

# Preservation of Carbon Dioxide Clathrate Hydrate Coexisting with Sucrose at Temperatures below the Water Freezing Point under Atmospheric Pressure

Tadaaki Sato, and Ryo Ohmura

**Abstract**—This paper reports the influence of sucrose on the preservation of CO<sub>2</sub> hydrate crystal samples. The particle diameter of hydrate samples were 1.0 and 5.6–8.0 mm. Mass fraction of sucrose in the sample was 0.16. The samples were stored at the aerated condition under atmospheric pressure and at the temperature of 253 or 258 K. The results indicated that the mass fractions of CO<sub>2</sub> hydrate in the samples with sucrose were  $0.10 \pm 0.03$  at the end of 3-week preservation, regardless of temperature and particle diameter. Mass fraction of CO<sub>2</sub> hydrate in the samples with sucrose was higher than that of pure CO<sub>2</sub> hydrate for 1.0 mm particle diameter, while was lower than that of pure CO<sub>2</sub> hydrate for 5.6–8.0 mm particle diameter. Discussion is made on the influence of sucrose on the dissociation of CO<sub>2</sub> hydrate and the resulting formation of ice.

**Keywords**—Clathrate hydrates, Carbon dioxide

## I. INTRODUCTION

CARBONATED beverages are known around the world as a association of refreshment by carbonation. There are carbonated frozen foods or jellylike carbonated foods. However, the extremely low solubility of CO<sub>2</sub> in ice, 10–8 g/g [1] compared to liquid water, 10–3 g/g [2] is the problem to produce a solid carbonated foods with refreshing feeling. To achieve CO<sub>2</sub> concentrations in solids similar to the CO<sub>2</sub> concentration in carbonated beverage, we need to find a method other than solution in ice. One attractive method of storing the gas to a high concentration is the use of hydrate.

Clathrate hydrates, also called gas hydrate, are icelike crystalline compounds consisting of hydrogen-bonded water molecules. The water molecules, generally called “host molecules”, build a network with hydrogen bonds to stabilize molecules other than water, generally called “guest molecules”. Three crystallographic structures of hydrates have been known to exist in nature— structure I, structure II, and structure H—which have different lattice various to accommodate the respective guest molecules. Hydrate formation generally requires low temperatures and high pressures. Clathrate hydrates have found several applications in various areas. Clathrate hydrates can contain a great quantity of gas. For example, the volume of CO<sub>2</sub> gas stored in 1 m<sup>3</sup> of CO<sub>2</sub> hydrate

is more than 150 m<sup>3</sup> at standard temperature and pressure [3], [4]. Using the large gas-storage capability of clathrate hydrates, novel applications, such as the storage and transportation of natural gas and hydrogen [5]–[7], have been considered.

One of their most amazing characteristics is often called “self-preservation” or “anomalous preservation” [8]. As the name of this phenomenon indicates, some kinds of clathrate hydrates prevent themselves from further decomposing above their equilibrium dissociation temperature but below the freezing point of water. Although the mechanism of this phenomenon was still not profoundly understood, numerous observations of slow or incomplete decomposition of clathrate hydrates have been reported in the past 2 or 3 decades [9]–[14]. Recently, an experimental study was performed on the dissociation behavior of CH<sub>4</sub> hydrate at temperature ramping from 250 to 268 K and under atmospheric pressure [15], and the combination of in situ neutron diffraction studies and ex situ scanning electron microscopy (SEM) observation on CO<sub>2</sub> hydrate at temperatures from 200 to 270 K and pressures between the hydrate stability limit and 0.6 kPa [9] has been reported. Takeya and Ripmeester reported that anomalous preservation may depend on the interaction between guest and water molecules [16]. Giavarini et al. experimentally investigated the preservation of CO<sub>2</sub> hydrate at pressure between 0.1 and 0.3 MPa and temperature between 270 and 273 K and compared it to that of CH<sub>4</sub> hydrate [17]. All of these previous studies indicate that some clathrate hydrates, especially the CO<sub>2</sub> and CH<sub>4</sub> hydrates, could have an unexpected good stability at the thermodynamic conditions out of the equilibrium conditions.

Besides storage and transportation, CO<sub>2</sub> hydrate formed with a kind of harmless guest molecule, the CO<sub>2</sub> molecule, may find application in food products. This is because that CO<sub>2</sub> hydrate is relatively easily formed. Makiya et al. reported that the CO<sub>2</sub> + H<sub>2</sub>O system suggested the formation of a new hydrate containing both CO<sub>2</sub> and ethanol as guest molecules in the hydrate [18]. Peters et al. reported their attempt to produce a frozen dessert mixed with CO<sub>2</sub> hydrate by a rapid formation method [19]. CO<sub>2</sub> hydrate in the product can be stable for a relatively short time such as several hours. Marketing carbonated water generally contains 4 mass % of CO<sub>2</sub> gas, calculated based on CO<sub>2</sub>/ water vapor liquid equilibrium at 0.5 MPa and 278 K. The mass fraction of CO<sub>2</sub> hydrate in a hydrate + water mixture corresponding to the CO<sub>2</sub> concentration in carbonated water is 0.14 (in this case, 71% and 100% for the small and large cage occupancies of CO<sub>2</sub> hydrate were assumed) [20]. Sun et al. indicated that mass fraction of the

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remaining CO<sub>2</sub> hydrate in the samples at the end of the 3-week preservation exceeded 0.14 [21]. These results indicated that the concentrations of CO<sub>2</sub> in these CO<sub>2</sub> hydrate samples were more than those in carbonated water in the market.

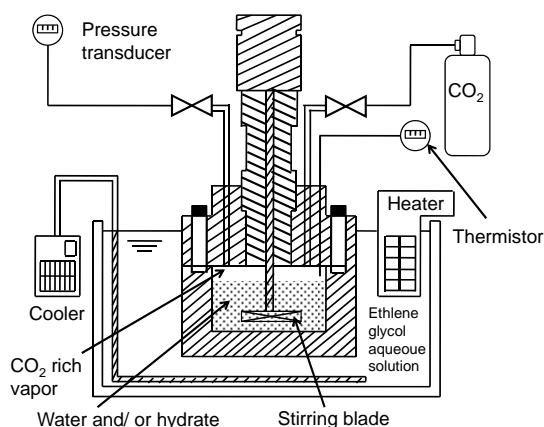


Fig. 1 Schematic of the experimental apparatus for CO<sub>2</sub> hydrates with sucrose

For the development of novel food/ drink products, the preservation of CO<sub>2</sub> hydrate with disaccharide or alcohol needs to be investigated. In any previous studies, preservation of CO<sub>2</sub> hydrate with the additives was not measured. In this study, we experimentally investigated the preservation of CO<sub>2</sub> hydrate co-existing with sucrose. The particle diameter of the samples was 1.0 and 5.6-8.0 mm. Mass fraction of sucrose in the sample was 0.16. The sample was stored at the aerated condition under atmospheric pressure and at the temperature of 253 or 258 K. Discussion is made on the influence of sucrose on the dissociation of CO<sub>2</sub> hydrate and the resulting formation of ice is discussed.

## II. EXPERIMENTAL SECTION

**Sample Preparation.** CO<sub>2</sub> hydrate crystal samples were synthesized in a stainless-steel apparatus with inner dimensions of 80 mm diameter and 40 mm height, about a volume of 200 cm<sup>3</sup>. 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  $\pm 0.1$  K) to measure the inner temperature. A pressure transducer (VPMC-A4-A-(-100 ~ 1000)-1, Valcom, Inc., with an uncertainty of  $\pm 1.8$  kPa) was set to measure the inner pressure of the apparatus during the CO<sub>2</sub> hydrate synthesis experiment. First, we supplied about 50 g of aqueous solution with mass fraction of sucrose 0.16 to the apparatus and then carefully sealed it. The air inside the apparatus was discharged by a vacuum pump. CO<sub>2</sub> gas was supplied into the apparatus and discharged three times, with these procedures, the particle repeated until no further pressure reduction was observed. The hydrate samples were removed from the apparatus at an pressure of the residual air in the apparatus was less than 0.01 kPa. The apparatus was set into the bath at temperature of 276 K. Then, the apparatus was

recharged with CO<sub>2</sub> gas until 3 MPa (higher than the phase equilibrium condition of the CO<sub>2</sub> + water system hydrate). The CO<sub>2</sub> gas recharging procedure was environment of about 218 K under atmospheric pressure, by using a liquid nitrogen bath, to prevent dissociation of CO<sub>2</sub> hydrate. The samples were immediately crushed in a chilled mortar and sieved into two types of particle diameters of 1.0 and 5.6 - 8.0 mm.

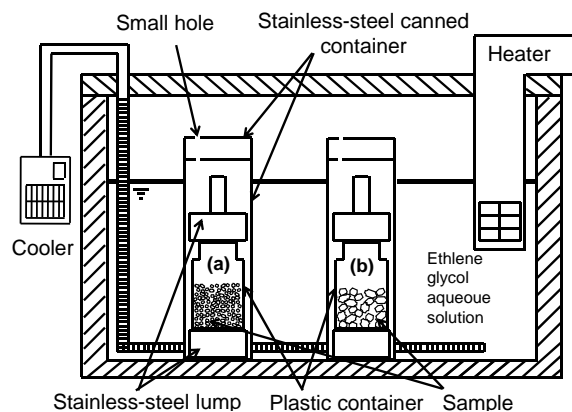


Fig. 2 Schematic of the apparatus for CO<sub>2</sub> hydrate with sucrose preservation tests. The particle diameter of hydrate samples was (a) 1.0 mm, (b) 5.6-8.0 mm. Mass fraction of sucrose in the sample was 0.16. The samples were stored at the aerated condition under atmospheric pressure and at the temperature of 253 or 258 K

**Preservation Experiment.** Before starting the preservation experiment, we have first measured the initial mass fraction of CO<sub>2</sub> hydrate in the sample. First, we removed the sample from the apparatus and put into a closed container. The sample was then heated to dissociate all the hydrate in the sample. During this hydrate dissociation, the container was once opened and the CO<sub>2</sub> gas evolved from the hydrate was released into the surrounding air. The mass of the sample was measured before and after the hydrate dissociation using an electronic balance (sefi IUW-200D, with an uncertainty of  $\pm 0.004$  g). We calculated the mass fraction of CO<sub>2</sub> hydrate based on a decrease in the mass of the sample, which should be equal to the mass of CO<sub>2</sub> released upon the dissociation of CO<sub>2</sub> hydrate. To calculate the mass of CO<sub>2</sub> hydrate based on this mass measurement, the hydration number was needed. Udachin et.al [20] reported that the hydration number was 6.2. We used this value. The mass of CO<sub>2</sub> hydrate in the sample was calculated with the following equation,

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

where  $m_{\text{Hyd}}$  is the mass of CO<sub>2</sub> hydrate,  $m_{\text{CO}_2}$  is the 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 is defined as  $m_{\text{Hyd}} / m_{\text{Total}}$ , where  $m_{\text{Total}}$  is the mass of the sample. During the preservation experiment, the sample was stored at the aerated condition under atmospheric pressure and at the temperature of 253 or 258 K. The stainless-steel canned containers to hold the sample were set in the temperature- controlled bath. Plastic containers with the samples were set into the stainless-steel

canned containers. The mass of each sample was intermittently measured during three weeks.

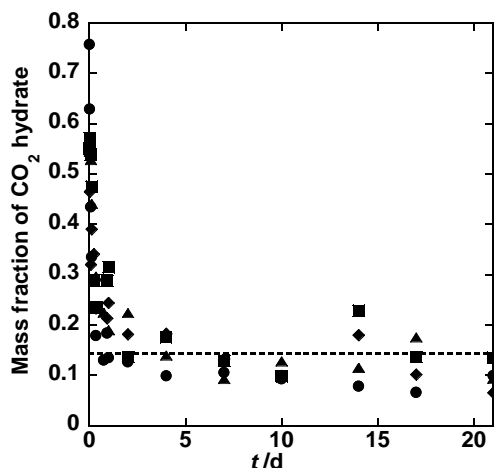


Fig. 3 Time evolution of CO<sub>2</sub> hydrate in samples with sucrose. The samples were stored at the aerated condition under atmospheric pressure and at the temperature of 253 or 258 K. Particle diameter (●) 1.0 mm, 258 K; (■) 5.6-8.0, 258 K; (▲) 1.0 mm, 253 K; (◆) 5.6-8.0 mm 253 K; (-) CO<sub>2</sub> hydrate mass fraction of Carbonated water expected 0.14

### III. RESULTS AND DISCUSSION

**Characterization of CO<sub>2</sub> hydrate samples.** The sample of CO<sub>2</sub> hydrate with sucrose was prepared at the temperature of 276 K, at the pressure of 3.0 MPa, the mass fraction of CO<sub>2</sub> hydrate in the sample was measured preceding experimental method. The results indicated that the mass fraction of CO<sub>2</sub> hydrate in the sample with sucrose was 0.75, while that of pure CO<sub>2</sub> hydrate in the samples was 0.95. As CO<sub>2</sub> hydrate is formed in the reactor, water in the aqueous phase decreased. The sucrose concentration in the aqueous solution increased with the progress of the hydrate formation. The sucrose solution of high concentration in the sample inhibited the water-to-hydrate conversion, but still the mass fraction of CO<sub>2</sub> hydrate was secured at 0.75.

**Preservation tests.** The samples were stored at the aerated condition under atmospheric pressure and at the temperature of 253 or 258 K. Samples of 0.2 g were removed from apparatus and measured the mass fraction of CO<sub>2</sub> hydrate in the samples with sucrose. Mass fraction of sucrose in the samples was 0.16. The samples were stored at the aerated condition under atmospheric pressure and at the temperature of 253 or 258 K. The results indicated that the mass fractions of CO<sub>2</sub> hydrate in the samples with sucrose were  $0.10 \pm 0.03$  at the end of 3-week preservation, regardless of temperature and particle diameter. The mass fraction of CO<sub>2</sub> hydrate in the samples with sucrose was higher than that of pure CO<sub>2</sub> hydrate for 1.0 mm particle diameter, while was lower than that of pure CO<sub>2</sub> hydrate for 5.6-8.0 mm particle diameter. It is inferred from the results that the high concentration sucrose aqueous solution coexisting with CO<sub>2</sub> hydrate in the sample influenced the dissociation of CO<sub>2</sub> hydrate and the resulting formation of ice, thereby negatively affecting the preservation of CO<sub>2</sub> hydrate.

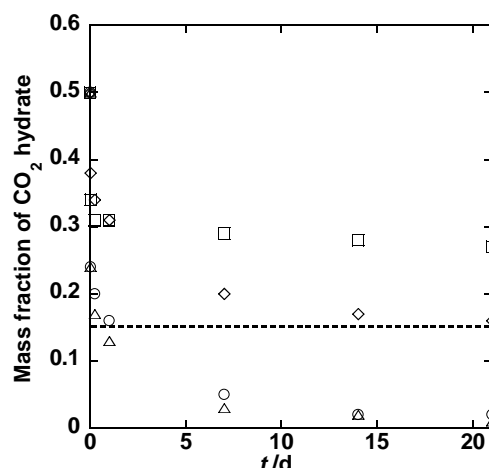


Fig. 4 Time evolution of CO<sub>2</sub> hydrate in samples. The samples were stored at the aerated condition under atmospheric pressure and at the temperature of 253 or 258 K. Particle diameter (○) 2.8 mm, 258 K; (□) 5.6-8.0, 258 K; (△) 2.8 mm, 253 K; (◇) 5.6-8.0 mm 253 K; (-) CO<sub>2</sub> hydrate mass fraction of Carbonated water expected 0.14

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