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Preservation of carbon dioxide clathrate hydrate in the presence of fructose or glucose and absence of sugars under freezer conditions

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ABSTRACT

To investigate the preservation of CO_2 clathrate hydrate in the presence of fructose or glucose and absence of sugars, CO_2 hydrate samples were preserved at 238.2 K, 253.2 K and 258.2 K under atmospheric pressure for three weeks. The preservations of CO_2 hydrate with those two monosaccharide sugars at both 238.2 K and 253.2 K were lower than that of the pure CO_2 hydrate without the sugars. The results indicated that the viscosity of super-cooled or stable sugar aqueous solution and occurrence of super-cooled water in the sample hydrate particles are significant factors in the preservation of CO_2 hydrate.

Introduction

Carbonated beverages are consumed as refreshments worldwide, *e.g.*, in the form of soda, beer, and champagne. Solid carbonated foods (jellies, gummies, *etc.*) are not as commercially widely spread as the carbonated beverages. This unavailability of the solid foods may be due to the low CO_2 solubility in ice or other edible solids. A candidate ingredient for inclusion in solid carbonated food is the CO_2 clathrate hydrate.

Clathrate hydrates (hereafter called as hydrates) are ice-like inclusion compounds composed of "host" water molecules and "guest" molecules such as methane, nitrogen, carbon dioxide, and noble gases. For example, the ice-like appearance of chunks of CO_2 hydrate is shown in Fig. 1(a). Clathrate hydrates have high gas storage capacity, *e.g.*, the CO_2 concentration in CO_2 hydrate formed around 276 K and 3 MPa is 298 kg/m^3 [1], and upon dissociation of the hydrate, large amounts of gas can be released as shown in Fig. 1(b). This CO_2 concentration in clathrate hydrates is approximately 50 times higher than that in carbonated water, which is 6 kg/m^3 at 0.3 MPa of CO_2 and 283.15 K [2]. Due to the high gas storage capacity, hydrates can be utilized for natural gas transportation [3,4], fire extinction [5], and as materials for solid carbonated foods [6].

For solid carbonated desserts using hydrate, a test for a rapid production process [6], a test for a packaging of the dessert subject to heat shock [7] and a sensory taste test for the dessert [8] were reported. According to the previous studies, the hydrate dessert could be commercialized. However, preservation of the hydrate-based dessert under thermodynamically stable equilibrium conditions of CO_2 hydrate, 516 kPa at 253.0 K and 963 kPa at 269.4 K [9] raises some practical difficulties. These difficulties may be overcome using the unique phenomenon in the hydrate called "self-preservation" or "anomalous preservation".

Dissociation of some clathrate hydrates, such as CH_4 hydrate, CO_2 hydrate *etc.*, is anomalously slow below the water freezing temperature, despite the hydrate phase being under thermodynamically unstable pressure–temperature conditions [10,11]. The detailed mechanism of the anomalous preservation is yet to be determined. An ice layer was observed on CO_2 hydrate particles under anomalous preservation using diffraction-enhanced X-ray imaging [12]. It is considered that the ice layer formed with the partial dissociation of the outer layer of the hydrate sample may play an important role for the anomalous preservation, *e.g.*, avoiding the guest diffusion from hydrate [13]. Takeya and Ripmeester [14] revealed that the occurrence of the anomalous preservation depends on the interaction strength between guest molecules and water. For example, in H_2S hydrate the guest may have strong interactions with water and the hydrate did not show the anomalous preservation between 160 K and 270 K [14].

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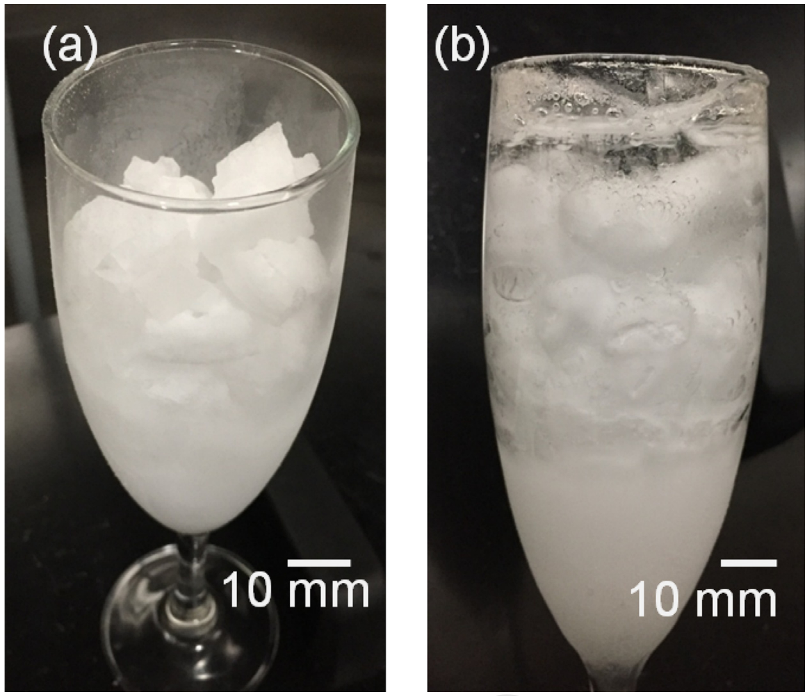

Fig. 1. (a) CO_2 hydrate particles. (b): CO_2 hydrate particles in liquid water. CO_2 bubbles from decomposing hydrate were observed which can be used for carbonation of beverages or other desserts.

The preservation experiments on CO_2 hydrate were performed for various diameters of CO_2 hydrate particle samples under domestic freezer conditions (atmospheric pressure and 253.2 K) [10]. Better preservation of CO_2 hydrate was observed for larger particles [10]. The dependency of preservation on the particle diameter may be due to the volume-to-surface ratio and is in agreement with the proposed model for the anomalous preservation [13]. The preservations of CO_2 hydrate dessert samples coexisting with sucrose [15] and trehalose [16] were reported and CO_2 concentrations in those hydrate dessert samples exceeded that in carbonated water after a three-week preservation period. However, CO_2 concentration in the samples with sucrose was lower than that in the pure CO_2 hydrate samples without sugars, whereas CO_2 concentration in the samples with trehalose was comparable to that in the samples without sugars. From this comparison it was inferred that the existence of thermodynamically stable aqueous solution in the hydrate samples is a significant factor of the preservation of CO_2 hydrate [16]. Glucose and fructose are also commercially utilized as sweeteners in combination with sucrose due to the relatively higher sweetness of fructose and easy production of these monosaccharides from starch. Although glucose and fructose can be utilized as a sugar for hydrate dessert, no CO_2 hydrate preservation test with these sugars has been reported to date.

The dependency of the CO_2 hydrate preservation on temperatures is yet to be determined. The preservation temperatures in the previous studies with the disaccharides were limited around to 253.2 K (243.2 K–258.2 K). At 253.2 K, it is observed that CO_2 hydrate with trehalose dissociated first to super-cooled water then to ice [16]. Around 235 K, it is reported that dissociation mode of the pure CH_4 hydrate may change, that is, whereas the CH_4 hydrate dissociates to super-cooled water at higher temperatures, it

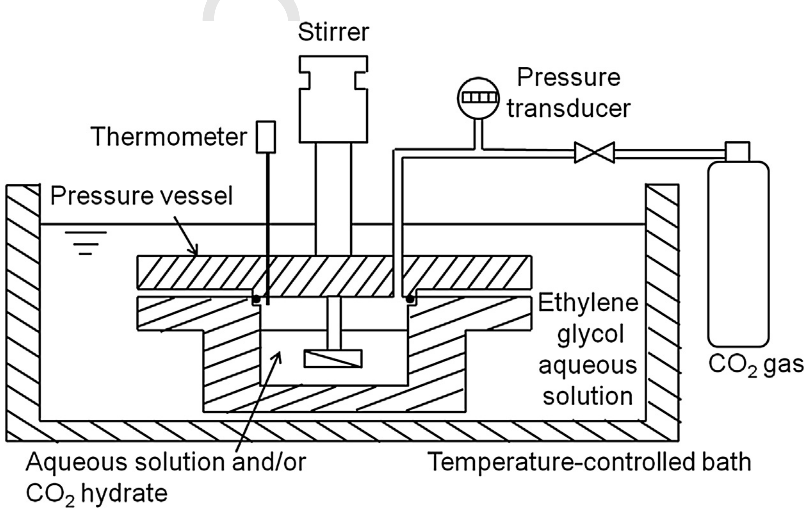

Fig. 2. Schematic of the experimental apparatus for hydrate dessert sample preparation.

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