



# Preservation of carbon dioxide clathrate hydrate coexisting with sucrose under domestic freezer conditions



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## ABSTRACT

We report an experimental study of the preservation of CO<sub>2</sub> hydrate in the presence of sucrose. We measured the mass fraction of CO<sub>2</sub> hydrate coexisting with sucrose for three weeks. The CO<sub>2</sub> hydrate sample was produced from an aqueous solution of sucrose with a mass fraction of 0.16 or 0.12. The particle sizes of the samples were 5.6–8.0 mm and 1.0 mm. The samples were stored at 253 or 258 K under atmospheric pressure. It was found that preservation of the CO<sub>2</sub> hydrate was better for the lower sucrose mass fraction and lower temperature. The effect of particle size was not clearly observed. The mass fractions of CO<sub>2</sub> hydrate in the samples at the end of three weeks exceeded 0.02, which is equivalent to carbonated water. These results indicate that CO<sub>2</sub> hydrate coexisting with sucrose can be stored for three weeks under domestic freezer conditions.

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## 1. Introduction

Carbonated drinks are enjoyed around the world because carbonation makes the drinks refreshing. Jelly-like carbonated foods are commercially available. However, the extremely low solubility of CO<sub>2</sub> in ice, a mass fraction of 10<sup>-8</sup> (Rohde and Price, 2007) compared with that of 10<sup>-3</sup> in liquid water (Diamond and Akinfiev, 2003), is an obstacle to producing solid carbonated foods with refreshing qualities. To overcome this obstacle, clathrate hydrates formed with CO<sub>2</sub>, which can contain high concentrations of CO<sub>2</sub>, could be used.

Clathrate hydrates, also called gas hydrates, are ice-like crystalline compounds consisting of hydrogen-bonded water molecules and other molecules. The water molecules, generally called “host molecules”, build a hydrogen-bonded network to stabilize molecules other than water, generally called “guest molecules”. High-capacity molecular storage by the guest is one of the attractive applications of clathrate hydrates. For example, the concentration of CO<sub>2</sub> in CO<sub>2</sub> hydrates, 296 kg/m<sup>3</sup>, is 20–50 times higher than that of CO<sub>2</sub> in carbonated water, 6–15 kg/m<sup>3</sup> (Descoins et al., 2006), corresponding to the CO<sub>2</sub> solubility in water at 278–293 K under a pressure of 0.5 MPa (Dodds et al., 1956). Application of the large molecular-storage capacity of clathrate hydrates to solid carbonated foods using CO<sub>2</sub> hydrates has been considered (Makiya et al., 2010; Peters et al., 2010, 2012, 2013).

Hydrate formation generally requires low temperatures and high pressures. The equilibrium temperature of CO<sub>2</sub> hydrates is 219 K under atmospheric pressure (Sloan and Koh, 2008); this is significantly lower than the temperatures in domestic freezers, which are typically 253–258 K. CO<sub>2</sub> hydrates are therefore thermodynamically unstable under domestic freezer conditions. Nevertheless, we expect long-term storage of CO<sub>2</sub> hydrates under domestic freezer conditions to be possible, because clathrate hydrates can prevent themselves from decomposing further above their dissociation temperature but below the freezing point of water. This characteristic is often called “self-preservation” or “anomalous preservation”. Although the mechanism of this phenomenon is still not understood in detail, numerous observations of the decomposition of clathrate hydrates have been reported. Flenty and Kuhs (2009) observed CO<sub>2</sub> hydrate surfaces at temperatures from 200 to 270 K and pressures between the hydrate stability limit and 0.6 kPa. They reported that anomalous preservation may depend on the presence of hexagonal ice above 240 K. Takeya and Ripmeester (2008) reported that the dissociation rate of CO<sub>2</sub> hydrate decreased at temperatures from 220 to 260 K under atmospheric pressure. Giavarini et al. (2007) experimentally investigated CO<sub>2</sub> hydrate preservation at pressures between 0.1 and 0.3 MPa and temperatures from 270 to 273 K. They reported that dissociation of the CO<sub>2</sub> hydrate was retarded in ice-rich samples (Giavarini et al., 2007). All of these previous studies indicate that CO<sub>2</sub> hydrates could have good stabilities under non-equilibrium thermodynamic conditions.

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There have been several efforts at producing frozen desserts containing CO<sub>2</sub> hydrates. Previous studies on producing desserts containing CO<sub>2</sub> hydrates are reviewed below. Peters et al. (2010, 2012, 2013) reported attempts to produce a frozen dessert mixed with CO<sub>2</sub> hydrates using a rapid formation method (Peters et al., 2010, 2012, 2013). CO<sub>2</sub> hydrates in the samples were stable for 10 min under atmospheric pressure. Makiya et al. (2010) reported the formation of clathrate hydrates containing CO<sub>2</sub> + ethanol at temperatures from 254 to 268. Sun et al. (2011) reported the preservation of CO<sub>2</sub> hydrates at 253 or 258 K under atmospheric pressure for three weeks (Sun et al., 2011). After preservation for three weeks, the mass fraction of CO<sub>2</sub> hydrate exceeded 0.02, which is equivalent to carbonated water containing 6 kg/m<sup>3</sup> of CO<sub>2</sub>.

As indicated above, the preparation of CO<sub>2</sub> hydrates with ethanol or sucrose and preservation of the CO<sub>2</sub> hydrates are possible under domestic freezer conditions. The preservation of CO<sub>2</sub> hydrates with disaccharides and ethanol needs to be investigated to develop carbonated foods containing CO<sub>2</sub> hydrates. Investigation of the preservation of CO<sub>2</sub> hydrates in the presence of disaccharides involves examining the relationship between ice formation and disaccharide concentration (Sei et al., 2002; Gonda and Sei, 2005; Uchida et al., 2007; Uchida and Takeya, 2010).

In the present study, we experimentally investigated the preservation of CO<sub>2</sub> hydrates coexisting with sucrose for three weeks. The CO<sub>2</sub> hydrate samples were produced from aqueous solutions of sucrose with a sucrose mass fraction,  $w_{sc}$ , of 0.16 or 0.12. The particle sizes of the samples,  $d$ , were 5.6–8.0 and 1.0 mm. The samples were stored under aerated conditions under atmospheric pressure at a temperature,  $T$ , of 253 or 258 K. The mass fraction of CO<sub>2</sub> hydrate in the samples was intermittently measured during three weeks.

## 2. Materials and methods

### 2.1. Sample preparation

CO<sub>2</sub> hydrate crystal samples were synthesized in a stainless-steel apparatus; the inner dimensions were diameter 80 mm and height 40 mm, and the volume was about 200 cm<sup>3</sup> (see Fig. 1). This apparatus was placed in a temperature-controlled bath filled with an aqueous ethylene glycol solution. The apparatus was equipped with platinum resistance thermometers (with an uncertainty of ±0.1 K) to measure the inner temperature. A pressure transducer (VPMC-A4-A-(-100 to 1000)-1, Valcom Inc., with an uncertainty of ±1.8 kPa) was used to measure the inner pressure of the apparatus during the CO<sub>2</sub> hydrate synthesis experiments. To produce CO<sub>2</sub> hydrates containing sucrose, we supplied about 50 g of an aqueous sucrose solution with a sucrose mass fraction of 0.16 or 0.12 to the apparatus, and then carefully sealed the apparatus. The air inside the apparatus was discharged using a vacuum pump. CO<sub>2</sub> gas was supplied to the apparatus to a pressure of 1.0 MPa and discharged from the apparatus to a pressure of 0.1 MPa three times. After this process, the pressure of the air inside the apparatus was less than 0.01 kPa. The apparatus was set in the bath at 276 K. Then CO<sub>2</sub> gas was supplied to the apparatus to form a hydrate at a temperature of 276 K and a pressure of 3.0 MPa; this is higher than the phase equilibrium pressure at 276 K for the CO<sub>2</sub> + water system hydrate (Yasuda and Ohmura, 2008). In the high-pressure apparatus, an impeller was driven at 400 rpm to agitate the fluid and the hydrate. On formation of the CO<sub>2</sub> hydrate, the pressure decreased from 3.0 to 1.7 MPa (the equilibrium pressure at this temperature), typically in 6–7 h. The apparatus was then recharged with CO<sub>2</sub> gas. The CO<sub>2</sub> gas recharging procedure was repeated five to six times, until no further pressure reduction was observed. The apparatus was transferred to a liquid-nitrogen

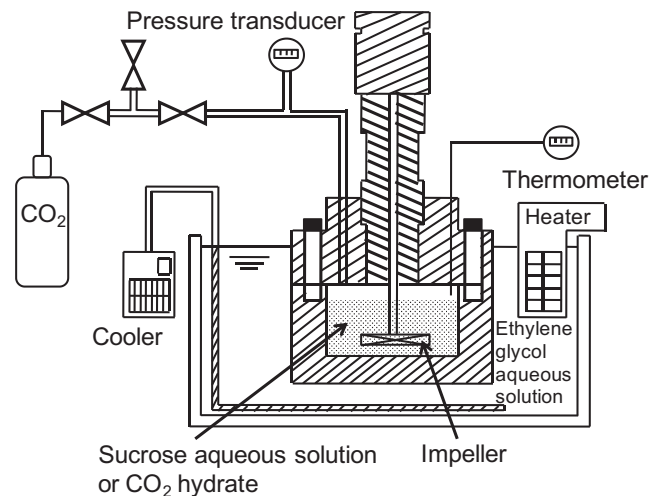


Fig. 1. Schematic diagram of experimental apparatus used to prepare CO<sub>2</sub> hydrate samples containing sucrose.

bath, and cooled to 219 K. During the cooling procedure, the pressure in the apparatus was reduced in a stepwise manner, approximately along the pressure–temperature line of the CO<sub>2</sub> hydrate equilibrium. The CO<sub>2</sub> hydrate sample was removed from the apparatus at 219 K under atmospheric pressure using a liquid-nitrogen bath. The samples were immediately crushed in a chilled mortar and sieved into particles with diameters of 1.0 and 5.6–8.0 mm.

### 2.2. Preservation experiments

Before starting the preservation experiments, we measured the initial mass fraction of CO<sub>2</sub> hydrate in the sample. A portion of the prepared CO<sub>2</sub> hydrate sample was placed in a closed container. The sample was then heated to 295 K for dissociation of all the hydrate in the sample. During hydrate dissociation, the container was opened once and the CO<sub>2</sub> gas evolved from the hydrate was released into the surrounding air. To calculate the mass of CO<sub>2</sub> in the sample, the mass of the sample was measured before and after hydrate dissociation, using an electronic balance (Sefi IUW-200D, with an uncertainty of ±0.004 g). The mass measurements before and after the hydrate dissociation were performed in a cold room at 253 K. To calculate the mass of CO<sub>2</sub> hydrate based on the mass of CO<sub>2</sub>, the hydration number was needed. Udachin et al. (2001) reported that the hydration number was 6.2 for a CO<sub>2</sub> hydrate prepared at 276 K and 3 MPa (Udachin et al., 2001). Based on this value, the mass of CO<sub>2</sub> hydrate in the sample was calculated using the following equation:

$$m_{\text{Hyd}} = m_{\text{CO}_2} \times M_{\text{Hyd}}/M_{\text{CO}_2} \quad (1)$$

where  $m_{\text{Hyd}}$  is the mass of CO<sub>2</sub> hydrate,  $m_{\text{CO}_2}$  is the total mass of CO<sub>2</sub>,  $M_{\text{CO}_2}$  is the molar mass of CO<sub>2</sub>, and  $M_{\text{Hyd}}$  is the molar mass of CO<sub>2</sub> hydrate. The mass fraction of CO<sub>2</sub> hydrate was defined as  $m_{\text{Hyd}}/m_{\text{Total}}$ , where  $m_{\text{Total}}$  is the mass of the sample before hydrate dissociation.

During the preservation experiments, the samples were stored in a temperature-controlled bath at 253 or 258 K under atmospheric pressure (see Fig. 2). Stainless-steel cans were placed in the bath and plastic containers with the samples were placed in the stainless-steel cans. Stainless-steel blocks were used as sinkers to mechanically stabilize the containers and cans. All of the containers, cans, and blocks were cooled prior to the experiments. The temperature inside the container was intermittently measured using a platinum resistance thermometer to confirm that the

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