Adsorption and Dehydration of Water Molecules from α, β and γ Cyclodextrins-A study by TGA analysis and gravimetry

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Abstract. The adsorption and desorption of water molecules from α, β and γ-cyclodextrins were studied by gravimetric and thermogravimetric analysis. Cyclodextrins like all the other carbohydrates have tendency to adsorb water molecules. However, their cyclic nature tends to affect the adsorption patterns. The cyclic nature of the cyclodextrins facilitates the formation of hydrogen bondings between OH groups of the neighbouring glucose units. The C2(1)-OH forms hydrogen bonding with C3(2)-OH. The extent of the hydrogen bond formation and strength of the hydrogen bond affect the way the adsorption and dehydration of water molecules from cyclodextrins take place.

All the three α, β and γ-cyclodextrins were subjected to thermogravimetric (TGA) and gravimetric analysis. The results show that the dehydration and adsorption pattern of β–cyclodextrin are different from the other two cyclodextrins at 50% humidity. An attempt was made to explain the anomalous behaviour of the β–cyclodextrin. The decomposition of the α–cyclodextrin takes place in three steps and, β and γ –cyclodextrins take place in two steps.

Introduction

Cyclodextrins are cyclic oligosaccharides and the cyclodextrins containing six, seven and eight glucose units are called α, β and γ-cyclodextrin respectively [1]. The action of enzyme on starch leads to the formation of β–dextrin in abundance [2]. The formation of oligosaccharides containing six and eight glucose units is less common. The structural features of the glucose units in cycle give them torus shape for the molecules [3]. The primary OH groups at C2 and C3 are at the top rim of the torus and the OH group at C6 is at the bottom rim of the torus. Furthermore, these molecules contain cavities and can accommodate organic molecules of suitable size. Because of this feature cyclodextrins are used as drug delivering agents.

The three primary OH groups in the cyclodextrins are sites for polar molecular adsorption. They also have different reactivities. The C6-OH group in a 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 of the OH groups.

The bench cyclodextrin always contain adsorbed water molecules. They can be removed and the molecules can be dehydrated by heating under vacuum. There are different types of water molecules and they leave the molecular matrix at different temperatures. Thermogravimetric analysis (TGA) of cyclodextrins has revealed the nature of these water molecules [1]. My intention in this article is not only to study the dehydration and thermal decomposition by TGA but also the adsorption of water molecules on cyclodextrins using gravimetry at a humidity of 50%. The study will reveal the adsorption behaviour of the three cyclodextrins and their affinity to water molecules.

Experimental

Samples and procedures

Dehydration

All the three cyclodextrins were purchased from Sigma-Aldrich. They all were ground and sieved to give 80 µm particles. The thermal analyses of the cyclodextrins were carried out with a Perkin Elmer

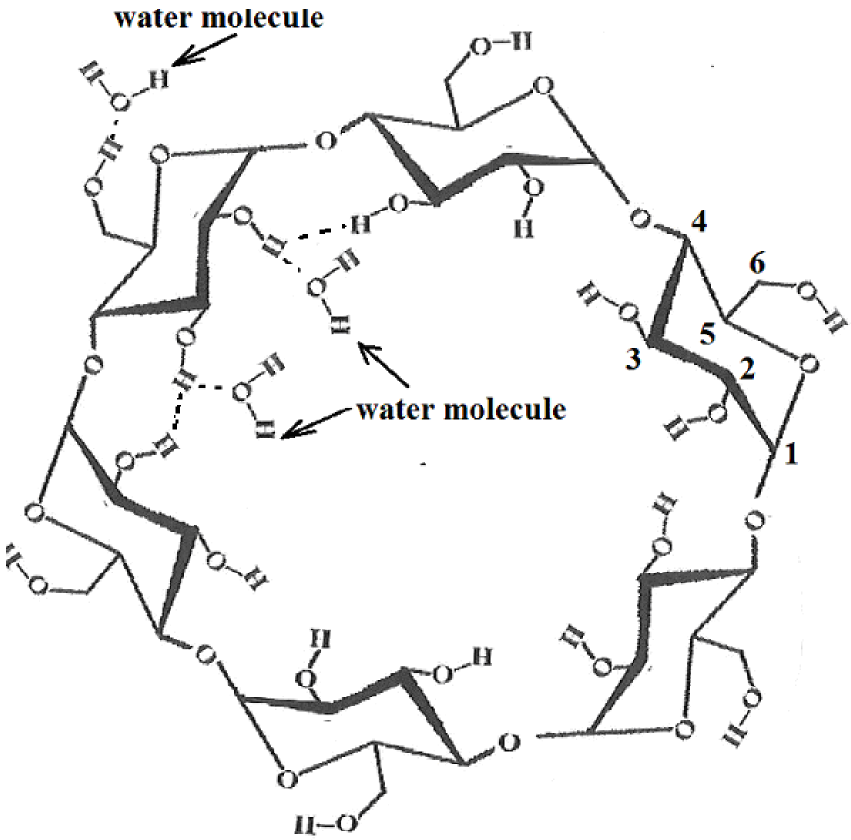

Fig. 1. Molecular structure of β-cyclodextrin. Possible water molecular adsorption sites are shown for one glucose unit in the molecule

TGA 7 thermal analyzer in a platinum measuring cell. The data handling was carried out by the use of Pyris program. The measurements were performed in air atmosphere (flow rate 10 ml/min) at a heating rate of 10 ^{o}C/min. The samples were heated from room temperature to 600 ^{o}C. All the measurements were repeated at least three times.

Adsorption experiments

All the three cyclodextrin 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. 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 measurements. 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.

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. The spectra were recorded in the range of 10000–4000 cm^{-1}. A total of 30 scans were obtained at a resolution of 16 cm^{-1}.

Results and discussion

The chemical structure of α-dextrin with possible water adsorption sites is shown in Fig. 1. The thermal decomposition curves of the three cyclodextrins are shown in Fig. 2. The derivative curves are presented in Fig. 3.

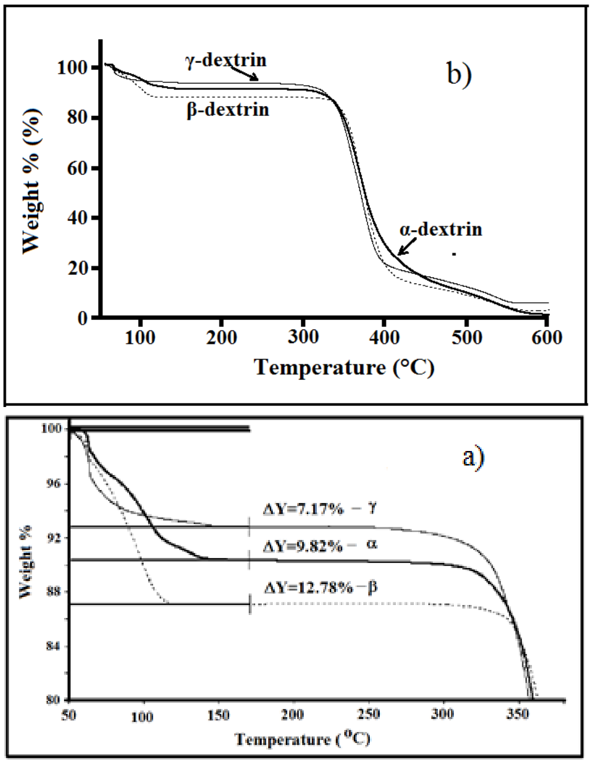

Fig. 2. TGA curves of α, β and γ-cyclodextrins

The Figures 2a and 2b show clearly that the dehydration ranges of the three cyclodextrins. A calculation based on the amount of dehydration gives a molecular formula of α–CyD.7H_2O for α–dextrin and β–CyD.10H_2O for β-cyclodextrin and γ–CyD.6H_2O for γ–cyclodextrin. The dehydration is complete before the temperature reaches 150 °C. The decomposition of the cyclodextrins starts after 325 °C. Detailed dehydration patterns of the cyclodextrins are shown in Fig. 3. An expanded figure (Fig. 3b) of the dehydration curves in the region 50-200 °C show the patterns clearly. All the cyclodextrins have different dehydration profiles. Γ-Dextrin has one step, β-dextrin has two steps and α-dextrin has three steps dehydration. The dehydration is complete at 144 °C in γ-cyclodextrin, at 138 °C in α-cyclodextrin and at 120 °C in β-cyclodextrin. The dehydration temperature interval of γ-cyclodextrin indicates that the molecule form strong hydrogen bondings with some of the water molecules. There was no dehydration of the water molecules at higher temperatures as reported in Ref 4. The samples used in these experiments were vacuum dried and left to adsorb water for some days. It is possible that the samples have not acquired enough cavity water at this stage. The TGA curve of α–cyclodextrin shows endothermic peaks at 68, 98 and 128 °C. These correspond to 1, 5 and 1 moles water molecules respectively. The TGA curve of β–dextrin shows two endothermic peaks at 54 and 89 ^{o}C and this corresponds to 2.5 and 7.5 water molecules respectively. TGA curve of γ-dextrin shows no definite peaks. The elimination of water from γ-dextrin takes place in one step.

Thermal degradation of all the cyclodextrins takes place in the same temperature range 320-450 ^{o}C in two stages (Fig. 5). The degradation takes place in three steps. It is difficult to predict the degradation products using the derivative curves.

The water adsorption on cyclodextrins as determined by gravimetry is shown in Fig. 5. The α–cyclodextrin has a relatively high rate of adsorption of water molecules compared to α and γ cyclodextrins. This agrees with the TGA analysis dehydration curves showing that the water content in β–dextrin is higher than in α and in γ-cyclodextrins. In α–cyclodextrin, the molecular shape strains the C2 and C3-OH groups and the Oh groups tend to be far apart from each other. This facilitates the adsorption of water molecules by OH groups. In β –cyclodextrin the C2 and C3 OHs are in optimal position and form intra-molecular hydrogen bondings. This makes the OH groups less available for interaction with water molecules [5]. However, the two steps dehydration of water molecules from

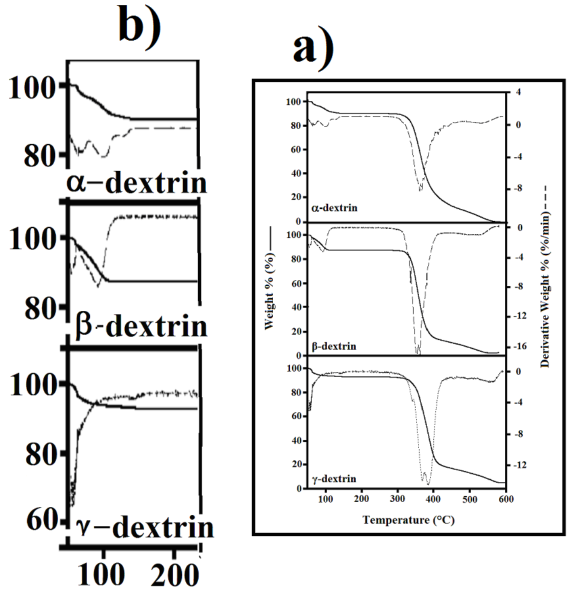

Fig. 3. DTG curves for the dehydration and decomposition of α, β and γ-cyclodextrins. Fig. 3b shows the expanded area in the temperature range 50-200 ^{o}C

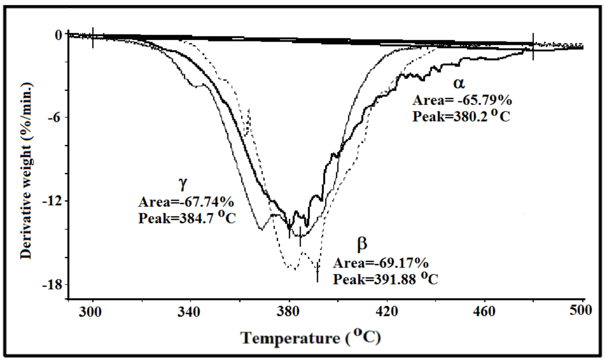

Fig. 4. DTG curves for the decomposition of α, β and γ-cyclodextrins.

β–cyclodextrin shows that the molecules contain cavity water. In γ-cyclodextrin C2 and C3 OHs are far apart from each other and are available for water adsorption. The single step dehydration of γ-cyclodextrin shows that the molecule contains only adsorbed water.

The gravimetric adsorption results of the cyclodextrins show that the β–cyclodextrin adsorbs more water compared to α and γ-cyclodextrins at a humidity of 50%. The results agree with the work reported by Tanada et al. [5]. The adsorption of water by γ–cyclodextrin exceeds that of β–dextrin at higher humidities (over 65%) [5].

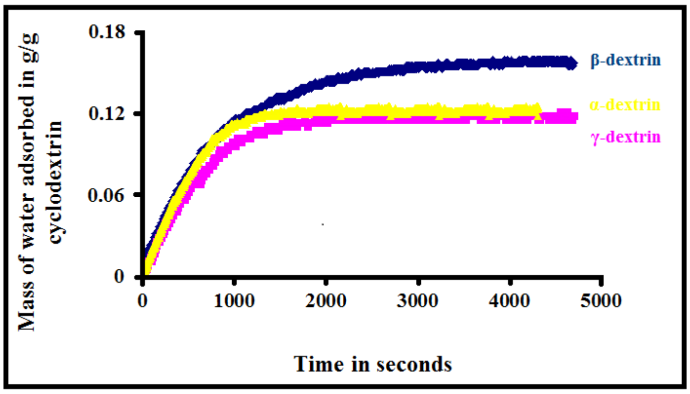

Fig. 5. Water adsorption evolution on α, β and γ-cyclodextrins.

Conclusion

The dehydration, decomposition and adsorption characteristics of α, β and γ- cyclodextrins have been enlightened in this article. The dehydration of the cyclodextrins takes place in steps and indicates that the cavity of β-cyclodextrin may contain more cavity water molecules compared to the other two cyclodextrins.

The water molecules are adsorbed by the polar OH groups attached to C2, C3 and C6 of the glucose units in the molecules. The adsorption of water molecules progresses with slightly different rates in the beginning with β-cyclodextrin having a higher rate of adsorption compared to the other two cyclodextrins. The study also shows that at a humidity of 50%, the β-cyclodextrin adsorbs more water than the other two cyclodextrins.

The degradation of cyclodextrin also takes place in steps. The cyclodextrins undergo three steps decomposition. This may indicate the preferred order of dehydration of primary OH groups and formation of gaseous products. A careful study of thermal decomposition evolution using near infrared spectroscopy may reveal the answers for these questions.

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