

Structure and stability of columnar cyclomaltooctaose (γ -cyclodextrin) hydrate

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Received 10 January 2005; accepted 16 March 2005

Abstract—Rapid recrystallization of cyclomaltooctaose (γ -cyclodextrin, γ -CD) from aqueous solution resulted in formation of a columnar structure with only water as the guest molecule. Upon vacuum drying at 90 °C for 15 h, γ -CD, which was initially in the columnar structure, became amorphous. Complementary water vapor sorption and wide-angle X-ray diffractometry experiments were performed on columnar γ -CD in its vacuum dried and as-precipitated states to elucidate its stability in humid environments and the crystal structure present at varying sorption levels. These experiments show that both types of γ -CD transform to the cage crystal structure upon exposure to water vapor at 40 °C and with an activity of 1.0. Sorption equilibrium is reached long before the crystal structure transformation is complete, indicating that a significant amount of molecular mobility exists in the various hydrated γ -CD crystal structures.

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Keywords: γ -Cyclodextrin; Water vapor sorption; Wide-angle X-ray diffraction; Phase transformation

1. Introduction

Cyclomaltooligosaccharides (cyclodextrins, CDs) are cyclic oligosaccharides capable of forming inclusion complexes with small molecules and macromolecules due to their hollow, truncated cone structure. CD molecules may be composed of 6, 7, or 8 glucose units, which correspond to α -, β -, and γ -CD, respectively. These molecules have a hydrophilic surface and a hydrophobic cavity in which the guest molecule resides. γ -CD can exist in two classes of crystal structures called cage and columnar.¹ In the cage structure (Fig. 1a), the CD cavities are not aligned, whereas they stack on top of each other in the columnar structure (Fig. 1b) to form long cylindrical channels in which, for example, guest polymer molecules can reside.^{2–9}

The as-received γ -CD cage structure has a ‘herringbone’ arrangement (Fig. 1a) in which the cavity of each

molecule is blocked by neighboring molecules. It is obtained upon recrystallization of γ -CD from water. Harata¹⁰ assigned the γ -CD hydrate unit cell to the monoclinic space group $P2_1$. He reports that 14.1 water molecules are distributed over 23 sites per γ -CD molecule while 7.1 of those water molecules are located inside the γ -CD cavity. Only the water molecules outside the cavity are involved in hydrogen bonding with γ -CD.

Nakai et al.¹¹ characterized γ -CD in the cage structure by isothermal water vapor sorption experiments at 40 °C and complementary wide-angle X-ray diffractometry (WAXD) to determine the effect of water content on the WAXD pattern. They confirm the existence of a hydrate containing seven water molecules per γ -CD molecule that forms from $a = 0.3$ to 0.5, where a represents the water vapor activity. Another hydrate containing almost 17 water molecules per γ -CD molecule was characterized at $a = 0.93$. Using the same sorption technique, Tanada et al.¹² also report that γ -CD forms two hydrates at intermediate and high activities.

The γ -CD inclusion compounds (ICs) form the columnar structure in which the cavity of each molecule

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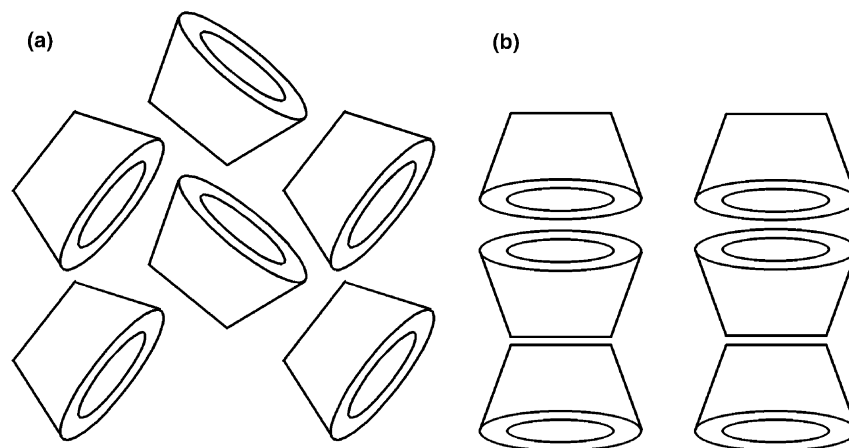


Figure 1. Schematic representation of the packing of γ -CD molecules in the cage (a) and columnar (b) crystal structures.

is aligned in a columnar fashion. For example, Kamitori et al.¹³ assigned the γ -CD·12-crown-4-LiSCN inclusion compound unit cell to the tetragonal space group $P4_21_2$. They report that 14.1 water molecules are distributed over 23 sites per γ -CD molecule, while 7.1 of those water molecules are located inside the γ -CD cavity. The orientation of γ -CD in the columns is head–head:tail–head, resulting in a 3-molecule repeating unit (Fig. 1b). Rusa et al.¹⁴ first prepared γ -CD in the columnar structure with only water as the guest molecule. This was done by rapidly precipitating γ -CD from an aqueous solution using acetone. In the same publication, Rusa et al. also reported preparation of columnar α -CD in a similar way by rapid precipitation from water using chloroform.

Miyake et al.¹⁵ have recently reported that CD molecules in the columnar structure with a polymer guest are arranged in both head-to-head and head-to-tail configurations in a ratio of 2:1, respectively. In contrast, Becheri et al.¹⁶ suggest that polymer–CD IC crystal precipitation is preceded by the formation of wormlike aggregates of CD in aqueous solution, which are most likely oriented in a head-to-head fashion. This explains how CD in the columnar structure with no guest molecule other than water can be obtained from rapid precipitation.

In a previous paper,¹⁷ we characterized the structure and stability of rapidly precipitated columnar α -CD, using water vapor sorption and complementary WAXD measurements. In this paper, we report similar measurements for the rapidly precipitated columnar structure of γ -CD. It is found that γ -CD undergoes a crystal structure transformation from the columnar to the cage structure at elevated water vapor activities. Vacuum-drying the as-precipitated columnar structure transforms it to an amorphous phase, which also undergoes a crystal structure transformation at elevated water activities.

2. Experimental

2.1. Materials

The γ -CD was purchased from Cerestar in powder form. Acetone was obtained from Aldrich Chemical Co. and used without further purification. Deionized water used for all recrystallizations was purified with a US Filter system.

2.2. Preparation of γ -CD columnar structure

A solution containing 11.6 g of γ -CD in 50 mL of deionized water was stirred continuously at 50 °C for 2 h. The clear solution was then poured into 250 mL of stirred acetone at room temperature. The precipitate was immediately vacuum filtered and is henceforth referred to as ‘as-precipitated’.¹⁴ As-precipitated γ -CD columnar structure which was then vacuum dried at 90 °C for 15 h is referred to as ‘vacuum dried’.

2.3. Thermogravimetric measurements

Thermogravimetric analysis (TGA) was carried out with a Perkin–Elmer Pyris 1 Thermogravimetric Analyzer on samples weighing 5 mg. Samples were placed in an open platinum pan that was hung in the furnace. The weight percentage of the remaining material in the pan was recorded during heating from 25 to 600 °C at a heating rate of 10 °C/min. Nitrogen was used as the purge gas.

2.4. Water vapor sorption isotherms

A custom-built gravimetric balance was used to measure the sorption of water vapor in dehydrated γ -CD. Samples weighing 0.2–0.5 g were first vacuum dried at 90 °C and then vacuum dried in the balance chamber at 40 °C to remove any water adsorbed after removal

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