Comparison of Water adsorption characteristics of oligo and polysaccharides of α-glucose studied by Near Infrared Spectroscopy

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Abstract. The adsorption properties of water molecules on oligo and polysaccharides are attributed to the OH groups of the glucose rings in the molecules. The water molecules are adsorbed onto OH groups by hydrogen bond formation. Near infrared spectroscopic and gravimetric techniques were used in analysing the adsorption characteristics of malto-oligosaccharides and some polysaccharides. Near infrared spectra of the dry oligo and polysaccharides were acquired during the adsorption of water molecules at a relative humidity of 50-55%. The amounts of water adsorbed by the samples were also recorded by an analytical balance. Second derivative techniques were used in decomposing the OH combination frequencies of the adsorbed water molecules in the region 5300-5000 cm^{-1}.

The results indicate that the water molecules are adsorbed on to C2 and C3-OH groups at a higher rate compared to the adsorption onto C1-OH groups in the molecules. Adsorption also takes place onto the ethereal oxygen atoms in the glucose rings in malto-oligosaccarides. The gravimetric results show that the adsorption of water molecules increases with the number of glucose units in the malto-oligosaccharides except maltotriose which has the highest adsorption over a period of 75 minutes. Furthermore, the adsorption characteristics of amylose and amylopectin are similar.

Introduction

Oligo and polysaccharides are saccharide polymers containing simple sugar monomers. There are several different varieties of oligo and polysaccharides containing different sugar monomers. Oligosaccharides are found in plants as free compounds and in the form of glycosides. Some plants house large amounts of oligosaccharides. Amylose, amylopectin, glycogen and cellulose are some of the carbohydrate polymers of glucose molecules. Amylose is a polymer of α–glucose molecules with α-1, 4- glycosidic bondings between the monomer units. The polymer is mostly un-branched and the number of glucose units in the polymer chain may vary from 300- 20,000. The polymer molecule winds up in the form of α–helix because of the angle formed during the formation of α-1, 4- glycosidic bondings. Amylopectin has similar polymer chains like amylose with branches at every 20 to 30 units. The branching points are with α-1, 6- glycosidic bondings. Glycogen has a structure similar to amylopectin but highly branched. The branching in amylopectin occur every 10-15 glucose units. Starch is a mixture of 20% amylose and 80% amylopectin.

Malto-oligosaccharides are polymers α-glucose monomers that are found in partially hydrolysed starch and can contain from 1 to 12 glucose units [1]. The glucose units in these oligosaccharides are bonded by 1, 4-glycosidic bondings. Maltose, maltotriose, maltotetraose, maltopentaose, maltohexaose and maltoheptaose contain 2, 3, 4, 5, 6 and 7 glucose units respectively in them. The nature of the chemical bondings between α-glucose units in the molecules gives the OH groups in them characteristic orientations in space.
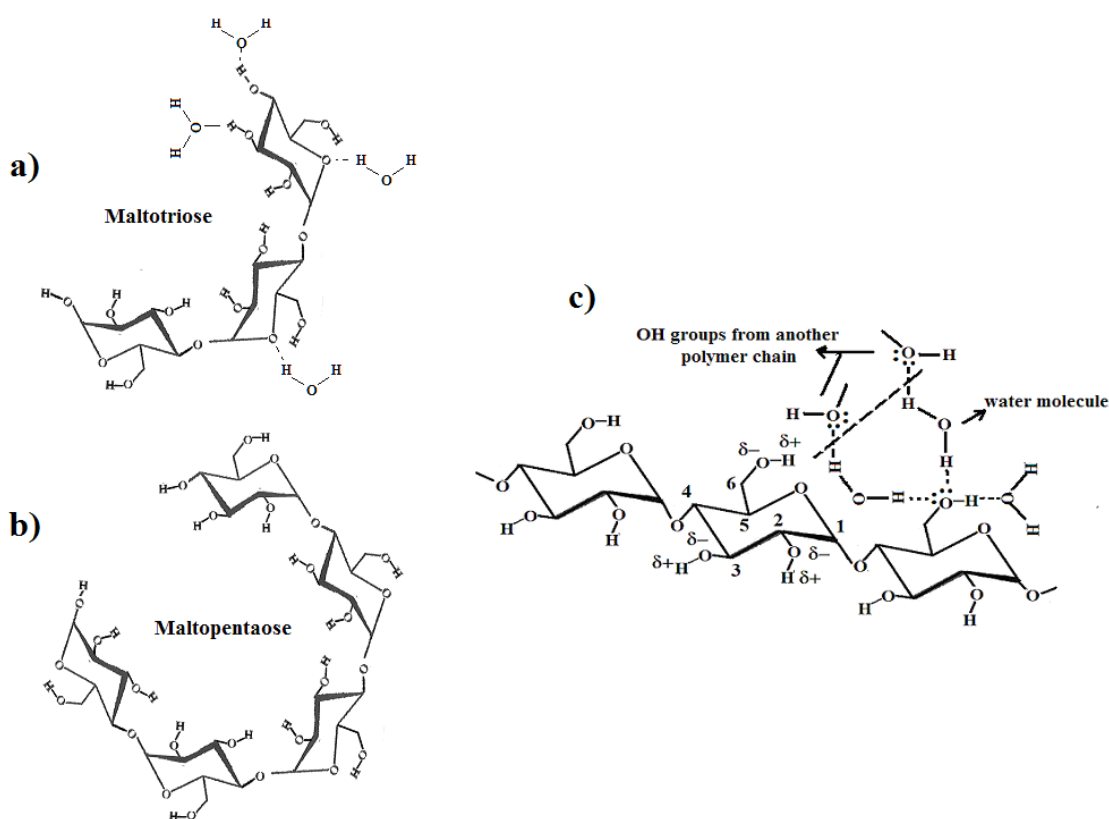
Fig. 1. Chemical structures of maltotriose, maltopentaose and amylose. The sites for possible adsorption of water molecules are also shown for maltotriose and amylose. Fig 3c reproduced from ref 10 with permission from ACS.

Carbohydrate polymers and oligosaccharides have tendency to adsorb water molecules by forming hydrogen bonds with OH groups on the glucose rings. However, the mechanism of adsorption can be different. In carbohydrate polymers, the adsorption takes place at the solid/solid interface but in the oligosaccharides the adsorption takes place at the solid/vapour interface. Desiccant properties of malto-oligosaccharides [1, 2] and polysaccharides [3-6] have been studied in the past by several authors. The humectant properties of the malto-oligosaccharides and polysaccharides are attributed to the primary and secondary OH groups in the molecules. However, the study of chemistry and the progress during the adsorption of water molecules by these compounds are rare in the literature.

Table 1. The NIR band assignments for the water molecules hydrogen bonded to the OH groups of the carbohydrate molecules

Band position cm^{-1}	Assignment-Combination frequency of the (OH stretching and bending vibrations) of the water molecules hydrogen bonding to groups in the glucose units
5246	OH groups at C2 and C3
5210	OH group at C4
5194	OH group at C6
5165	OH group at C1
5130	-O- ring O of the glucose units

The NIR spectrum of an adsorbent containing OH groups exhibits a unique peak in the region 5300-5000 cm^{-1} when water molecules hydrogen bond to the OH groups on the adsorbent. The absorption arises due to the combination frequency of the water molecular OH stretching and bending vibrations. Since this absorption is purely from water molecules adsorbed on to the OH groups on the surface of the adsorbent, the band structure of the above peak revealed by the second and fourth derivative techniques can be directly connected to the different types of surface OH groups. With the help of near infrared reflection spectroscopy combined with second and derivative techniques, Christy has published a series of articles [7-10] regarding the nature of OH groups and their affinity to water molecules in different substances. Christy was able to distinguish the near infrared absorption bands arising from the water molecules hydrogen bonded silanol groups and water molecules hydrogen bonded to vicinal silanol groups [7]. Furthermore, the near infrared absorption bands arising from the water molecules hydrogen bonded to different OH groups in the carbohydrate polymers were identified [10].

The intention in this article is to compare the adsorption characteristics of the hydroxyl groups in the oligosaccharides and polysaccharides containing α-glucose units and their adsorption properties towards water molecules as observed by the evolution of the NIR spectra during the adsorption of water molecules. Furthermore, Gravimetric method was used in studying the bulk properties of the saccharides. The characteristics of the OH groups in the saccharides were used in comparing the adsorption properties.

Experimental
Samples and procedures

Oligosaccharides maltose, maltotriose, maltotetraose, maltopentaose, maltoheptaose, amylose and amylopectin were purchased from Sigma-Aldrich. All the samples had purity over 95%. The samples were finely ground to achieve similar particle size distribution.

All the saccharide samples were first dried at 120 °C using a ceramic heater (BA Electric Bunsen from Electro thermal, Staffordshire, U.K.). A powerful vacuum pump was used in evacuating the water adsorbed on the samples. A K-type thermocouple was used in measuring the temperature in the sample during heating. After the evacuation process, each sample was cooled and controlled for any adsorbed water molecules by measuring the NIR spectrum of the sample. The absence of a peak in the 5300-5000 cm^{-1} region would confirm the total removal of the adsorbed water molecules.

The water adsorption evolution of each sample was followed by gravimetry and NIR spectrometry. Adsorption of water molecules by a carbohydrate molecule depends on the humidity of the surroundings and attempts were made to maintain the humidity at 50% during the gravimetric and NIR measurements.
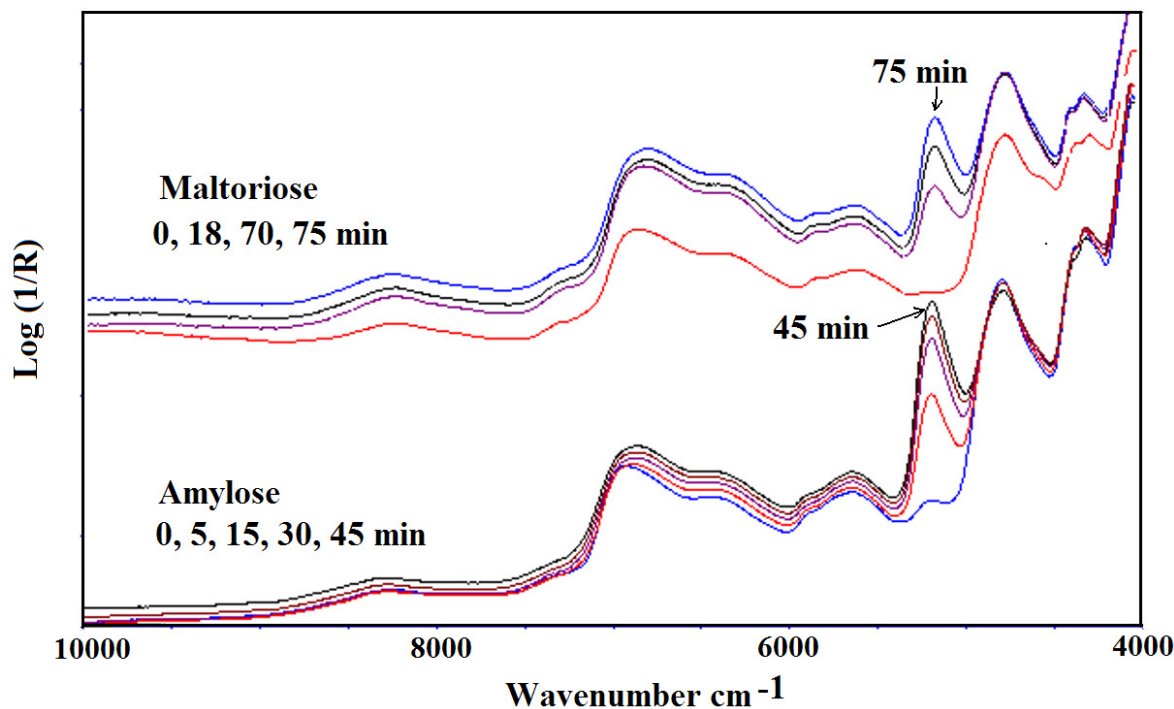
Fig. 2. The NIR spectra acquired during the adsorption of water molecules at a relative humidity of 50% by maltotriose and amylose at a relative humidity of 50%.

The gravimetric determination of water sorption was carried out by quickly spreading a small amount of a dry sample in the NIR sample cup and placing it on a Mettler electronic balance that is capable of recording the weight increase of the sample up to 0.0001g. The balance was connected to a computer through a RS232 port and the data from the balance was recorded by communicating with the balance using locally made software. The increase in the mass of the sample was recorded twice each second. The data collected at the computer were imported into an Excel spread sheet and presented in the form of graphs for comparison and discussion.

The NIR 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 sulphate detector. A small amount of the dry sample was quickly placed and spread in the NIR sample cup and moved on the ZnSe crystal of the transflectance accessory that is covered by the chamber that provided an environment of air with 50% relative humidity. The spectral evolution was recorded frequently in the range of 10000–4000 cm^{-1}. A total of 30 scans were obtained at a resolution of 16 cm^{-1}. All the NIR spectra were transformed into log (1/R) format and 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.

Results and discussion

The samples used in the adsorption experiments in this article are compounds made up by α–glucose units. The chemical structures of maltotriose, maltopentaose and amylose are shown in Fig. 1. The possible interaction of water molecules with the OH groups on the maltotriose are also shown in Fig. 1. The NIR spectra of the dry maltotriose and amylose acquired during the adsorption of water molecules from the surroundings are shown in Fig. 2. The spectra show the general features appearing

in the NIR region. The characteristic NIR band assignments of the oligosaccharides with adsorbed water are similar to the carbohydrate polymers with adsorbed water and can be found elsewhere [10]. The NIR band assignment for the water molecules that are hydrogen bonding to the OH groups of the glucose units of the saccharide molecules can be found in Table 1.
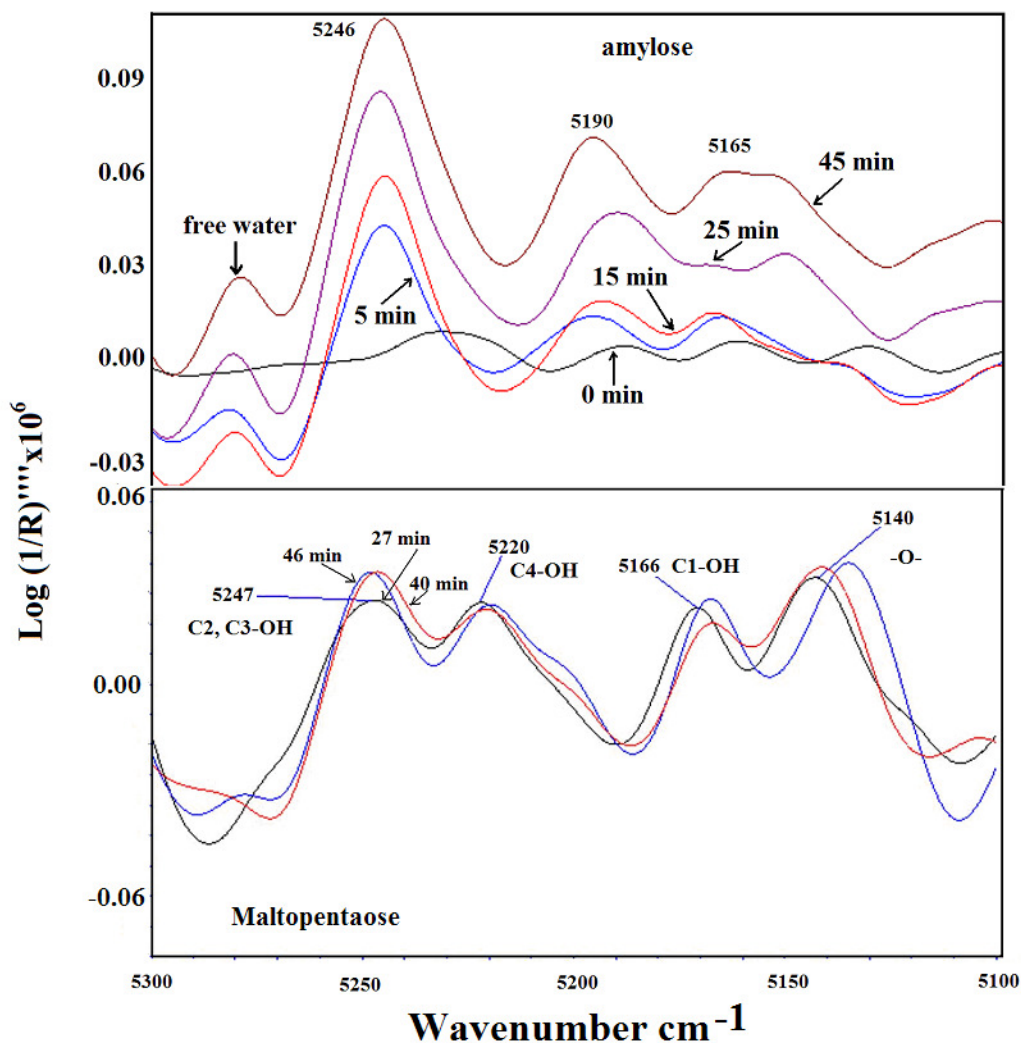

Fig. 3. The fourth derivative profiles of the NIR spectra acquired during the adsorption of water molecules by dry maltopentaose and amylose samples

The NIR spectra in Fig. 2 show that the intensity of the absorption band arising from the combination frequencies of the water molecules increases in the samples. This is also the case with the other oligosaccharides and amylopectin. However, the rates of increase vary in the samples. Fourth derivative profiles of the NIR spectra acquired during the water adsorption evolution on maltopentaose and amylose in the range 5300-5000 cm^{-1} are shown in Fig. 3. The variations in the absorption peaks arising from the combination frequencies of the OH groups of water molecules hydrogen bonding to OH groups in the glucose units of the above saccharides are clear. The water molecules adsorbed on to the OH groups of C2 and C3 give rise to an absorption band at 5246 cm^{-1}[10]. The combined rate of adsorption of water molecules on the C2 and C3-OH groups has a higher rate compared to the C1-OH group in both maltopentaose and amylose. This observation is

valid for other oligosaccharides and amylopectin. Absorption around 5130 cm^{-1} is an indication that some water molecules form hydrogen bonding with ethereal oxygen (-O-) in the glucose rings of the oligosaccharides.
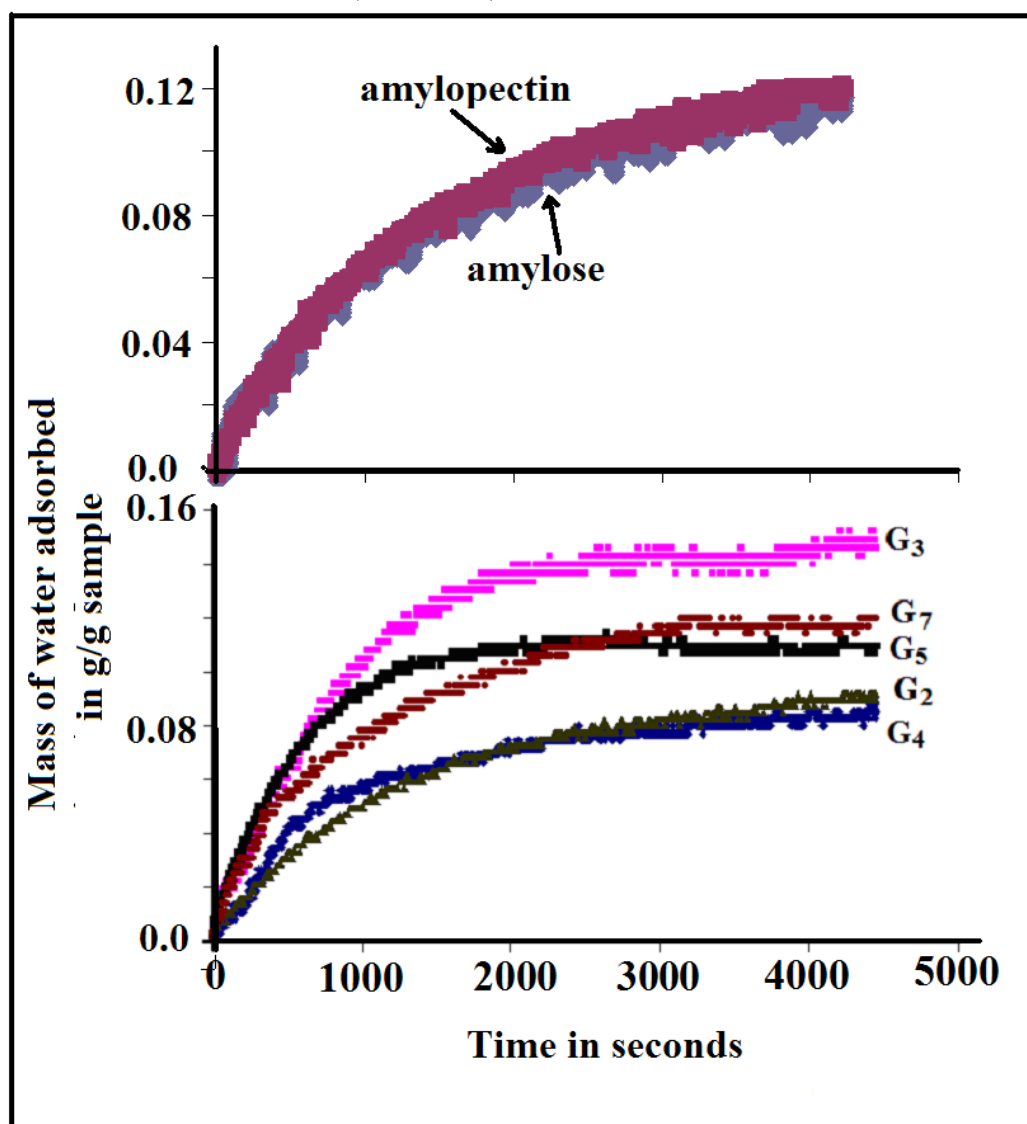

Fig. 4. Water adsorption profiles for a) maltose (G2), maltotriose (G3), maltotetraose (G4), maltopentaose (G5) and maltoheptaose (G7); b) amylose and amylopectin

The gravimetric adsorption results of the oligosaccharides are strange in terms of adsorption characteristics (Fig. 4). The maltose molecules have very low adsorption of water molecules. In contrast maltotriose has relatively high adsorption compared to all the other oligosaccharides. The fact that the maltose molecules engage in hydrogen bondings in crystalline state make the OH groups less available for hydrogen bonding with water molecules. In maltotriose the addition of one glucose unit makes it difficult for inter hydrogen bonding with other maltotriose molecules [2] and the ring OH groups are available for hydrogen bonding with water molecules. Maltopentaose and maltoheptaose adsorb less water compared to maltotriose. Maltose and maltotetraose have similar adsorption curves.

The amylose and amylopectin have similar water adsorption profiles. However their adsorption of water seems to increase even after 75 minutes. I the case of oligosaccharides the water adsorption gets saturated within the first 25 minutes. Maltotriose and maltopentaose adsorb water at a faster rate compared to amylose and amylopectin during the early part of the adsorption process.

Conclusion

The adsorption characteristics of malto-oligosaccharides containing 2 to 7 glucose units and carbohydrate polymers containing glucose monomers such as amylose and amylopectin have been enlightened in this article. The characteristics are similar. The OH groups attached to C2 and C3 adsorb water molecules at a higher rate compared to the primary OH group at C6. There is also evidence that some water molecules adsorb onto the ethereal oxygen of the glucose units of the oligosaccharides.

The gravimetric results show that the maltotriose adsorb more water than the other oligosaccharides. This result agrees with the results reported in the literature [1, 2]. Maltose adsorbs less water. In carbohydrate polymers amylose and amylopectin have similar adsorption profiles during the period of adsorption used in these experiments.

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