Water adsorption properties of free and dehydrated β-cyclodextrin studied by near infrared spectroscopy and gravimetry

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Abstract.

β-cyclodextrin, like other carbohydrates has a tendency to adsorb water molecules and the properties are attributed to the hydroxyl groups in the molecules. β-cyclodextrin, the cyclic oligomer of glucose has a hydrophobic interior and hydrophilic exterior. The cyclic structure favours the formation of hydrogen bonds between the OH groups on the adjacent glucose units and affects the formation of hydrogen bonds with water molecules. The hydoxyl groups engaged in hydrogen bondings can be eliminated at high temperatures and the adsorption properties of the dehydrated β-cyclodextrin will depend on the new functional groups formed. The aim of the report is to discuss the issue of the water adsorption properties of free and dehydrated β-cyclodextrin.

Dry β-cyclodextrin and dehydrated β-cyclodextrin at temperatures 250, 300 and 350 ^{o}C were allowed to adsorb water from a humidity controlled air environmennt and the evolving near infrared spectra were measured using a near infrared spectrometer equipped with a transflectance accessory. The near infrared spectra in the region 10,000-4000 cm^{-1} and their second and fourth derivative profiles were used in studying the variation in the adsorption characteristics of dehydrated β-cyclodextrin. The absorption profiles and their derivative profiles in the first OH overtone region (7200-6900 cm^{-1}) and the combination frequency of the First OH overtone and OH bending (in the region 5300-5100 cm^{-1}) could give clues regarding the changes that had taken place in the β-cyclodextrin molecule during dehydration.

The results of the analyses show that the adsorption of water by β-cyclodextrin decreses at 300 ^{o}C compared to 200 and 250 ^{o}C. Dehydration forms more of the ethereal type –O—bonds in the molecule and explains the decrease in the water molecular adsorption at higher dehydration temperatures.

Introduction

Cyclodextrins are a family of cyclic oligosaccharides, consisting of a number of (1,4)-linked d-glucopyranose subunits, obtained by degradation of starch by the enzyme cyclodextrin glucosyltransferase [1] . The most common CDs, named α-,β - and γ-CDs, are composed of six, seven and eight glucose unites, respectively. The structural features of the glucose units in cycle give them torus shape for the molecule [2]. Polar molecular adsorption takes place in three basic cyclodextrin OH groups. These groups have different reactivities. The C6-OH group in favourable position in the cyclodextrin molecules and has higher reactivity compared to C2-OH and C3-OH. All the three cyclodextrins adsorb water molecules and the amount of water molecules adsorbed onto the cyclodextrin molecules vary depending on the availability of the polar sites in the molecules and the reactivity on the OH groups [3].

The presence of glucose units in the cyclodextrin shapes the molecule like a truncated cone. The secondary OH groups C2-OH and C3-OH are located at the larger edge of the cone and the primary groups C6-OH are located at the narrower edge of the cone. This results in a molecule with a

hydrophilic outside, which can dissolve in water, and an apolar cavity, which provides a hydrophobic matrix, described as a 'micro heterogeneous environment' [4]. Due to these interesting properties, cyclodextrin can form inclusion complexes.

My intention in this article is to study the dehydration effects on the adsorption of water molecules by β-cyclodextrin. The experiments were carried out at a humidity of 30%.

Experimental

Samples and procedures

Dehydration and adsorption of water

β-cyclodextrin was purchased from Sigma-Aldrich. The presence of water molecules on β-cyclodextrin was studied by using Near infrared spectroscopy. The results were analyzed by Perkin Elmer Spectrum software. All measurement were carried out in air atmosphere (temperature: 24,7°C ; humidity: 30%).

A portion of the β-cyclodextrin was dried under vacuum at around 120°C. A powerfull vacuum pump was used in the evacuation of water from the sample. Then the sample was first heated to 200°C in a ceramic oven and evacuated to remove any eliminated water from the surface. 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.

Near infrared spectroscopic and gravimetric analysis

The water adsorption evolution of each sample was followed by both near infrared spectroscopy and gravimetry. 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. Around 0,1g of the β-cyclodextrin sample was quickly placed in a NIR sample cup and moved on to the ZnSe crystal of the transflectance accessory. The spectral evolution was recorded in the range of 10000–4000 cm^{-1}. A total of 30 scans were obtained at a resolution of 16 cm^{-1}. All NIR spectra were transformed to 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.

The gravimetric determination of water sorption was carried out by quickly spreading a small amount of a dry sample in the sample cup and placing it on a Mettler electronic balance that is capable of recording the weight increase of the sample up to 0.0002 g. 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.

Results and discussion

A partial chemical structure of β-cyclodextrin with possible water adsorption sites is shown in Fig. 1. The near infrared spectra of dry β-cyclodextrin samples acquired on the samples heated and evacuated at 200, 250 and 300 ^{o}C are shown in Fig. 2. The fourth derivative profiles of NIR spectra acquired on the above β-cyclodextrin samples during adsorption of water molecules are shown in Fig. 3.

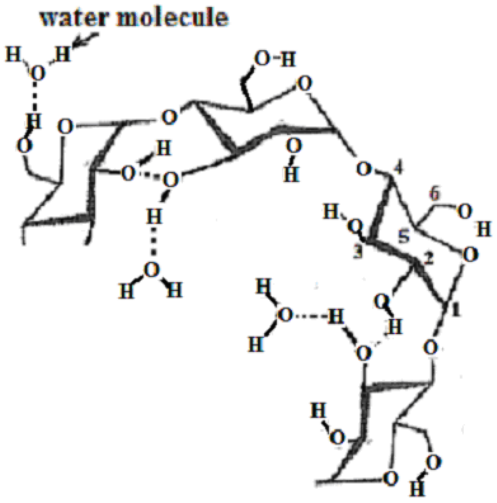

Fig. 1. Partial structure of β-cyclodextrin with possible water adsorption sitesin β-cyclodextrin

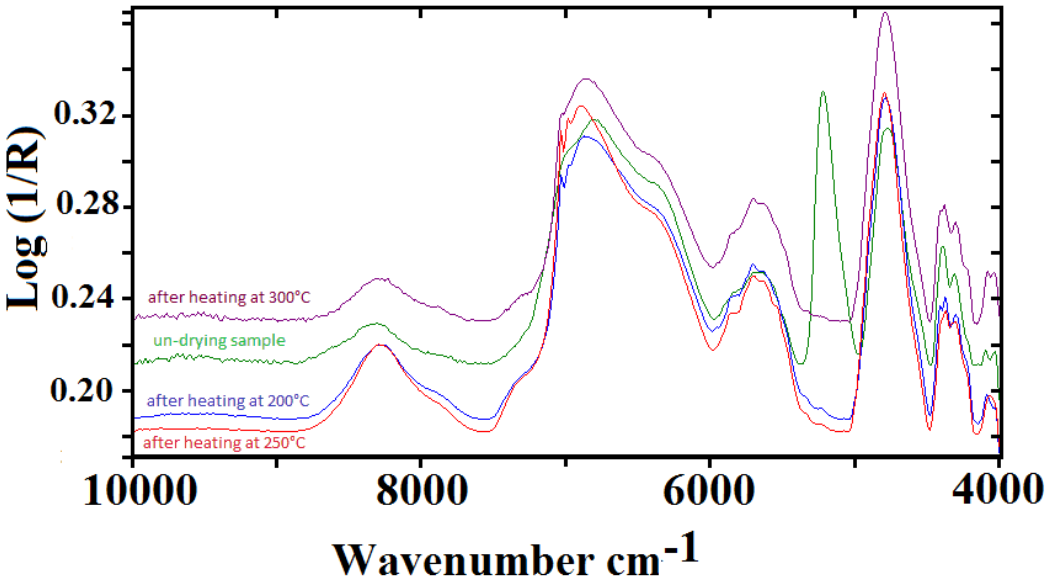

Fig. 2. Near infrared spectra of bench, dry and, heated and evacuated β-cyclodextrin samples

The changes taking place in the β-cyclodextrin samples are very difficult to identify in the spectra except the chages in the OH overtone absorption around 7100 cm^{-1}. The adsorption of water takes place in all the samples (Fig. 3). However, the adsorption rates are different depending on the dehydration temperature.

The fourth derivative profiles of the absorption spectra acquired during the adsorption of water are given in Fig. 4. The absorption peak around 5200 cm^{-1} in the figures indicate the water molecules adsorbed by C2, C3-OH groups and the absorption around 5280 cm^{-1} is due to OH groups of free water molecules accumulated in the cavity of β-cyclodextrin samples. All the three treated β-cyclodextrin samples have acquired water by adsorption and diffusion processes. The peak around 7030 cm^{-1} is due to the first overtone of the OH stretching vibration of the C2, C3-OH groups and the

absorption around 6980 cm^{-1} is due to the first overtone of the C6-OH group. During the adsorption of water the intensity of the peak at 7030 cm^{-1} decreases. This is because the OH groups in the β-cyclodextrin samples engage in hydrogen bonding with some of the water molecules and the first overtone absorption shifts to a lower wavenumber.

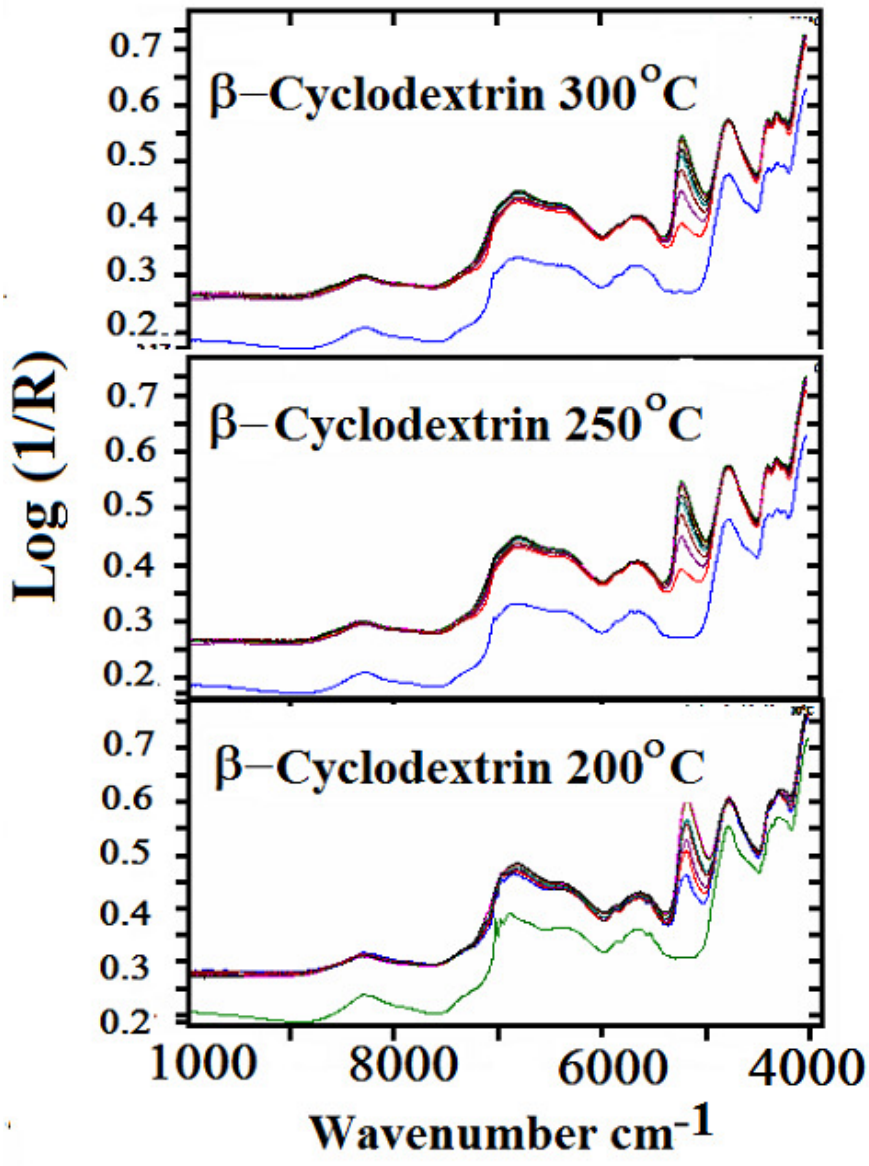

Fig.3. The evolution spectra of thermally treated β-cyclodextrin during adsorption of water over time (200 °C- 0 to278 minutes, 250 °C-0 to 249 minutes and 300 °C-0 to 188 minutes)

A plot of the amount of water adsorbed by the β–cyclodextrin samples with time is shown in Fig. 5. The differences in adsorption properties are clear. The sample heated at 250 °C adsorbs more water than the samples heated at 200 and 300 °C. Heating at 300 °C condense OH groups and eliminates water molecules from the β–cyclodextrin molecules and form ethereal bonds in the molecules (Fig. 6). The oxygen atoms in the ethereal bonds are less polar compared to OH groups and adsorbs less water. This is evident in the fourth derivative profile of the sample treated at 300 °C. The intensity of absorption of the first overtone of the OH stretching is much lower than the other two samples. The mass of water acquired by diffusion is also different. The sample heated at 250 °C acquires more water by diffusion than the samples heated at 200 and 300 °C. The OH groups in the samples heated at

200 and 250 °C remain the same and the amounts of water adsorbed by the OH groups in the glucose units are the same.

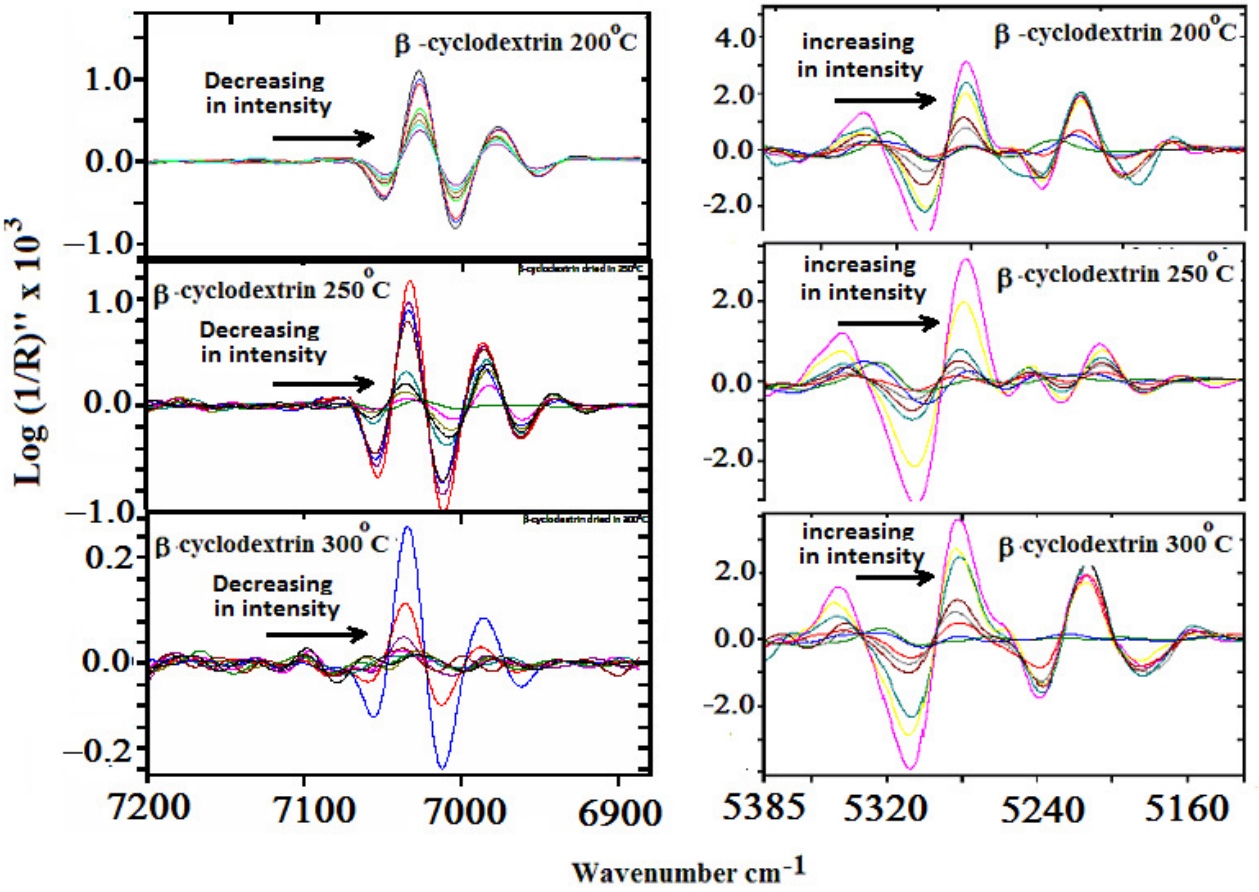

Fig. 4. Fourth derivative profiles of the absorption spectra acquired during the adsorption of water by the heat treated β–cyclodextrin samples

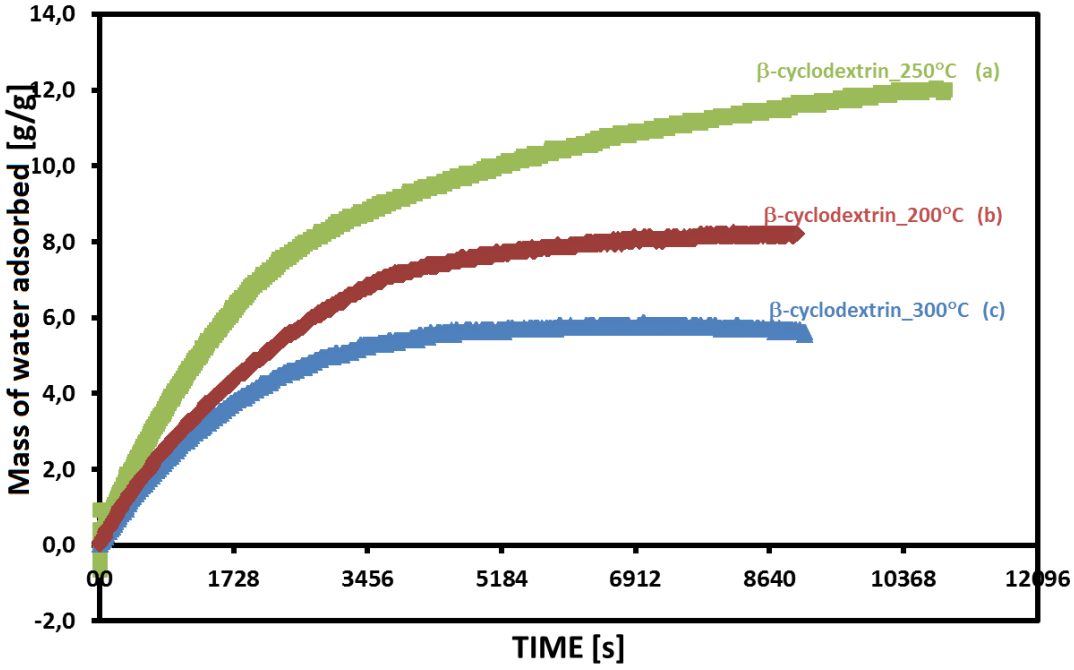

Fig. 5. Mass of water adsorbed by the β–cyclodextrin samples against time

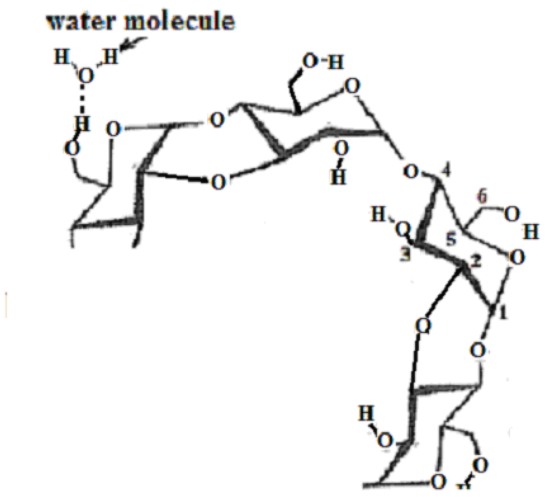

Fig. 6. Possible structural changes in the β-cyclodextrin molecules after heating the sample at 300 °C

Conclusion

The dehydration and adsorption characteristics of β- cyclodextrin have been enlightened in this article. The water molecules are adsorbed by the polar OH groups attached to C2, C3 and C6 of the glucose units in the molecules. The mass of water adsorbed depends on the temperature used for dehydration.

The results show that the β- cyclodextrin sample cannot be dehydrated at a temperature of 200 °C. The same is true for sample heated at 250 °C. However, the sample acquires more water than the sample heated at 200 °C. It appears that the sample acquires more cavity water through diffusion.

The dehydration of the β- cyclodextrin indicates that the molecule undergo condensation of OH groups to form ethereal type bonds connecting the glucose units in of β-cyclodextrin. The sample heated at 300 °C acquires less water than the other two samples. Ethereal oxygen is less polar than the OH groups and hence adsorbs less water.

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