

# HYDRATION AND DEHYDRATION PROCESSES OF $\beta$ -CYCLODEXTRIN: A RAMAN SPECTROSCOPIC STUDY

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## ABSTRACT

A linear relationship between the integrated intensity of the Raman OH stretching band ( $I_{OH}$ ) and ambient humidity in equilibrium with a sample of a crystalline  $\beta$ -Cyclodextrin ( $\beta$ CD) hydrate, for humidities between 15% and 100%, was obtained. In addition, hydration and dehydration processes were monitored by measuring  $I_{OH}$  as a function of time. For the normally hydrated crystal, both hydration and dehydration processes present essentially continuous and similar variations with hysteresis for times shorter than 20 min.

## 1. INTRODUCTION

The water content of crystalline  $\beta$ -cyclodextrin (cyclomaltoheptaose,  $\beta$ CD) hydrate is known to establish fast equilibria with atmospheric humidities in the range 15%-100%. The overall crystal structure is conserved, though with a small percentual reduction of the cell volume from the 100% humidity level [1]. The number of water molecules per  $\beta$ CD varies continuously from about 9.4 to 12.3 in the humidity range 15-100% [1]. In fully hydrated  $\beta$ CD, 7 water molecules occupy the cyclodextrin cavity as a cluster, and 5.4 occupy interstitial spaces [1-3]. Below 15% humidity, the crystal structure collapses. At very low humidities, a distinct phase II is formed [4]. Although the crystal lattices of  $\beta$ CD hydrates do not have permanent channels, fast diffusion of water molecules occurs due to transient fluctuations in the lattices [1]. Exchange experiments carried out with water marked either with D or with  $^{18}O$  showed that the H/D exchange is complete, hence extending also to sterically inaccessible O-H groups, and that the long-range transport of hydrogen takes place by diffusion of intact water molecules [5].

In this work, the relative integrated intensity under the Raman OH stretching band envelope ( $I_{OH}$ ) is measured for  $\beta$ CD hydrates in equilibria with different relative humidities. From this, a relationship is established between  $I_{OH}$  and the relative ambient humidity, for

humidities between 15% and 100%. In addition,  $I_{OH}$  is measured as a function of time, during a hydration-dehydration sequence of experiments on crystalline  $\beta$ CD.

## 2. MATERIALS AND METHODS

### 2.1. Materials

$\beta$ CD, kindly offered by Wacker Chemie, Munchen, Germany, was recrystallized by cooling concentrated aqueous solutions from *ca.* 80 °C in a Dewar flask. Crystals were taken from the solvent and exposed to atmosphere of moderate temperature and humidity (*ca.* 22°C and 70% relative humidity). After equilibration with the atmosphere, the crystals were grounded to obtain a micro-crystalline powder.

### 2.2. Methods

Two series of experiments were performed. The first aimed at correlating  $I_{OH}$  with atmospheric humidity, for  $\beta$ CD hydrates in equilibria with constant humidities.  $\beta$ CD powder was exposed to the atmosphere over suitable saturated salt solutions [1]. After equilibration, some powder was sealed in a Kimax capillary tube (inner diameter 0.8 mm).

In the second set-up,  $I_{OH}$  was followed as a function of time during the process of hydration and dehydration. In the hydration experiment, dehydrated  $\beta$ CD powder was introduced in a cell with the bottom filled with pure water. For dehydration, fully hydrated  $\beta$ CD was introduced in the same cell with water replaced by silica gel. The cell was positioned in the laser beam for Raman spectra recording.

The Raman spectra were recorded on a T64000 Jobin Yvon spectrometer, working in the subtractive configuration, with relevant slit widths set to 300  $\mu$ m and intermediate slit between premonochromator and spectrograph wide open (14 mm). The detecting device was a CCD, and an integration time of 15 s was used. Spectral data for the 2800-3800  $\text{cm}^{-1}$  overall region were collected in 10 subregions, hence corresponding to a total acquisition time of 150 s. An Ar ion laser (Innova 300-05 model with power track, from Coherent) provided *ca.* 100 mW at the sample position. Integrated intensities were determined using the machine software.

## 3. RESULTS AND DISCUSSION

### 3.1. Raman $\nu$ OH intensity vs. ambient humidity

The Raman OH stretching band of crystalline hydrated  $\beta$ CD corresponds to a moderately intense and very broad band, centred around 3350  $\text{cm}^{-1}$ . This band is assigned to the OH stretching vibration from  $\beta$ CD hydroxyl groups and from water molecules. The most intense band in the 2800-3800  $\text{cm}^{-1}$  region is the peak intensity of the complex of  $\nu$ CH bands which occurs at a Raman shift of 2908  $\text{cm}^{-1}$ . The peak intensity at this frequency was taken as internal reference for measurement of the relative  $\nu$ OH Raman band intensity (the corresponding frequency was found to be constant over the different conditions of the study). With this internal reference,  $I_{OH}$  was measured for  $\beta$ CD hydrates in equilibria with saturated salt solutions of different relative humidities, using the first set-up described in the Methods Section.

Fig.1 presents the Raman spectra of five samples of crystalline  $\beta$ CD hydrate in equilibrium with ambient humidities of 0, 58, 79, 88, 98%. The inset shows  $I_{OH}$  vs. ambient humidity. Except for the lowest humidity which should correspond to  $\beta$ CD in a different phase (phase II, mostly dehydrated form) [4], all points fall on a straight line ( $I_{OH} = 24 \cdot h + 52$ ,  $R=0.99$ ). The constant term in this relationship corresponds to the hydroxyl groups in the  $\beta$ CD molecules and to water molecules possibly retained in the  $\beta$ CD structure at 0% humidity.

The data in Fig.1 show that in the humidity range 15%-100%, the water content of crystalline  $\beta$ CD hydrates exhibits a linear response to variations of ambient humidity. This is consistent with crystallographic data [1].

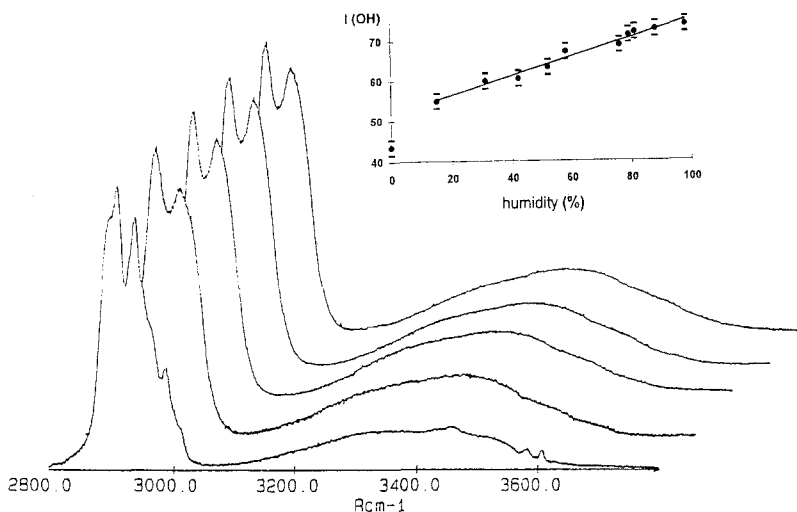


Figure 1. Raman spectra of crystalline  $\beta$ CD hydrates for different water activities. The inset shows  $I_{OH}$  vs. ambient humidity ( $h$ ).  $I_{OH}$  is drawn on an arbitrary scale.

### 3.2. Hydration and dehydration processes

In the second experiment,  $I_{OH}$  was observed as a function of time during hydration and dehydration of  $\beta$ CD. During dehydration, the relevant kinetic variable is the *occupied fraction of removable water sites* ( $\theta$ ) in  $\beta$ CD, whereas for hydration the unoccupied fraction of removable water sites ( $1-\theta$ ) is the relevant quantity. These quantities ( $1-\theta$  and  $\theta$ ) should be studied in their variations against time, for a comparison of hydration and dehydration on an equal footing.

On the reasonable assumption that all the OH oscillators have approximately the same intrinsic Raman intensity, the crystal water content per mole of  $\beta$ CD, *i.e.*,  $n(\text{H}_2\text{O})/\beta\text{CD}$ , is linear in  $I_{OH}$ . However,  $I_{OH}$  contains a constant term  $I_{OH}^{(\text{min})}$  which includes the contributions from the 21 hydroxyl groups and of possibly present non-removable water molecules. If this constant contribution is subtracted from  $I_{OH}$ , the relative quantity  $I_{OH} = [I_{OH} - I_{OH}^{(\text{min})}] / [I_{OH}^{(\text{max})} - I_{OH}^{(\text{min})}]$  ranges from 0 to 1. Then,  $I_{OH}$  represents the quantity  $n = [n - n^{(\text{min})}] / [n^{(\text{max})} - n^{(\text{min})}]$  that is the occupied fraction of the removable water

molecules,  $\theta$ .  $I_{OH}$  is therefore a suitable and observable variable in hydration/dehydration experiments. This redefinition of variables is all the more necessary since definite and precise values for  $n^{(max)}$  and  $n^{(min)}$  are not yet well defined, as they seem to depend on crystallization conditions, and  $I_{OH}^{(max)}$  and  $I_{OH}^{(min)}$  are expected to depend on current instrumental conditions.

Fig. 2 presents  $1-\theta$  vs. time (hydration set of experiments) and  $\theta$  vs. time (dehydration) for  $I_{OH}$  above the corresponding 15% ambient humidity value. This restriction excludes the initial value of the hydration experiment and long-time values of the dehydration experiment. As mentioned above, these points correspond to  $\beta$ CD in a different phase (phase II, mostly dehydrated form).

As it can be seen from Fig.2, both hydration ( $1-\theta$ ) and dehydration ( $\theta$ ) exhibit continuous and similar time variations. Hysteresis occurs for times between zero and 20 min., with the dehydration curve (occupancy curve) decaying faster than the hydration curve (unoccupancy curve), i.e., the results show a different time behaviour for the occupied-to-unoccupied and the unoccupied-to-occupied changes, with the latter being slower for short times.

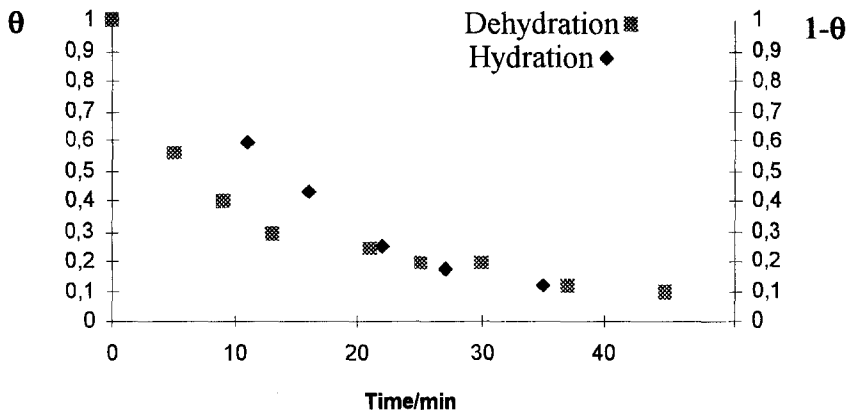


Figure 2. Quantities  $1-\theta$  (for the hydration experiment) and  $\theta$  (for the dehydration experiment) shown as functions of time, for  $I_{OH}$  above the corresponding 15% ambient humidity value (see text).

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