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Inclusion complexes of starches with hydrocarbons

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Abstract

Starch formed inclusion complexes with aliphatic and aromatic hydrocarbons. The amount of included hydrocarbons depended on the starch variety. Waxy maize starch was superior for this purpose as it included over 7% of hydrocarbons. Tapioca, maize and potato starches included gradually lesser amount of hydrocarbons. Oven-dried starches performed better than air-dried ones. Aromatic hydrocarbons complexed more readily. Polarity is, perhaps, the most essential factor governing the complexation. Less polar hydrocarbons were complexed more readily. The FT-IR spectra taken in the Kubelka–Munk mode and CLBM studies (the hedgehog effect) revealed that complexing hydrocarbons expelled part of the amorphous content of starch granules to form internal empty domains. In such domains, hydrocarbons were held with involvement of local van der Waals and dispersion forces of D-glucose units rather than by formation of helical complexes with amylose and amylopectin. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Hydrocarbon blends; Inclusion complexes; Maize starch; Potato starch; Tapioca starch; Waxy maize starch

1. Introduction

Starch is known to form capillary, surface sorption and/or inclusion complexes with inorganic (Tomasik & Schilling, 1998a) and organic (Tomasik & Schilling, 1998b) guest molecules. Among several organic guest molecules, hydrocarbons are also listed. Studies carried out on complexes of hydrocarbons with amylose and amylopectin (Kuge & Takeo, 1967) suggested that hydrophobicity of chains of hydrocarbons could be a driving force for coiling amylose around hydrocarbon to form helical complexes. For the same sake formation of surface sorption complexes was unlikely and, indeed, it was observed (Koda, 1928). The idea of the formation of amylose helical complexes with hydrocarbons suggested potential selectivity of complexation of hydrocarbons dependent on their molecular size and it was experimentally proved (Kuge & Takeo, 1967). In addition, amylopectin exhibited a weak ability towards formation of inclusion complexes with hydrocarbons (French, Pulley & Whelan, 1963). The mode of complexation of hydrocarbons by granular starch appeared to be less straightforward. Studies (Osman-Ismail & Solms, 1973) on the complexing ability of starch varieties in respect, among others, limonene and β-pinene revealed that the starch variety is essential. The amylose-to-amylopectin ratio was considered as the critical factor. Another essential factor is the time necessary to reach the sorption equilibrium and related to it, is the possibility of desorption of the guest molecules from the host (Maier & Bauer, 1972). The amount of hydrocarbons complexed to starch depended on their structure and ranged from 23.4% for benzene to 5.4% for hydrocarbons of petroleum ether (French et al., 1963; Kuge & Takeo, 1968; Schierbaum, 1959; Solms, Osman-Ismail & Beyler, 1973; Ulmann & Schierbaum, 1958). In our recent studies on complexes of granular starch with aliphatic alcohols (Polaczek, Starzyk & Tomasik, 1999) evidence was given that the complexation of these alcohols within amylose and amylopectin helices might be of lesser importance. Alcohols penetrated into the granule interior and occupied cavities liberated amorphous content of the granule interior expelled on the granule surface through the channels in the granule shell. Higher yield of complexation for aromatic than aliphatic hydrocarbons could be explained by the formation of azeotrops with water present inside the starch granules. The facilitated removal of water contributed to the formation of empty domains inside granules (Bączkowicz & Tomasik, 1986).

In this study the problem of the formation of complexes of hydrocarbons with potato, maize, waxy maize, and tapioca starches is revised. A potential possibility of selectivity in the hydrocarbon complexation as a tool in separation of hydrocarbon mixtures into pure individuals was also checked.

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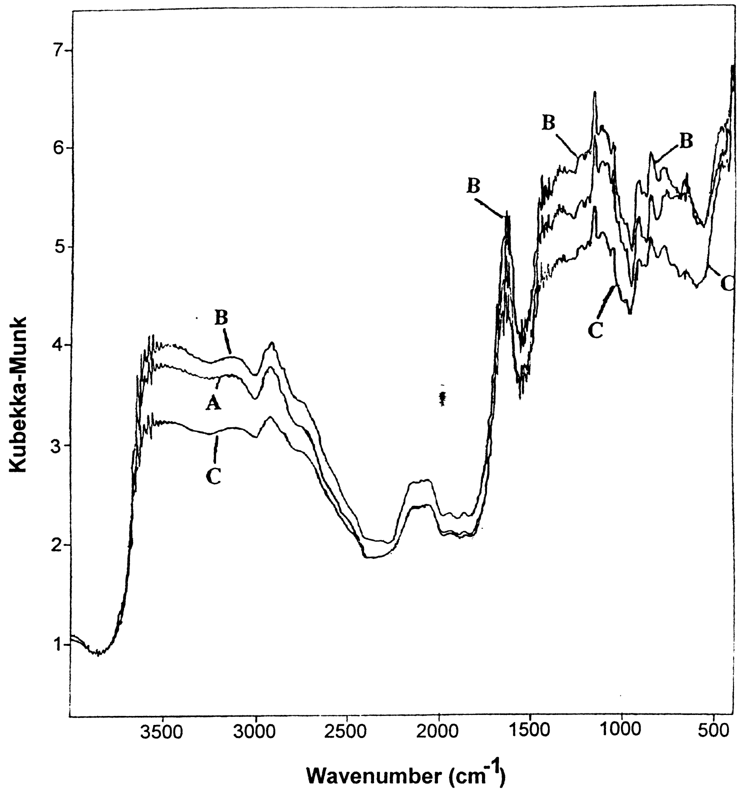

Fig. 1. Win-IR spectra of potato starch soaked in the 1:1:1 blend of three isomeric xylenes: (A) the spectrum of starch prior to soaking; (B) spectrum of starch after 3 days soaking in xylenes at room temperature; (C) the spectrum of starch after 1 h under boiling xylenes.

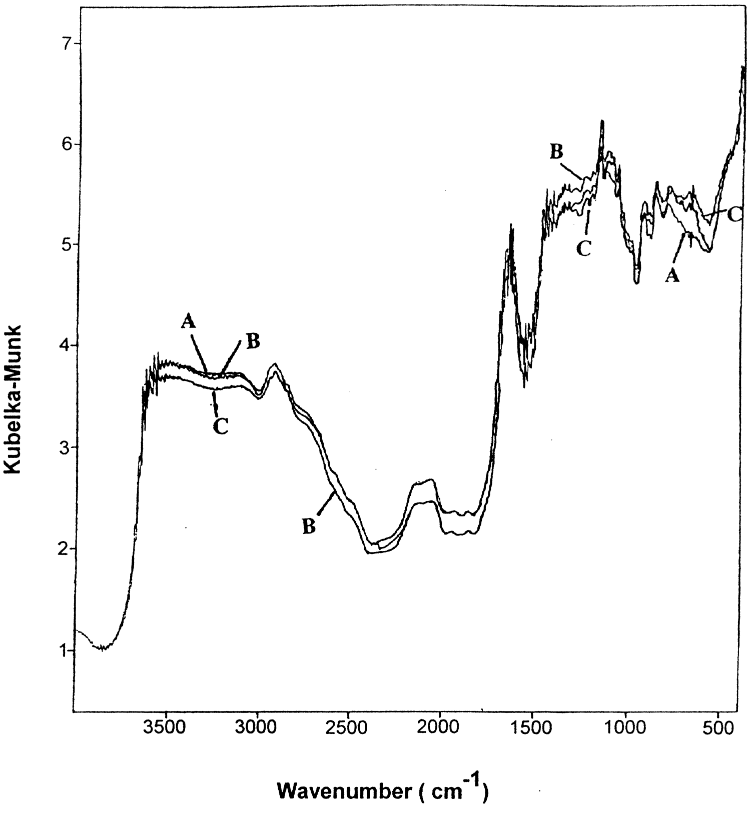

Fig. 2. Win-IR spectra of potato starch prior to soaking (A); after 3 days contact with extraction gasoline at room temperature (B); and after 1 h contact with boiling extraction gasoline (C).

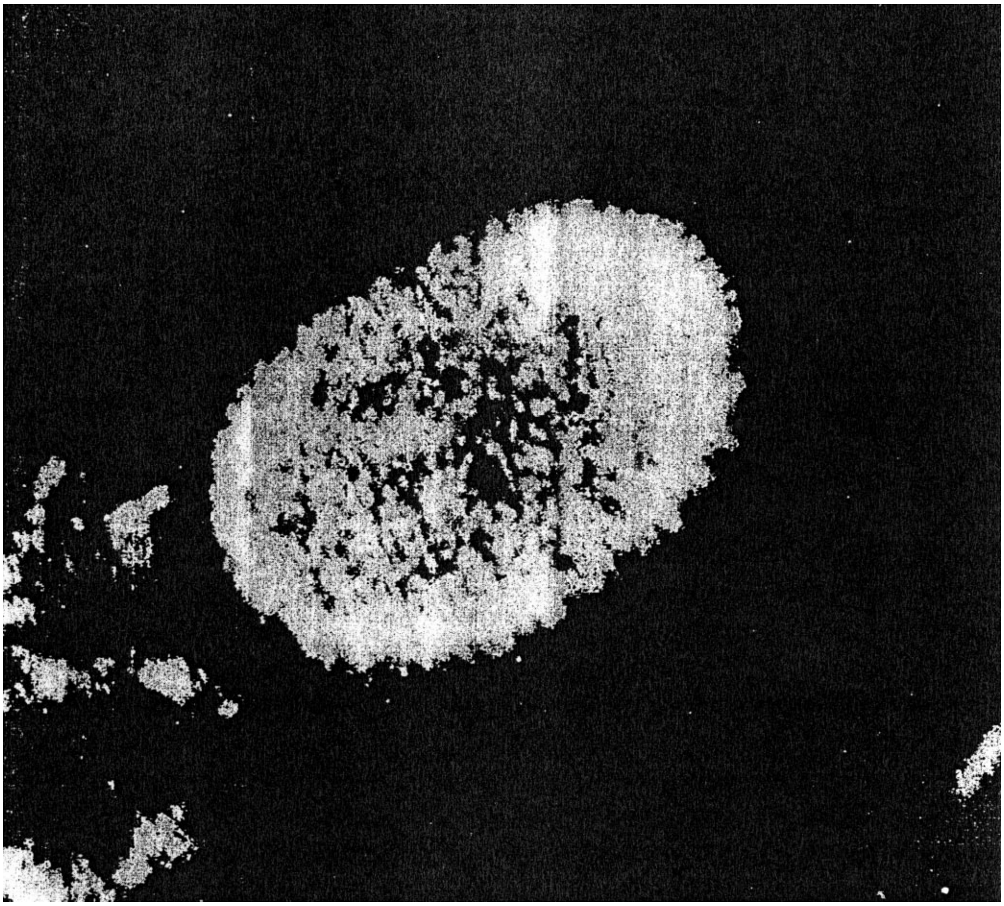

Fig. 3. Potato starch granule seen under optical microscope with illumination with polarised light beam from the bottom and simultaneous illumination with side beam of red laser. Excretions of amorphous content of the granule interiors resembled granules to small hedgehogs. Hence the effect observed was named the hedgehog effect.

2. Experimental

2.1. Materials

Potato starch was isolated in 1998 in NOVAMYL S.A., Nowogard, Poland. It followed Polish Standards for potato starch (PN-A-74710). As the air-dried product it contained 14.2% humidity. Maize starch and waxy maize starch were isolated in 1998 in NATIONAL STARCH & CHEMICAL GmbH (Germany). Both contained 15% humidity. (UE classification: E1422). Tapioca starch, Victoria Brand variety was isolated in 1997 in NATIONAL STARCH & CHEMICALS (Germany). It contained 12.8% humidity.

Extraction gasoline followed Polish Standards PN-56/6-96022; SWW: 0246-31 was purchased from Chemical Enterprise Szczyglowice (Poland). Its composition is given in Table 5.

2- and 4-xylenses of analytical grade were purchased from POCh, Gliwice (Poland) and 3-xylene, reagent grade, was purchased from REACHIM, USSR. They were used in 1:1:1 blend.

2.2. Preparation of complexes

Either air-dried or oven-dried (8 h at 130°C in blow-oven) samples of starch (2 g) were treated with extraction gasoline or mixture of xylenes (10 ml) and either stored in hermetically closed reaction flasks at room temperature for 24, 48, and 72 h or refluxed for 1 h. Then solid was filtered and left for drying in the open. Collected filtrate and solid were stored in tightly closed vessels.

2.3. Gas chromatography

PYE–UNICAM (GLV) Cambridge, UK was used at 30 ml/min flow of argon. Glass 5.5 m × 2 mm column was packed with 10% Carbowax 20 M on Ozaxome Q 90/100 M. Temperature of the column and FID detector was 30 and 80°C, respectively.

2.4. Capillary chromatography

HEWLETT PACKARD 57-10A, Boeblingen, Germany, gas chromatograph was used. Helium at 230 kPa was applied. Capillary, 100 m × 0.25 mm column was lined

Table 1
Range of pasting temperatures for air-dried, oven-dried and hydrocarbon–starch complexes

Sample	Pasting range (°C)	
	Beginning	End
Potato starch		
Air-dried	59–60	68–70
Oven-dried	54–56	64–66
Complexed (1 h reflux in gasoline)	54–55	64–65
(72 h, RT[a] in gasoline)	55–56	64–67
(1 h reflux in xylenes)	54–56	62–65
(72 h, RT[a] in xylenes)	55–56	63–66
Maize starch		
Air-dreid	64–66	68–70
Oven-dried	58–60	65–67
Complexed (1 h reflux in gasoline)	59–60	66–68
(72 h, RT[a] in gasoline)	57–60	67–68
Waxy maize starch		
Air-dried	55–58	60–63
Oven-dried	51–54	56–58
Complexed (1 h reflux in gasoline)	52–53	57–58
(72 h, RT[a] in gasoline)	51–54	57–59
Tapioca starch:		
Air-dried	64–67	70–72
Oven-dried	60–63	66–69
Complexed (1 h reflux in gasoline)	60–62	67–69
(72 h, RT[a] in gasoline)	61–63	67–69

[a] Room temperature.

with 0.5 μm layer of Petrocol DH. The feed and detector were maintained at 200°C. The temperature of the thermostat varied from 30 to 200°C with the increase rate of 2°C/min. The initial isotherm was 25 min. The precision of estimations of the area under peaks was 0.1%.

2.5. Range of pasting temperature

This estimation was carried out according to Gambus and Nowotna (1992) using the Rheostat-2 rotary viscometer VEB-MLV Pruefgeraete-Werk, Medingen, Germany.

2.6. Thermogravimetric analysis

The analyses were performed on computerised a Paulik–Paulik–Erdey Derivatograph Q 1500 D machine (Budapest, Hungary). Samples of complexes (200 mg) were heated in ceramic crucibles in the air. The rate of temperature increase from room temperature to 450 was 4°C/min. Corrundum (8 μm) was the standard.

2.7. WIN-IR spectrophotometry

Spectra were recorded using a BIORAD FT-IR 175C spectrophotometer with a diffusive-reflectance accessory manufactured by Pike Technologies Inc. and 1.6 mm sample cups of 4.7 mm diameter. The band intensities were presented in Kubelka–Munk units f (*R*) (compensating differences).

2.8. Optical microscopy

Optical microscope BIOLAR PI made in PZO Warsaw was used. Laser DLS25M1, 670 ± 0.2 nm of Spindler & Hoyer GmbH & Co. Goetingen, Germany was used in co-operation with the microscope.

3. Results and discussion

Observations under optical microscope involving the crossed polarised-non-polarised light beams technique (CLBM) (Starzyk, Lii & Tomasik, 1999a) revealed that granules of starch changed their image depending on hydrocarbon, starch variety and moisture content in the granules. In xylenes, regardless of the contact of granule with the medium, which lasted either 3 days at room temperature or 1 h on reflux, only hilum of granules expanded. This effect was not accompanied by any vanishing of Maltese crosses and interference. The Kubelka–Munk Win-IR spectra showed that 3 days contact of starch with xylenes slightly reduced the volume of starch granules and the spectroscopic cell could be filled with higher portion of starch. As the result of contact with boiling xylenes, relatively strong association of starch granules was observed. A smaller portion of starch could be put into the spectrophotometric cell which means that material from the granule interior leached and covered the granule surface (Fig. 1).

Deformation of granules due to contact with aliphatic hydrocarbons of extraction gasoline was stronger than with xylenes. The tendency of granules for association was negligible when soaked in gasoline at room temperature for 3 days and it appeared after keeping starch granules for 1 h under reflux (Fig. 2).

Using the CLBM technique conditions with red laser (Starzyk, Lii & Tomasik, 1999b) the so-called "hedgehog effect" could be observed (Fig. 3).

Starch granules exhibited nanometric needles on their surface resembling hedgehogs. These needles were formed by the content of granule the interior expelled by the solvent and deposited on the granule surface. One might see that the material from starch granules was expelled not only through the hilum. This process was responsible for the formation of empty domains inside granules, into which solvent could penetrate and reside therein. This observation rationalised results of our former microscopic observations (Bączkowicz & Tomasik, 1989) of starch granules contacted with various solvents.

Changes in starch granules under the influence of hydrocarbons were, generally, not essential and definitely they influenced solely the starch macrostructure. Estimated range of pasting temperature for original, air-fried potato starch, the same starch after drying and for the same starch contacted with extraction gasoline showed negligible

Table 2
Thermogravimetric analysis of starches and their complexes with aliphatic hydrocarbons from gasoline

Sample	Temperature, (°C)		
	Mass loss[a]		Maximum of transition[b]
	First	Second	(DTG)[c]
Potato starch			
Air-dried	50–117(13.4)	250–272(58.2)	252, 277, 330
Complexed (1 h reflux)	55–122(13.5)	245–270(61.1)	250, 270, 320
(72 h, RT[d])	55–115(12.0)	247–270(57.0)	250, 270, 330
Oven-dried	52–117(13.8)	250–272(61.2)	240, 273, 350
Complexed (1 h reflux)	60–123(12.9)	253–276(62.2)	257, 277. 350
(72 h, RT[d])	55–125(14.3)	252–275(59.7)	244, 277, 362
Maize starch			
Oven-dried	to 285(4.5)	285–298(64.7)	275, 292, 319
Complexed (1 h, reflux)	to 288(8.1)	291–302(65.5)	277, 295, 325
(72 h, RT[d])	to 291(8.2)	291–303(64.4)	279, 295, 326
Waxy maize starch			
Oven-dried	to 277(2.2)	277–312(70.3)	230, 299, 330
Complex (1h, reflux)	to 281(9.2)	281–315(64.8)	257, 300[e], 329
(72 h, RT[d])	to 283(10.0)	283–323(66.2)	250, 306[e], 335
Tapioca starch			
Oven-dried	to 292(3.9)	292–307(69.5)	274, 297[e], 340
Complex (1 h, reflux)	to 289(9.2)	289–305(64.5)	275, 295[e], 336
(72 h, RT[d])	to 290(6.9)	290–305(66.7)	279, 297[e], 337

[a] The mass loss in % is given in parentheses.
[b] All effects were endothermic.
[c] The middle effect in differential thermal analysis was the principal effect.
[d] Room temperature.
[e] The peak split, additional weak peak appeared.

changes in measured parameters (Table 1). Drying in the oven but not contact with hydrocarbons was that operation which influenced pasting of starch.

Pasting temperatures of tapioca, waxy maize, and potato starch were similarly affected by contact with extraction gasoline. Only maize starch after contact with gasoline exhibited a noticeable depression of the pasting temperature. It could be rationalised in terms of the extraction of lipids present in granules (see, for instance, Tegge, 1988).

Thermogravimetric analysis (Table 2) of starch varieties prior to and after contact with hydrocarbons showed that undoubtedly complexes were formed. However, in order to achieve complexation, drying starch in the oven prior to complexation was recommended. Among starch varieties potato starch took the least amount, ~1%, of aliphatic hydrocarbons from extraction gasoline, whereas waxy maize starch, tapioca starch, and maize starch held over 7, 5.5, and slightly below 4% hydrocarbons, respectively.

Table 3
Chromatographic analysis (glc) of the xylene blend prior and after treatment with oven-dried potato starch

Sample	Peak			
	R_f	Area (%)	R_f	Area (%)
Unprocessed blend	2.6	63.6	2.9	36.4
After 1 h reflux	2.6	60.3	2.9	39.7
After 72 h at room temp.	2.6	58.9	2.9	41.2

Reflux was more effective than prolonged contact of starch with hydrocarbons at room temperature. Differences

Table 4
Effect of the mode of processing of extraction gasoline with potato starch (chromatographic analysis)

Treatment mode	Peak area[a] at R_f					
	0.62	0.81	1.02	1.20	1.91	3.39
None (unprocessed gasoline)	0.09	0.61	1.0		0.017	0.13
Air-dried starch						
24 h at room temp.	0.097	0.67	1.0	0.005	0.015	0.13
48 h at room temp.	0.115	0.70	1.0		0.02	0.14
72 h at room temp.	0.13	0.75	1.0		0.02	0.14
1h reflux	0.086	0.95	1.0	0.013	0.011	0.16
15 min reflux	0.146	1.0	0.994		0.018	0.147
Oven-dried starch						
72 h at room temp.	0.065	0.52	1.0		0.12	0.125
10 h reflux	0.1	0.83	1.0	0.015	0.01	0.15
1 h reflux	0.086	0.97	1.0		0.013	0.16
15 min reflux	0.092	0.75	1.0		0.014	0.14

[a] The peak areas are given as the ratio in respect to the most intensive peak on chromatogram.

Table 5
Composition of extraction gasoline and selectivity of oven-dried potato starch in complexation of its components

Component	Chromatographic peak area (%)		
	Unprocessed	Processed 72 h at RT[a]	1 h reflux
C_5-hydrocarbons			
Cyclopentane	< 0.1	< 0.1	< 0.1
Iso-pentane	< 0.1	< 0.1	< 0.1
n-Pentane	0.1	0.1	0.1
C_6-hydrocarbons			
Benzene	0.7	0.6	0.7
Cyclohexane	5.2	5.2	5.4
2,3-Dimethylbutane	0.1	0.1	0.1
n-Hexane	4.1	4.1	4.2
Methylcyclopentane	2.9	3.0	3.1
2-methylpentane	0.9	0.9	1.0
3-methylpentane	0.8	0.8	0.8
C_7-hydrocarbons			
Cycloheptane	trace	trace	trace
trans-1,2-Dimethylcyclopentane	4.6	4.6	4.7
cis-1,2-Dimehylcyclopentane	0.7	0.7	0.7
cis-1,3-Dimethylcyclopentane	2.8	2.8	2.8
2,2-Dimethylpentane	0.5	0.5	0.5
2,3-Dimethylpentane + 1,1-dimethylcyclopentane	1.8	1.8	1.7
2,4-Dimethylpentane	0.1	0.1	trace
3-Ethylpentane + *trans*-1,2-dimethylcyclopentane	2.4	2.4	2.4
n-Heptane	16.2	16.1	16.0
Methylcyclohexane + 2,2-dimethylhexane	18.9	18.8	18.7
2-Methylhexane	5.2	5.2	6.3
3-Methylhexane	5.5	5.5	5.5
Toluene	4.7	4.7	4.7
C_8-Hydrocarbons			
1,1-Dimethylcyclohexane	0.1	0.1	0.1
trans-1,2-Dimethylcyclohexane	0.6	0.6	0.6
2,3-Dimethylhexane + 3-methyl- and 3-ethylpentane	0.8	0.8	0.8
2,4-Dimethylhexane	1.0	1.0	1.0
2,5-Dimethylhexane + Ethylcyclopentane	1.5	1.5	1.5
3,3-Dimethylhexane	0.1	0.1	–
3,4-Dimethylhexane	0.5	0.5	0.5
Ethylbenzene	0.2	0.2	0.1
2-Methylheptane	2.9	2.9	2.8
3-Methylhexane + 3-methyl-and 3-ethylpentane	1.9	1.9	1.9
4-Methylheptane	0.8	0.8	0.8
n-Octane	2.3	2.3	2.3
1,1,2-Trimethylcyclopentane	0.4	0.4	0.4
1,1,3-Trimethylcyclopentane	0.3	0.3	0.3
1,2,3-Trimethylcyclopentane	1.5	1.5	1.5
1,2,4-Trimethylcyclopentane	1.6	1.6	1.6
2,2,3-Trimethylpentane	< 0.1	0.1	0.1
2,2,4-Trimethylhexane	0.4	0.4	0.4
2,2,5-Trimethylhexane	3.0	3.0	3.0
2,3,4-Trimethylpentane	0.1	0.1	0.1
3- and 4-Xylenes	0.1	0.1	0.1
C_9-Hydrocarbons			
Total	0.1	0.1	0.1
Unidentified components	1.7	1.9	0.6

[a] Room temperature.

in complexing ability between particular starches suggested that the amorphous content of starch granules was expelled from their interiors and the most amorphous waxy maize starch faced the biggest losses of internal amylopectin.

Studies on the complexation of xylenes confirmed that also aromatic hydrocarbons might be complexed. Less polar and smaller 2-xylene had a priority over more polar and larger 4-xylene in inclusion into granules (Table 3). One might see in Table 3 that after contact with starch the area under first peak of lower R_f decreased and, simultaneously, the area of the peak of higher R_f increased.

The same was found for extraction gasoline combined with potato starch. Gasoline fraction of lower R_f was slightly more readily complexed than fractions of higher R_f (Table 4).

Because these data for xylenes were related to potato starch, which poorly included aliphatic hydrocarbons one might say that aromatic hydrocarbons better complexed to starch than aliphatic. Data in Tables 3 and 4 reveal preference for the complexation by reflux.

Results of the study point to the importance of van der Waals and dispersion forces in holding hydrocarbons by starch. It is commonly accepted (see, for instance, Tomasik & Schilling, 1998a,b) that non-polar compounds as the whole or non-polar fragments of polar compounds used to be closed inside of amylose and amylopectin helices. It is also known that chains of amylose and linear terminal branches of amylopectin in starch are only randomly coiled. Under favourable conditions, such random coils reorient and envelope non-polar chain of a molecule to form a helical inclusion complex. Under experimental conditions applied in this study, reorientation of amylose and amylopectin branches enveloping hydrocarbons was rather unlikely. The priority for inclusion of more bulky 2-xylene over 4-xylene delivered additional argument that observed complexation involved van der Waals and dispersive forces of individual D-glucose units (Mazurkiewicz, 1997) rather than their coiling to form helical complexes. Therefore, it was not surprising that starches exhibited very limited selectivity in complexation of hydrocarbons of different structures and dimensions. Relevant data are collected in Table 5.

In view of the precision (0.1%) of applied capillary chromatographic method some slight changes in the composition of gasoline after reflux with starch might be carefully discussed.

Since areas of the peaks for 2,4-dimethylpentane, 2,2-dimethylhexane and *n*-heptane were reduced by the magnitude beyond the precision limit a weak preference for the complexation of these hydrocarbons could be postulated. Using the same arguments weaker inclusion could be postulated for methylcyclopentane, cyclohexane, and 2-methylhexane.

Complexation of hydrocarbons into starch should result in decrease in temperature of ignition of starch and improved starch flammability.

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