Preservation of Molecular Ozone in a Clathrate Hydrate : Three-Phase (Gas + Liquid + Hydrate) Equilibrium Measurements for $O_3 + O_2 + CO_2 + H_2O$ Systems

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Abstract—This paper reports the three-phase (gas + liquid + hydrate) equilibrium pressure *versus* temperature data for a ($O_3 + O_2 + CO_2 + H_2O$) system for developing the hydrate-based technology to preserve ozone, a chemically unstable substance, for various industrial, medical and consumer uses. These data cover the temperature range from 272 K to 277 K, corresponding to pressures from 1.6 MPa to 3.1 MPa, for each of the three different ($O_3 + O_2$)-to-CO_2 or O_2-to-CO_2 molar ratios in the gas phase, which are approximately 4 : 6, 5 : 5, respectively. The mole fraction of ozone in the gas phase was ~0.03 , which are the densest ozone fraction to artificially form O_3 containing hydrate ever reported in the literature. Based on these data, the formation of hydrate containing high-concentration ozone, as high as 1 mass %, will be expected.

Keywords—Clathrate hydrate, Ozone, Molecule storage, Sterilization.

I. INTRODUCTION

OZONE (O_3) is a strong oxidant and potent disinfecting agent. Due to this nature, there are vast applications of artificially generated ozone in industry, for example, decontamination of air and water, deodorization of exhaust gas, the sterilization perishables, the disinfection of medical instruments, and the cleaning or surface-conditioning processes in the semiconductor industry. Moreover, ozone is easy on the environment because of its nature of decomposing naturally into diatomic oxygen (O_2) with time. For these reasons, ozone is expected to utilize in various industrial processes and commercial activities. However, it is neither very easy nor economical to use ozone in consumer applications such as sanitizing foods and drinking water, removing pesticide residues from fruits and vegetables, treating water in aquariums for suppressing bacteria growth, etc. This is because, to artificially generate ozone, we need a high-voltage electric device such as a corona discharger or a cold plasma generator and, once generated, ozone in the gaseous state rapidly decomposes to oxygen. Thus, it is generally considered that ozone cannot be stored and transported like other industrial gases and must be produced on site.

On the other hand, clathrate hydrates (abbreviated hydrates) are expected to be new materials relating to the energy and the environment issues. Hydrates are crystalline solid compounds each composed of *host* water molecules hydrogen-bonded into a structure of interlinked cages. Unless the given pressure is extremely high (typically on the order of gigapascals), each cage contains at most one *guest* molecule of a substance other than water. That is, the guest molecules in a hydrate are isolated by the cage walls due to van der Waals forces and thereby prevented, in general, from mutual interactions. Based on this nature, the idea of storing ozone using a hydrate was proposed by McTurk and Waller [1] expecting that, hydrates have a high potential of storing chemically unstable substances, such as ozone, in the form of encaged guest molecules. For the limited consumer use of ozone, ozonated water (liquid water in which ozone is physically dissolved) and ozonated ice (water ice holding microbubbles of an ozone-containing gas) are commercially available. However, the initial ozone concentrations in such ozonated water or ice actually measured in previous studies are only of the order of 1 or 10 ppm , and rapidly decays with time. Storing ozone in a clathrate hydrate at a concentration much higher than that available using ozonated water or ice.

Ozone may form a hydrate by itself in the absence of any other hydrate-forming substances. However, the hydrate formation from pure ozone gas or an ozone + oxygen gas mixture (a typical ozone-containing gas available from commercial ozone generators) presumably requires a very high pressure and a low temperature, e.g., 13 MPa and 248 K, as reported by Yoshimura et al [2]. For decreasing the hydrate-forming pressure and for facilitating the ozone storage at atmospheric pressure, the use of an appropriate *help* guest (such as carbon tetrachloride, xenon and 1,1-dichloro-1-fluo-roethane [3]–[4]) has been considered to be necessary. For practical applications of ozone-containing hydrates, however, the use of a toxic or very expensive substance as the help guest should be avoided. On the other hand, the hydrates can be desirably formed at moderate pressures and preserved at a moderately cooled atmospheric-pressure condition. In order to satisfy these requirements, Nakajima et al. [5] selected carbon dioxide (CO_2) as the help guest, and formed an $O_3 + O_2 + CO_2$ hydrate from an

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$O_3 + O_2$ gas mixture (10–12 % in O_3 mole fraction) blended with pure CO_2 in a molar ratio of 1 : 7 at a pressure of 1.9 MPa and a temperature of 0.1 °C. Besides, they showed that the hydrate thus formed and stored in an aerated condition cooled to a temperature of 248 K can preserve ozone at a concentration on the order of 0.1 % (mass basis) for over 20 days. The $O_3 + O_2$ + CO_2 hydrate is expected to be an efficient medium for storing and transporting ozone for use in various industrial and consumer applications.

It is necessary to demonstrate the phase-equilibrium conditions relevant to these hydrates for the industrial generation of ozone-containing hydrates. Muromachi et al. [6] performed the first three-phase (gas + liquid + hydrate) equilibrium measurements for $O_3 + O_2 + CO_2 + H_2O$ systems. These data cover the temperature range from 272 K to 279 K, corresponding to pressures up to 4 MPa, for each of the (O_3 + O_2)-to-CO_2 or O_2-to-CO_2 molar ratios in the gas phase, which are approximately 1 : 9, 2 : 8, and 3 : 7, respectively. The mole fraction of ozone in the gas phase of the $O_3 + O_2 + CO_2 + H_2O$ system was from ~0.004 to ~0.02. By increasing in $O_3 + O_2$ fraction or decreasing in CO_2 fraction, in the hydrate, it will be expected to increase the concentration of ozone. Therefore, in this study, we performed the mesurements of the three-phase equilibrium pressure *versus* temperature data for a ($O_3 + O_2$ + $CO_2 + H_2O$) system at a higher ozone fraction in the gas phase exceeding the range covered by the preceding study. Considering the possible advantage of using liquid water over using ice in industrial hydrate-forming operations, we selected a temperature range above 272 K and pressures less than 4 MPa for our three-phase equilibrium measurements. According to the Gibbs phase rule, the number of intensive properties in our three-phase four-component system is three. Therefore, the equilibrium pressure at a given temperature can be determined when two of the four mole fractions (i.e., the mole fractions of O_3, O_2, CO_2 and H_2O) in the gas phase are specified. The molar ratios of ($O_3 + O_2$)-to-CO_2 or O_2-to-CO_2 in the gas phase, are approximately 4 : 6, 5 : 5, respectively. These data will be the basis for the formation of the hydrate containing highest-concentration of ozone as high as 1 mass % by using a commercial ozone generator.

II. EXPERIMENTAL

A. Materials

The raw materials used in the present experiments were deionized and distilled water, carbon dioxide having a certified purity of 0.99995 in mole fraction (Japan Fine Products Corp., Kawasaki, Kanagawa Prefecture, Japan) and oxygen having a certified purity of 0.999 in mole fraction (Japan Fine Products Corp., Kawasaki, Kanagawa Prefecture, Japan). The oxygengas was used as received from the supplier to generate ozone with the aid of an ozone generator.

B. Apparatus

The experimental apparatus used in this study is schematically illustrated in Fig. 1 This apparatus was modified from that used in our preceding study [6]. Because of the reactivity and
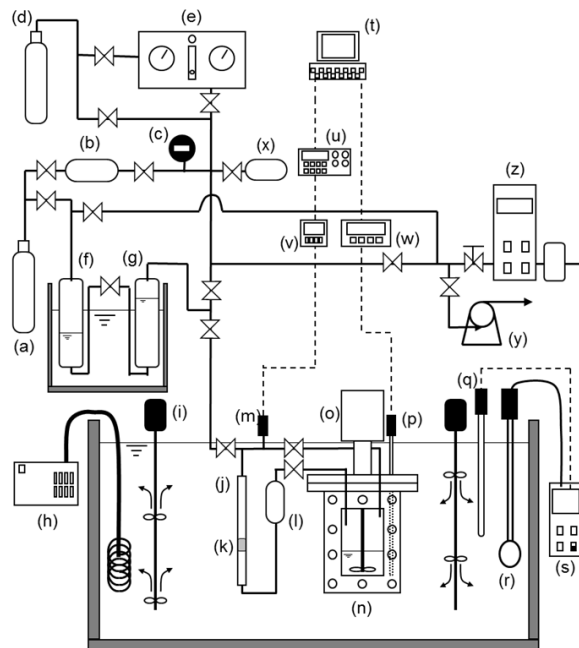

Fig. 1 Schematic of experimental setup for the phase-equilibrium measurements. This setup consists of (a) a carbon dioxide cylinder, (b) a carbon dioxide buffer reservoir, (c) a pressure gauge, (d) an oxygen cylinder, (e) an ozone generator, (f), (g) (h)a immersion cooler, (i) a stirring motor, (j) a 3/4 inch tube, (k) a Teflon-coated magnet cylinder, (l) a gas-sample reservoir, (m) a pressure sensor, (n) a hydrate-forming cell, (o) a stirrer, (p) a Pt-wire resistance thermometer, (q) a Pt-wire resistance thermometer, (r) a heater, (s) a PID-controlled heater, (t) a personal computer, (u) a digital voltmeter, (v) a volt amplifier, (w) a resistance-measuring bridge, (x) a gas-sample holder, (y) an exhaust pump, and (z) an ozone monitor

oxidativeness of ozone, the materials to be in contact with an ozone-containing gas were limited to stainless steel, borosilicate glass and Teflon. Hydrates were formed in a test cell (n), which was a cylindrical stainless-steel chamber, 35 mm ID and 120 mm height. Placed on the top lid of the cell was a stirrer (o). The cell had a 6-mm diameter cavity drilled in its sidewall. We newly assembled a gas-mixing loop which was composed of the test cell (n), a gas displacer made of a 3/4-inch stainless-steel cylinder (j) and a Teflon-coated magnet cylinder (k), and a gas-sample reservoir (l). This loop having an internal volume of ~190 cm^3 provided a continuous space. The Teflon-coated magnet cylinder (k) of the displacer could be reciprocated with the aid of a motor-driven crank mechanism. The major portion of the apparatus was immersed in a temperature-controlled bath equipped with an immersion cooler (h), a PID-controlled heater (r) and two alternate-flow stirrers (i). The pressure and temperature were measured by a strain-gauge pressure transducer (m) (PHB-A-10MP, Kyowa Electronic Instruments Co., Ltd., Tokyo, Japan) and a platinum-wire resistance thermometer (p) (NHRS1-0, Chino, Inc., Tokyo, Japan) connected to a measuring-resistance bridge (w), respectively. The obtained pressure and temperature data were collected by a personal computer (t). Gaseous ozone was generated by an ozone generator (e) (ED-OG-R4DA,

EcoDesign, Co., Ltd., Saitama Prefecture, Japan) using a continuous supply of oxygen gas from a high-pressure cylinder (d). This generator could provide an O_3 gas up to 0.3 MPa. For measurements at higher system pressures, we prepared a twin-cylinder gas pressurizer (f, g). For measuring the ozone fraction in each ozone-containing gas sample, we used an ultraviolet-absorptiometric ozone monitor (z) (Ebara Jitsugyo Co., Ltd., Tokyo, Japan) that allowed us to determine the ozone fraction up to 0.089 with an uncertainty of ±0.001 on a molar basis. The assembly for supplying carbon dioxide consisted of a high-pressure cylinder (a), a stop valve, a stainless-steel buffer reservoir ~300 cm^3 in volume (b), and a pressure gauge (c). For obtaining a gas sample for the purpose of determining the composition of the gas phase inside the test cell, the two valves through which the test cell was connected to the residual part of the gas-mixing loop were closed such that the gas in the latter part was separated from the aqueous solution and the hydrate left inside the test cell. The gas contained in the latter part, which was considered to be equal in composition to the gas phase inside the test cell, was then discharged to a gas-sample holder (x). A gas chromatograph (GC-3000A, Agilent Technologies Japan, Ltd., Tokyo, Japan) was used for determining the ratio of oxygen to carbon dioxide in the sample after the completion of the ozone-to-oxygen reaction in it. The expanded uncertainties in this study were estimated to be ±0.11 K for the temperature, ±6.0 kPa for the pressure and ±0.0015 for the mole fraction of each species in the sampled gas with a 95 % coverage.

C. The Principle of Phase−Equilibrium Measurement Method

We obtained the three-phase (gas + liquid + hydrate) equilibrium pressure *versus* temperature data for a (O_3 + O_2 + CO_2 + H_2O) systems and, for comparison, corresponding data for a (O_2 + CO_2 + H_2O) systems. For the O_2 + CO_2 + H_2O system, we applied the conventional temperature-search method [7]. In case of the conventional temperature-search method widely applied to hydrate-forming systems, the system temperature is stepwise increased at intervals long enough to thermodynamically equilibrate the system at each step until the hydrate having been coexisting with the aqueous and gas phases disappears.

If this method was applied to an ozone-containing system, the ozone decomposition would substantially progress during such intervals. Therefore, Muromachi et al. [6] recently developed a new phase-equilibrium measurement technique, a modified pressure-search method. Fig. 2 shows a conceptual illustration of the pressure change during each pressure-search process under a constant temperature. First we explain the variation of the system pressure illustrated as the solid line in the Fig. 2. After we supplied the mixture of gases to the hydrate-forming cell, the hydrate nucleation occurred, thereby resulting in a decrease in the system pressure. Simultaneously with this process, the partial pressure of ozone in the gas phase continues to decrease. As the partial pressure of ozone in the gas phase falls below the phase equilibrium condition and the
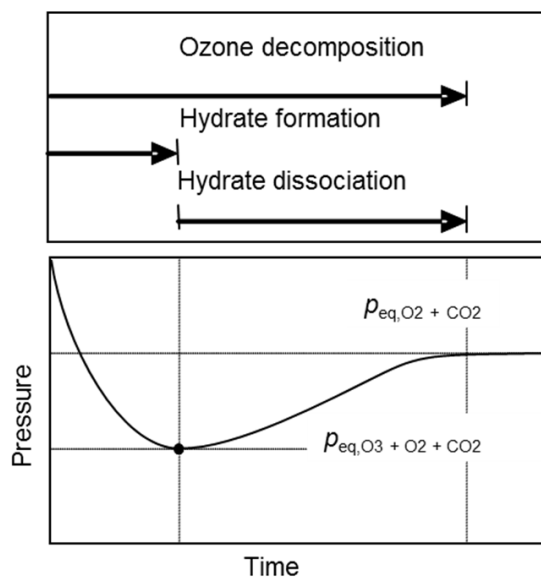

Fig. 2 Conceptual illustration of the thermodynamic-state evolution inside the test cell during the relaxation period subsequent to a gas-charging operation; the three rate processes that simultaneously or alternatively progress in the test cell during the relaxation period subsequent to a gas-charging operation (upper diagram) and the evolution of the system pressure and the three-phase equilibrium pressure corresponding to the instantaneous gas-phase composition inside the test cell (lower diagram). Illustrated is the case when the pressure p exhibits both a maximum and minimum during the relaxation period

hydrate formation ceases, the system pressure levels off only for a moment. Subsequently, the system pressure starts to increase as the result of the decomposition of ozone in the gas phase and of the partial hydrate-dissociation. These reactions result in a gradual increase in the system pressure until the ozone in the system has entirely decomposed to oxygen. Finally, the system pressure asymptotically approaches a constant value. Now we explain the variation of the equilibrium pressure, illustrated as the dotted line in the Fig. 2, corresponding to the ozone concentration in the gas phase. Because of the decomposition of ozone, the equilibrium pressure is expected to rise with time. This is because, owing to their molecular size, ozone may form a hydrate at a lower pressure than oxygen at a given temperature. Thus, we can expect that the equilibrium pressure for a (O_3 + O_2 + CO_2 + H_2O) systems is lower than that of a (O_2 + CO_2 + H_2O) systems. Since the system pressure always tends to approach the phase equilibrium condition, it is the only point, where the decrease and increase of the system pressure change, that the system pressure is equal to the equilibrium pressure of the ozone-containing hydrates. Thus, we determine that the minimum of the system pressure at this point represents the equilibrium.

D. Measurement Procedures

For the O_2 + CO_2 + H_2O system, we applied the conventional temperature-search method. The test cell was first charged with 20 g of liquid water, then immersed in the

temperature-controlled bath. After charging the loop with oxygen gas up to a prescribed pressure, carbon dioxide gas was supplied to the loop until the system pressure increased to a prescribed. The temperature of the loop was then decreased to ~263 K to induce hydrate nucleation inside the test cell. Once the hydrate formation inside the cell was detected during this cooling process, the temperature was increased in steps of 0.1 K. Responding to the stepwise increase in temperature, the pressure also stepwise increased due to the partial dissociation of the hydrate. At each step, the temperature was held constant until the pressure became constant. This process of the stepwise temperature rise was continued until the completion of the hydrate. We determined the pressure–temperature condition recorded during the step beyond which the pressure had leveled off as the three-phase equilibrium condition. After readjusting the system temperature at the level of the equilibrium condition, we then performed the gas-sampling procedure.

The actual procedure of the modified pressure-search method that we applied for the $O_3 + O_2 + CO_2 + H_2O$ system is described below. After charging the test cell with 20 g of liquid water, we removed the gas-mixing loop from the thermostatted bath installed in the experimental setup and immersed it into a separate cooling bath temperature-controlled at 263 K. Once we visually confirmed the ice formation in the bulk of the liquid pool inside the test cell, we moved the gas-mixing loop back to the former bath, which was controlled to a temperature at or above 272 K, and reconnected it to the setup. The gas-mixing loop was then charged with the $O_3 + O_2$ gas-mixture in the amount equal (on a molar basis) to that of the pure O_2 gas supplied to the test cell in the corresponding experiment for the $O_2 + CO_2 + H_2O$ system. Then, the smaller gas-pressurizing chamber and the test cell were charged with this mixture up to a pressure of 0.3 MPa. O_2 gas from the high-pressure cylinder was then injected into the larger gas-pressurizing chamber to pressurize the water stored in the smaller chamber, until the pressure inside the gas-mixing chamber increased to the prescribed level. Subsequently, the loop was charged with CO_2 gas until the system pressure increased to the level equal to the equilibrium pressure determined in the corresponding experiment for the $O_2 + CO_2 + H_2O$ system performed at the same temperature. We performed both the temperature monitoring and visual observation to confirm the vanishing of the ice phase during the hydrate-phase growth process. For a technical reason, we defined the system conditions at the stage when a minute increase in the system pressure (~3 kPa) from its minimum value was observed as the thermodynamic phase-equilibrium conditions; this is because we could not do the gas sampling just at time of the minimum pressure which we could not predict in advance. The gas-sampling procedure generally followed that we used for $O_2 + CO_2 + H_2O$ system. We discharged the gas in the former section into the gas-sample holder to increase the pressure inside the holder to ~500 kPa. The residual gas in the gas-sampling section was immediately forced to flow into the ozone monitor. The gas-sample holder was then heated to completely decompose the contained ozone to oxygen. The resultant $O_2 + CO_2$ mixture in the holder was subjected to a gas-chromatographic analysis to determine the
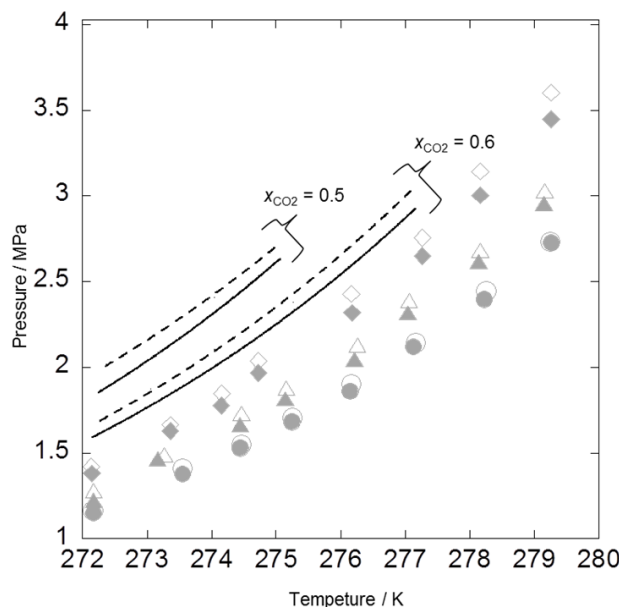
O_2 *versus* CO_2 molar ratio.

Fig. 3 Three-phase equilibrium p–T data for $O_3 + O_2 + CO_2 + H_2O$ system (solid line, ●, ▲, ◆) and $O_2 + CO_2 + H_2O$ system (dotted line, ○, △, ◇). The data points relevant to the five different levels of x_{CO2}, the CO_2 mole fraction in the gas phase, are discriminated by their geometries as follows: circles (●, ○) for $x_{CO2} \approx 0.9$; triangles (▲, △) for $x_{CO2} \approx 0.8$; rhombuses (◆, ◇) for $x_{CO2} \approx 0.7$; and (the upper line) for $x_{CO2} \approx 0.6$; (the lower line) for $x_{CO2} \approx 0.5$. The data for $x_{CO2} \approx 0.6$ and $x_{CO2} \approx 0.5$ were newly obtained in this study. Other data were obtained in our previous study [6]

III. Results and Discussion

We obtained the phase-equilibrium pressure *versus* temperature data for ($O_3 + O_2 + CO_2 + H_2O$) and ($O_2 + CO_2 + H_2O$) systems. These are not only the p and T values, but alsothe relevant values of the mole fractions x of O_3, O_2 and CO_2 in the gas mixture discharged from the gas-sampling. The p–T data that we obtained may be divided into two classes in reference to the nominal value of x_{CO2} (0.6 or 0.5). The p *versus* T conditions indicated by these data sets are lined in Fig. 3. We find that the p–T data points for each group are aligned on asingle smooth curve. The data shows consistent tendencies that, at a given temperature, the equilibrium pressure decreases with an increase in x_{CO2} and that even a small fraction of ozone ($x_{O3} \approx 0.02$). These tendencies is consistent with the results of the previous study in which Muromachi et al. [6] performed phase-equilibrium measurements for the ($O_3 + O_2 + CO_2 + H_2O$) and ($O_2 + CO_2 + H_2O$) systems, for each of the x_{CO2} were 0.9, 0.8, 0.7, respectively.

The three-phase equilibrium pressure *versus* mole fraction of ozone in the gas phase obtained in the system ($O_3 + O_2 + CO_2 + H_2O$) are divided into two classes in reference to the nominal value of x_{CO2} (0.6, 0.5) as depicted in Fig. 4. Here we note that the mole fraction of ozone in the gas phase increases in the higher system pressure and the data obtained in the present
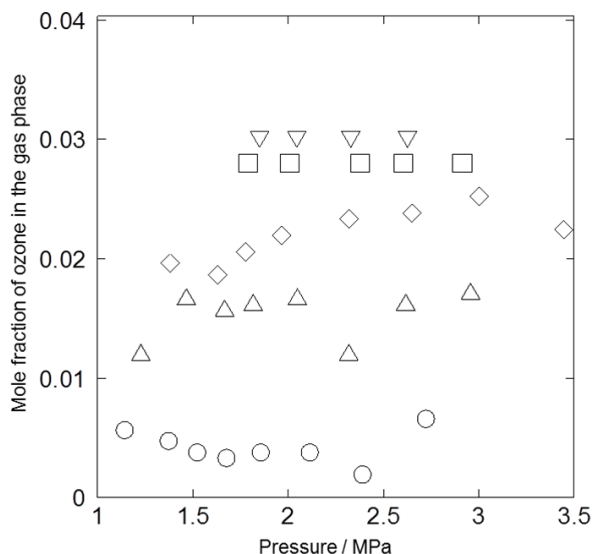
Fig. 4 Three-phase equilibrium pressure *versus* mole fraction of ozone in the gas phase for $O_3 + O_2 + CO_2 + H_2O$ system ($\circ$, $\triangle$, $\diamond$, $\square$, $\triangledown$). The data points relevant to the five different levels of x_{CO2}, the CO_2 mole fraction in the gas phase, are discriminated by their geometries as follows: circle ($\circ$) for $x_{CO2} \approx 0.9$; triangle ($\triangle$) for $x_{CO2} \approx 0.8$; rhombuse ($\diamond$) for $x_{CO2} \approx 0.7$; and square ($\square$) for $x_{CO2} \approx 0.6$; triangle ($\triangledown$) for $x_{CO2} \approx 0.5$. The data for $x_{CO2} \approx 0.6$ and $x_{CO2} \approx 0.5$ were newly obtained in this study. Other data were obtained in our previous study [6]

study shows the highest mole fraction of ozone in the gas phase in Fig. 4. It is generally acknowledged that the concentration of a *guest* substance in a hydrate increases with the increase in the *guest* concentration in the gas phase [8]. Thus, based on the data in Fig. 4, we can expect to form the hydrate containing highest-concentration ozone, yet reported.

ACKNOWLEDGMENT

REFERENCES

[1]   G. McTurk, J.G. Waller, "Ozone–carbon tetrachloride double hydrate" *Nature*, 20, 1964, 1107.
[2]   T. Masaoka, A. Yamamoto, K. Motoi, "Storing method of ozone, method of producing solid material incorporating ozone, food preservation material and food preserving method" *Patent Abstracts of Japan*, Publication 2007–210881, 2007. Released online in Patent and Utility Model Gazette DB of the Japan Patent Office(http://www.ipdl.inpit.go.jp/homepge.ipdl).
[3]   S. Muromachi, R. Ohmura, Y. H. Mori, "Clathrate hydrates for ozonepreservation" *J. Phys. Chem. B*, 114, 2010, 11430–11435.
[4]   S. Muromachi, T. Nakajima, R. Ohmura, Y. H. Mori, "Phase equilibrium for clathrate hydrates formed from an ozone + oxygen gas mixture coexisting with carbon tetrachloride or 1,1-dichloro-1-fluoroethane" *Fluid Phase equilib*, 305, 2011, 145–151.
[5]   T. Nakajima, S. Akatsu, R. Ohmura, S. Takeya, Y. H. Mori, "Molecular storage of ozone in a clathrate hydrate formed from an $O_3 + O_2 + CO_2$ gas" *Angew. Chem. Int. Edit*, 50, 2011, 1–5.
[6]   S. Muromachi, R. Ohmura, Y. H. Mori, "Phase equilibrium for ozone-containing hydrates formed from an (ozone + oxygen) gas mixture coexisting with gaseous carbon dioxide and liquid water" *J Chem Thermodyn*, 49, 2012, 1–6.
[7]   A. Danesh, B. Tohidi, R. W. Burgass, A. C. Todd, "Hydrate equilibrium data of methyl cyclo-pentane with methane or nitrogen" *Chem. Eng. Res. Des*, 72, 1994, 197–200.
[8]   Sloan ED, Koh CA, "Clathrate Hydrates of Natural Gases, 3rd ed. Boca Raton" *CRC Press*, 2008, 271.