M. Richter, S. Augustat, and F. Schierbaum, *Ausgewählte Methoden der Stärkechemie*, VEB Fachb, Leipzig, 1973.
13. R. V. Golovnya and T. A. Misharina, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 310 [*Russ. Chem. Bull.*, 1998, **47**, 303 (Engl. Transl.)].
14. R. V. Golovnya, A. L. Samusenko, and E. A. Mistryukov, *J. High Resol. Chromatogr. CC*, 1976, **2**, 609.
15. A. G. Filatova, A. I. Lapshin, N. I. Krikunova, T. A. Misharina, and R. V. Golovnya, *Tez. X Rossiiskogo simp. po rastrovoi elektronnoi mikroskopii i analiticheskim metodam issledovaniya tverdykh tel* [*Proc. X Russian Symp. on Scanning Electron Microscopy and Analytical Methods of Studying Solids*], Chernogolovka, 1997, 98 (in Russian).

*Received November 28, 1997*