



# Chemistry of Desiccant Properties of Carbohydrate Polymers as Studied by Near-Infrared Spectroscopy

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ABSTRACT: The combination frequency of water molecule in near-infrared spectroscopy is very useful for studying water molecular adsorption on solid surfaces. The absorption is purely from water molecules, and the variation in the absorption bands reflects the change in the environment of the water molecules on a surface. This variation, in turn, reflects the nature of the functional groups on the surface. Recently, Christy used this information in combination with second-derivative techniques to probe the surface of hydrothermally treated silica gel samples (Ind. Eng. Chem. Res. 2011, 50, 5543). In this work, a similar approach was used in studying the surface OH groups in carbohydrate polymers and their behavior toward water molecular adsorption. Not only second-derivative profiles but also fourth-derivative profiles of the near-infrared spectra were used in revealing the adsorption behavior of the OH groups on the polymer surface. Carbohydrate polymers such as amylose amylopectin, cellulose, and starch samples were used in this study. After being heated and evacuated at 120 °C, the samples were exposed to air, and the evolving changes on the surfaces of the samples were followed by near-infrared spectroscopy. Furthermore, the effectiveness of the samples in adsorbing water molecules was followed by monitoring the mass of water adsorbed. These investigations formed the basis for understanding how the OH groups on the carbohydrate polymers adsorb water molecules. The results clearly reveal that carbohydrate polymers such as amylose, amylopectin, and cellulose have three OH groups of different polarities and that the OH groups attached to C2 and C3 positions in the monomer glucose units adsorb water molecules faster than the C6-OH group. Furthermore, the adsorption of water molecules in amylose and amylopectin follows the same pattern during the first hour, irrespective of the variation in their structure.

# 1. INTRODUCTION

1.1. Carbohydrates and Their Desiccant Properties. Carbohydrate polymers are made up of monosaccharide units with different glycosidic or acetal bonds between the monosaccharide molecules. Amylose, amylopectin, glycogen, and cellulose are some of the carbohydrate polymers of glucose molecules. Amylose is a polymer of  $\alpha$ -glucose molecules with  $\alpha$ -1,4-glycosidic bonds between the monomer units. The polymer is mostly unbranched, and the number of glucose units in the polymer chain can vary from 300 to 20000. The polymer molecule winds up in the form of an  $\alpha$ -helix because of the angle formed during the formation of  $\alpha$ -1,4-glycosidic bonds. Amylopectin has polymer chains similar to those in amylose, with branches at every 20 to 30 units. The branching points involve  $\alpha$ -1,6-glycosidic bonds. Glycogen has a structure similar to that of amylopectin but highly branched. The branching in amylopectin occurs every 10-15 glucose units. Starch is a mixture of 20% amylose and 80% amylopectin. Cellulose is the major structural material of plants and is a polymer of  $\beta$ -glucose molecules with  $\beta$ -1,4-glycosidic bonds. The bonds in cellulose chains make them extend in linear chains. The chains are arranged in parallel rows and are held by hydrogen bonds between the OH groups in the chains.

Carbohydrate polymers generally have affinity for water molecules. 1-3 This property has been used in the dehydration of ethanol in industry. 4-7 The desiccant properties of carbohydrate polymers have been attributed to the free OH groups on the glucose units. 8-11 The hydroxyl groups interact with water molecules by hydrogen bonding. Studies on the adsorption of water by starch reveal that starch can take up to 30% of water by adsorption at 40% relative humidity.11

Furthermore, studies on the adsorption of water by cellulose propose 3-7% water adsorption at 40% humidity. 12 The remainder of the water that is found in cellulose beyond 40% relative humidity is capillary water.<sup>6,7</sup> Studies have also been performed to understand the adsorption of the amylose and amylopectin components in starch. Rebar et al. 13 followed the thermodynamics of the adsorption of water and ethanol to show the adsorption differences between amylose and amylopectin. They showed that water molecules are more strongly adsorbed to amylopectin than to amylose and attributed this behavior to the branched structure of amylopectin.

All of these studies addressed the adsorption behavior of carbohydrate polymers toward water molecules. Articles considering the chemistry of the adsorption of water molecules showing where and how water molecules are adsorbed in the polymer matrix are rare in the literature.

Infrared spectroscopy is one of the techniques used in the studies of water adsorption. Both mid- and near-infrared spectroscopies have been used successfully in studies of surface OH groups and their adsorption properties. Investigations of surface silanol groups in silica gel<sup>14–19</sup> and carbohydrate polymers and related substances<sup>20–24</sup> have been performed by infrared spectroscopy in both the mid- and near-infrared ranges. Recent investigations by Christy and co-workers<sup>25–27</sup> using

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near-infrared spectroscopy have provided insight into the types of OH groups on the silica gel surface, their fate during heating, their adsorption of water molecules, and the binding of water molecules to the surface OH groups. In these investigations, second-derivative techniques contributed to the resolution of differences between free and hydrogen-bonded OH groups on the silica gel surface.

Derivative spectroscopy is a widely used technique in absorption, fluorescence, and reflection spectroscopies. <sup>25,29–31</sup> The technique has been used in analytical spectroscopy for spectral discrimination to accentuate small structural differences, resolve overlapping spectral bands, and correct for various background absorptions in the spectra. The water molecules adsorbed on carbohydrate polymers give rise to a broad absorption peak containing absorption bands from the different OH groups in the carbohydrate polymers. The investigations of Christy and co-workers <sup>25–27</sup> on silica gel surfaces have demonstrated the potential of derivative spectroscopy and have opened possibilities for investigating surface OH groups on other chemical substances and their water adsorption behavior.

1.2. Polarization of Hydroxyl Groups in Carbohydrate Polymers. The monomer units in carbohydrate polymers contain OH groups, and because of the oxygen atoms in these groups, the monomers are polarized. The degree of polarization in each OH group depends on where the OH group is attached and the environment surrounding it. For example, amylose contains α-glucose units with OH groups in the C2, C3, and C6 positions. The extents of polarization in the OH groups appear to be comparable, and a ranking of OH groups according to polarity is difficult. Moreover, the degree of effective polarization depends on the secondary structure of polymers. Internal hydrogen bonds between neighboring OH groups can arise because of proximity given their structural arrangement in space. For example, cellulose with its linear secondary structure brings the C2-OH and C6-OH groups closer to each other, and this can lead to the formation of hydrogen bonds between some pairs of these two types of OH groups. The thus-formed hydrogen bonds can make some of these OH groups less available for strong water molecular adsorption.

The intention in this article is to show the characteristics of the OH groups in the biopolymers and their adsorption properties as observed by the evolution of the near-infrared spectra during the adsorption of water molecules. The adsorption of water molecules by OH groups in carbohydrate polymers gives rise to a peak that appears in the combination region of the near-infrared range around 5200 cm<sup>-1</sup>. This appears to be a broad peak containing several bands with their maxima close to each other. The fourth-derivative profile approach was used in addition to second derivative profiles to enhance the exposure of the band positions. Furthermore, it was also the intention to show how these OH groups behave from the start of water molecular adsorption by using secondand fourth-derivative approach with the near-infrared spectra.

## 2. EXPERIMENTAL SECTION

2.1. Materials, Equipment, and General Experimental Procedure. Carbohydrate polymer samples such as amylose, amylopectin, and starch from potato, microcrystalline cellulose, amylose acetate, dextran, dextrin, 2-dehydroxy-D-glucose, and 6-dehydroxy-D-glucose were all purchased from Sigma-Aldrich. A sugar substitute, sucralose was obtained from a local grocery store.

Finely ground amylose, amylopectin, and starch samples were sieved through 40- $\mu$ m sieve to control the particle size.

The desiccant properties of carbohydrate polymers were followed separately by NIR spectrometry and gravimetry. All samples were first evacuated and dried at 120 °C, and the evolutions of their adsorptions of water vapor were followed.

The adsorption experiments and infrared measurements were carried out simultaneously in the same room, which had a room temperature of 23.5 °C. The relative humidity during the water adsorption experiments and near-infrared measurements of amylose, amylopectin, cellulose, and starch samples were in the range of 55–57%. A small thermometer/hygrometer (Termometerfabriken Viking AS, Eskilstuna, Sweden) was used in humidity measurements.

2.2. Sample Drying, Water Sorption Experiments, and Near-Infrared (NIR) Measurements and Transformations. Each of the carbohydrate polymers used in the experiments was dried under a vacuum using a ceramic heater (BA Electric Bunsen from Electrothermal, Staffordshire, U.K.) controlled by an external power supply and a powerful vacuum pump (Edwards, West Sussex, U.K.) and cooled to room temperature before water sorption experiments.

Each of the dry carbohydrate polymers (around 0.15 g) was placed in the NIR transflectance sample cup and exposed to air in the room, and the evolution of the adsorption of water was followed by recording NIR spectra over a period of 60-70 min. The near-infrared measurements were made using a Perkin-Elmer Spectrum One NTS FT-NIR spectrometer (Perkin-Elmer Ltd., Cambridge, U.K.) equipped with a transflectance accessory and deuterated triglycine sulfate detector. The sample cup containing the carbohydrate polymer sample was placed directly on the crystal of the transflectance accessory, and NIR spectra were collected every 5 min in the range of 10000-4000 cm<sup>-1</sup>. A total of 30 scans were obtained at a resolution of 16 cm<sup>-1</sup>. All NIR spectra were transformed to log(1/R) format and saved. The second-derivative profiles of the spectral data were calculated by an algorithm developed by Savitzky and Golay with a 19-point derivative width. The fourth-derivative profiles of the spectra were obtained in the same manner from the second-derivative profiles after performing a smoothing operation using the automatic smoothing option in the spectrum software of the instrument.

The gravimetric determination of water sorption was carried out on each dry carbohydrate polymer by placing the NIR sample cup containing 0.15 g of dry carbohydrate polymer sample on a Mettler electronic balance connected to a computer through an RS-232 port for data collection. The increase in the mass was recorded twice every second by locally written software that communicated with the Mettler balance through the RS-232 port. The data collected at the computer were plotted using an Excel spread sheet and presented in the form of graphs for comparison and discussion.

### 3. RESULTS AND DISCUSSION

3.1. General Remarks on the Near-Infrared Spectra of Carbohydrate Polymers. Water molecules are found adsorbed in the carbohydrate polymer samples in their natural state. A general band assignment for the carbohydrate polymers are given in Table 1. The table reveals some of the regions where the carbohydrate skeleton and OH groups absorb. The carbohydrate polymers do not have absorptions in the range of 5400–5000 cm<sup>-1</sup> where the combination frequencies (O–H) of the hydrogen-bonded water molecules absorb. This range is

Table 1. Near-Infrared Band Assignments for a Natural Carbohydrate Polymer Sample in the Range of 10000-4000 cm<sup>-1</sup>

peak (cm <sup>-1</sup> )	band assignment
9200-7600	CH second overtone and OH combination
7500-5950	CH combinations, first overtone -OH stretchings
5950-5300	first CH overtone
5300-5000	combination frequencies of OH groups from water molecules hydrogen-bonded to carbohydrate OH groups, to other water molecules, and to other sites in the polymer
4500-4100	CH combination frequencies

of great interest, and the nature of the OH groups on carbohydrate polymers can be indirectly identified using the bands appearing in this region.

As mentioned in the Experimental Section, the near-infrared spectra acquired from the carbohydrate samples were converted to  $\log(1/R)$  format. Their second-derivative and fourth-derivative profiles were acquired using the Perkin-Elmer spectrum software.

**3.2.** Water Adsorption by Carbohydrate Polymers. The molecular adsorption of water using hydrogen bonding in amylose is shown in Figure 1. The figure shows only part of the

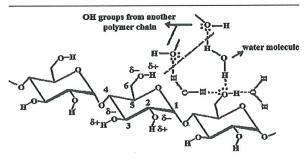


Figure 1. Model for water molecular adsorption on amylose. The possible adsorption of water molecules is shown for only one C6-OH group.

amylose polymer molecule. The OH groups in the glucose units of an amylose molecule can adsorb water by donating or accepting hydrogen bonds. Theoretically, three water molecules can form hydrogen bonds with each OH group in the glucose units. Calorimetric measurements of hydration of cellulose in both microcrystalline and amorphous states show that the adsorption of water is exothermic  $^{32}$  and support the formation of saturated hydrogen bonds during the adsorption of water. The formation of only unsaturated hydrogen bonds would have resulted in an endothermic reaction. The presence of OH groups in the polymer molecule or in the neighborhood of the molecule helps the water molecules in forming saturated hydrogen bonds. The numbers of water molecules that can be adsorbed by each OH group varies depending on whether the group is engaged in intermolecular hydrogen bonds with other OH groups in the polymer chains or intramolecular hydrogen bonds with OH groups in the neighboring polymer chains.

Near-infrared spectra of amylose, amylopectin, and cellulose acquired during the molecular adsorption of water when dry samples were exposed to surrounding air are shown in Figure 2. It appears that the adsorption nears saturation within 45 min of exposure. All of these spectra reveal an increase with time in the intensity of the water OH combination frequencies around 5200 cm<sup>-1</sup>. Their rate of increase reflects the rate of adsorption

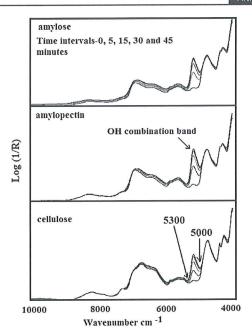


Figure 2. NIR absorption spectra of the evolution of water adsorption on amylose, amylopectin, and cellulose.

of water molecules. The peak representing the OH combination frequencies appears as a single peak. However, the second-derivative profiles of the peak reveal more structure lying under the peak (Figure 3). This is further enhanced in the fourth-derivative profiles of the peak. The second derivative gives an impression that there are three bands around 5200 cm<sup>-1</sup>. These three bands are revealed clearly in the fourth-derivative profiles in the range of 5300–5000 cm<sup>-1</sup>. The carbohydrate polymers amylose, amylopectin, and cellulose and several other carbohydrate polymers and their derivatives exhibit similar spectral structures in the near-infrared range of 5300–5100 cm<sup>-1</sup>. The range of 5100–5000 cm<sup>-1</sup> seems to be very broad and complicated and appears to be coming from the water molecules of different hydrogen bonds with carbohydrate polymers.

3.3. Peak Assignments. The intensities of the bands under the peak at 5200 cm<sup>-1</sup> appear to be similar in structure in all three carbohydrate polymers. The band at 5246 cm<sup>-1</sup> has the highest intensity compared to the other bands at 5190 and 5165 cm<sup>-1</sup>. The band positions shown in Figure 3 are for amylose polymer, and the exact positions of the bands in the other carbohydrate polymers and monosaccharides might vary slightly. From Figure 1, it is clear that there are possibilities for three water molecules to bind each of the OH groups of the three carbohydrate polymers. The OH combination frequencies of the water molecules binding in this way give rise to bands close to each other. Assigning these bands to water molecules bound to specific OH groups in the carbohydrate polymer matrix is not easy because of their similarity in polarity. An indirect method for the assignment was thus explored.

A selection of saccharide monomers and carbohydrate polymers were made with the aim of differentiating these three absorption bands. On the basis of the absorptions in the near-infrared range, an attempt was made to assign the bands to different OH groups. Two sets of near-infrared spectra of these samples in the range of 5300–5000 cm<sup>-1</sup> are shown in Figures

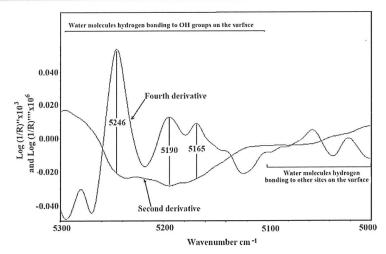


Figure 3. Second- and fourth-derivative profiles of NIR spectra of an amylose sample with adsorbed water molecules in the range of 5300-5000 cm<sup>-1</sup>.

4 and 5. The spectra of 2-deoxy-D-glucose, 6-deoxy-D-glucose, and amylose are shown in Figure 4, and the spectra of

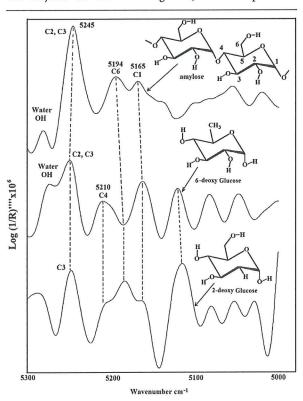


Figure 4. Fourth-derivative profiles of NIR spectra of 2-deoxy-D-glucose, 6-deoxy-D-glucose, and amylose with adsorbed water molecules in the range of 5300–5000  $\rm cm^{-1}$ .

sucralose, dextran, and cellulose acetate are shown in Figure 5. The spectra of 2-deoxy- D-glucose, 6-deoxy-D-glucose, sucralose (Figure 5), and amylose show clearly that the three absorption bands in the range of 5300–5100 cm<sup>-1</sup> are due to the water molecules adsorbed by the OH groups in the molecules and the pattern of these bands are not affected by the three-dimensional

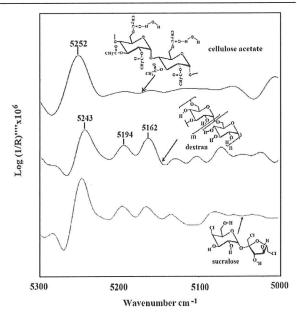


Figure 5. Fourth-derivative profiles of NIR spectra of sucralose, dextran, and cellulose acetate with adsorbed water molecules in the range of 5300-5000 cm<sup>-1</sup>.

network of the polymer molecules. The positions of the absorption bands in all of these compounds are nearly the same. A comparison of the bands around 5250 cm<sup>-1</sup> for the molecules 2-deoxy-D-glucose (OH group at C2 is missing), 6-deoxy-D-glucose (OH group at C6 is missing), and amylose clearly shows that the band at 5190 cm<sup>-1</sup> comes from the water molecules adsorbed on OH groups at C6. Furthermore, a comparison of the relative intensities of the band at 5246 cm<sup>-1</sup> for amylose and 2-deoxy-D-glucose shows that this band is a contribution from the water molecules adsorbed on C2-OH and C3-OH groups. The large relative intensity of the band at 5246 cm<sup>-1</sup> for dextran (Figure 5; OH group at C6 is missing because of the 1,6 linkages in dextran) also excludes the contributions from the water molecules attached to C6-OH groups. It is also clear from the comparison of the bands in

Figure 4 that the bands at 5210 and 5165 cm<sup>-1</sup> come from the water molecules attached to C4-OH and C1-OH groups, respectively.

The monomers 6-deoxy-D-glucose and 2-deoxy-D-glucose adsorb water molecules under saturated vapor pressure (21 mmHg at 23 °C). The adsorption was not significant even after several days. These compounds are incapable of adsorbing water molecules when they are exposed to the same conditions as the carbohydrate polymers. This suggests that the three-dimensional network of the carbohydrate polymers provides an environment that can sustain the adsorbed water molecules. The three-dimensional network provides a solid/solid interface in the polymer matrix, <sup>32</sup> and the water molecules are adsorbed by forming saturated hydrogen bonds with OH groups in the polymer chains of the carbohydrate molecules and between the OH groups on the surfaces formed by the carbohydrate polymer chains. These observations again support the formation of saturated hydrogen bonds during the adsorption of water molecules.

The OH combination absorption for hydrogen-bonded water molecules is around 5280 cm <sup>-1</sup>, and a band appearing around 5280 cm<sup>-1</sup> for amylose and amylopectin is an indication of the presence of free water molecules and water molecules in a network with the adsorbed water molecules. There is no band at 5280 cm<sup>-1</sup> for the cellulose sample, indicating that free water molecules were not found under the experimental conditions used in this experiment.

Cellulose acetate (Figure 5), in which all of the OH groups in the cellulose matrix are esterified by the acetate group, was also used to confirm the adsorption behavior of the OH groups. The fourth-derivative profiles of the near-infrared spectrum of a cellulose acetate sample with water molecules adsorbed is shown in Figure 5. There is only one intense adsorption of the water molecule at 5252 cm<sup>-1</sup>. When all of the OH groups are esterified, the water molecules can only be adsorbed onto the carbonyl group (Figure 5). In this case, the OH combination frequencies of the adsorbed water molecules have the same frequencies, and hence, there is only one band in the spectrum.

**3.4.** Detailed Analysis of Water Adsorption. The near-infrared spectra acquired during the exposure of dry amylose polymer at four different time intervals are shown in Figure 6. The increase in the band intensities at 5246 and 5190 cm<sup>-1</sup> is very clear. However, the band peak position at 5165 cm<sup>-1</sup> experiences a slight gradual red shift and overlaps with another

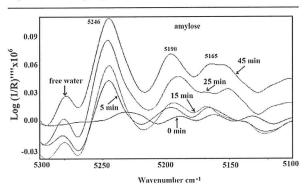


Figure 6. Fourth-derivative profiles of NIR spectra of amylose in the range of 5300–5100 cm<sup>-1</sup> acquired during the evolution of the adsorption of water molecules. The scales of the spectra at 25 and 45 min were adjusted for clarity.

band appearing in the neighborhood at 5150 cm<sup>-1</sup>. It is difficult to provide an explanation for the merger of this band at this point.

The mass of water adsorbed by dry amylose during the first 70 min of exposure is plotted in Figure 7a. A comparison plot

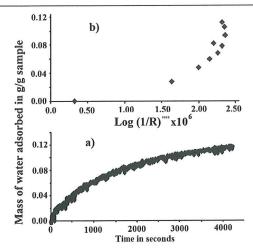


Figure 7. Correlations between the mass of adsorbed water and the (a) time and (b) intensitiy of the fourth derivative of the band at 5246 cm<sup>-1</sup>.

showing the relationship between the water adsorbed and the value of  $[\log(1/R)]^{\prime\prime\prime\prime}$  (according to theory, this is proportional to the absorbance and will be called the NIR absorbance hereafter) for the absorption band at 5246 cm<sup>-1</sup> is shown in Figure 7b. The plots clearly show that the water adsorbed is nonlinear with time and nonlinear with the NIR absorbance. The absorption intensities of the bands due to the OH combination frequencies of the water molecules adsorbed onto the C2-OH + C3-OH, C6-OH, and C1-OH groups in the amylose polymer are shown in Figure 8. The rates of increase in

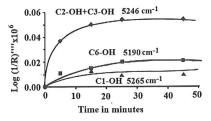


Figure 8. Time correlations of the intensities of the fourth-derivative bands at 5246, 5190, and 5165 cm<sup>-1</sup> relating to the adsorption of water molecules by OH groups attached to C2 + C3, C6, and C1, respectively, in the glucose units of amylose.

the intensities reflect the rate of adsorption of water molecules on the surface of the amylose sample. The C2-OH + C3-OH and C1-OH groups have the highest and lowest rates of adsorption, respectively. A rough estimate shows that the peak at 5246 cm<sup>-1</sup> has a rate four times higher than the peak at 5190 cm<sup>-1</sup>. The low rate of adsorption by C6-OH can be attributed to its unfavorable energetic position in the glucose unit. <sup>32,33</sup> Stagnation in adsorption activity on C1-OH groups after the initial few seconds is not surprising because there are only a few C1-OH groups available in the amylose polymer chains. Similar

behaviors were observed with amylopectin and cellulose samples.

Comparison plots for the water adsorbed as determined by gravimetry for the three carbohydrate polymers are shown in Figure 9. The plots clearly show that there is not much

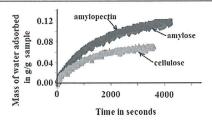


Figure 9. Plot showing the masses of water adsorbed by amylose, amylopectin, and cellulose as functions of time.

difference in the adsorption of water molecules from the vapor phase by amylose and amylopectin during the first hour. The cellulose sample used in the adsorption experiments was microcrystalline. It had an extended ribbon structure, and the proximity of the ribbons allowed for the possibility of interchain hydrogen bonds between the OH groups in the glucose units. Several of these chains form flat sheets, these sheets lie on top of one another, and the sheets are held firmly by hydrogen bonds.<sup>32</sup> This explains the low adsorption of water molecules by cellulose (Figure 9).

The fourth-derivative profiles of the near-infrared spectra of the polymers amylose, amylopectin, and cellulose acquired after 45 min of exposure to air are shown in the range of 5300–5100 cm<sup>-1</sup> in Figure 10. The polymers amylose and cellulose show

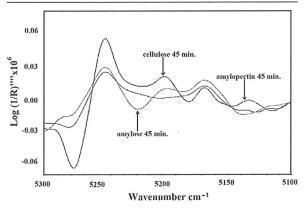


Figure 10. Comparison of the fourth-derivative NIR profiles of water adsorbed (after 45-min exposure) by amylose, amylopectin, and cellulose in the range of \$300-\$100 cm<sup>-1</sup>.

similar profiles compared to amylopectin. These features confirm the similarity in the molecular structures with respect to the OH groups in the matrix. The OH groups are present at the same positions in these two polymer molecules. The fourth-derivative profile of amylopectin resembles that of dextrin, which has a similar molecular structure (Figure 11).

The amount of water adsorbed can be used to predict the surface coverage by water molecules. For example, the water adsorbed by 1 g of amylose (or amylopectin) during the first 70 min is about 0.118 g. The mass of water adsorbed during these experiments at the humidity mentioned is in a range that can be

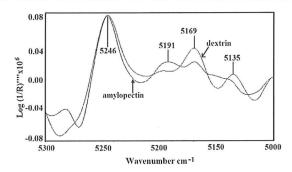


Figure 11. Comparison of the fourth-derivative NIR profiles of water adsorbed by amylopectin and dextrin in the range of \$300–\$5000 cm<sup>-1</sup>.

described by monolayer adsorption.  $^{23,24,32}$  Theoretically, one glucose unit can adsorb nine water molecules (three on each OH group) in the first layer of adsorption. Glucose units of mass of 162 g (180 - 2 - 16 g for two hydrogen atoms missing from carbon positions 1 and 4 and one O atom eliminated from the condensation of OH groups at C1 and C4) can adsorb 9  $\times$  18 g of water. Using this information, the surface coverage of amylose or amylopectin can be calculated as (162  $\times$  0.118  $\times$  100)/(9  $\times$  18). The estimation reveals that only around 12% of the OH groups are engaged in adsorbing water molecules. This behavior is an indication that extensive hydrogen bonds exist among the OH groups in carbohydrate polymers and such OH groups are not available for interaction with water molecules.

The amounts of water adsorbed by dry potato starch and dry corn starch are shown in Figure 12. The adsorption curves are

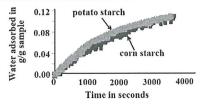


Figure 12. Plot showing the masses of water adsorbed by potato starch and corn starch as functions of time.

similar for the two samples. This again confirms the lack of variation in the adsorption properties of amylose and amylopectin during the first hour of the molecular adsorption of water.

# 4. CONCLUSIONS

Near-infrared spectroscopy and second- and fourth-derivative techniques were used to study the molecular adsorption of water on the surface of carbohydrate polymers. The presence of three different OH groups on the surface was confirmed for the first time by near-infrared spectroscopy. Furthermore, the chemistry of desiccant properties of carbohydrate polymers has been brought to light. Evidence has been presented to show how water molecules are adsorbed onto different OH groups in the polymer matrix of a dry carbohydrate sample.

The absorption of the first water molecules by the OH groups in the carbohydrate polymers falls in the range of 5300–5100 cm<sup>-1</sup>. Water molecules adsorbed on other possible sites in the polymer matrix give rise to absorptions in the range of 5100–5000 cm<sup>-1</sup>. The absorption pattern seems to be

complicated, and it is difficult to assign these to definite groups on the surface.

The adsorption of water molecules onto the surface of a carbohydrate polymer takes place simultaneously on all three OH groups (in the case of amylose, amylopectin, and glucose) but at different rates. The C2- and C3-OH groups combined have a high rate of adsorption compared to the C6-OH groups. It has also been shown that the water molecules are preferentially adsorbed by C2- and C3-OH groups. Furthermore, the carbohydrate polymers provide a suitable environment to sustain the adsorbed water molecules.

The adsorption of water by cellulose proceeds at a lower rate compared to the adsorption of water by amylose and amylopectin.

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#### Notes

The authors declare no competing financial interest.

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