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Measurement of CO_2 solubility in pure water and the pressure effect on it in the presence of clathrate hydrate

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Abstract

The solubility of CO_2 in pure water was investigated under high-pressure conditions, from 7 to 12 MPa. Temperature varied between 2.5–20 °C. CO_2 clathrate hydrate formed at temperatures below approximately 10 °C. Saturated concentrations of CO_2 were determined from expanding dissolved gas. The solubility in the presence of the hydrate decreased with decreasing temperature and with decreasing pressure, although some researchers reported it decreased with higher-pressure conditions at about 7 °C. Many other researchers reported that the pressure conditions did not affect the solubility in the presence of the hydrate. Although this is mostly correct, we did confirm a small difference in solubility due to pressure conditions.

Keywords: Carbon dioxide; Solubility; Clathrate hydrate; Pressure effect; Temperature effect; Gas expansion method

1. Introduction

Particular attention of the world is focused on the effects of global warming due to increased concentrations of carbon dioxide (CO_2) in the atmosphere. New energy technologies that will not produce CO_2 are expected in the future. The control and mitigation of the CO_2 concentrations in the atmosphere is a pressing need. CO_2 sequestration is a realistic option that addresses this problem.

The sequestration of CO_2 into the ocean, first proposed by Marchetti [1], has been recognized as an effective and practical mitigation strategy for CO_2 disposal. The oceans have a large capacity for keeping an enormous amount of CO_2 away from the atmosphere. Recently, many specific strategies have been proposed. For example, the Japanese organization, the Research Institute of Innovative Technology for the Earth (RITE) proposes one scheme, i.e., dilution of multiple droplets at mid-depth in the ocean using a moving ship. The National Maritime Research Institute in Japan proposes the COSMOS system, in which a large CO_2 droplet with a hydrate is kept at the sea-bottom, released at a depth of about 800 m.

Several on-site experiments for CO_2 sequestration into the ocean were performed to observe the dissolution behavior of liquid CO_2 droplets in seawater. Droplets were injected into the ocean at a depth of about

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800 m. Many other experiments have been performed in laboratories in quiescent pools or streams of water at high-pressure conditions (5–40 MPa), e.g., Hirai et al. [2] and Aya et al. [3]. Every experiment has shown that the liquid CO_2 droplet is covered with a film of clathrate hydrate in lower temperature conditions (<10 °C).

Geological CO_2 sequestration into deep aquifers is also important. The technical feasibility was demonstrated at the Sleipner gas field in the North Sea, where 1×10^9 kg of CO_2 have been injected annually into sands saturated with saline water at depths below 800 m. If CO_2 is injected into an aquifer just below the seafloor, the temperature is low enough for the hydrate to form.

To achieve CO_2 sequestration with minimal environmental impact and with public support, understanding the properties of CO_2 dissolution with hydrates is essential. The clathrate hydrate is a non-stoichiometric crystalline compound. Guest molecules of suitable size are caged inside bonding water molecules without chemical reactions. Sloan [4] provided a detailed summary of hydrate characteristics. Englezos et al. [5] also discussed details about hydrate formation.

Hirai et al. [2] and Someya et al. [6] estimated the CO_2 solubility with hydrates from the dissolution velocity of a CO_2 droplet. Aya et al. [3] measured the CO_2 solubility from the gas volume which expanded from the CO_2 saturated solution. These experiments also clarified qualitatively the effects of the pressure, the temperature and the salinity on the solubility with or without the hydrate. Teng et al. [7], and Teng and Yamasaki [8], measured the solubility from a volume difference before and after the CO_2 dissolution in a narrow tube, in which water and CO_2 stratified. Without the hydrate formation, their results corresponded with those reported by other researchers. The solubility increased with decreasing the temperature, as first reported by Dodds et al. [9].

Teng et al. [7] and Teng and Yamasaki [8], however, concluded that the solubility with the hydrate also increased with decreasing the temperature, contrary to most other reports. In their experiments, they continuously vibrated a narrow tube for forming the hydrate, as had been done by Ohgaki et al. [10]. Their solubility data seemed to be suspect, as pointed out by Ohmura and Mori [11]. The solubility with the hydrate would decrease with decreasing the temperature as measured by Yang et al. [12] and Servio and Englezos [13]. Theoretical calculation [13] supported this observation.

Yang et al. [12] and Servio and Englezos [13] made good experiments. An ambiguity, however, still exists about the pressure effect on the CO_2 solubility with the hydrate. Yang et al. [12] concluded that the solubility with the hydrate at about 7 °C decreased with increasing the pressure, while Servio and Englezos [13] concluded that the pressure effect was slight.

The aim of the present paper is, therefore, to clarify the pressure effect on the solubility, on the basis of a large number of experiments. Here, the solubility into pure water is only considered, although seawater and underground water are saline water, with different kinds of ions, because the pressure effect seems to be similar in pure water and in saline water, qualitatively.

2. Experiments

The solubility was measured at different temperatures (from 2.5–20.0 °C) and pressures (7, 10, 12 MPa). Fig. 1 shows a schematic of the experimental apparatus used for measuring the CO_2 solubility with and without the hydrate. The main section of the phase equilibrium system was a high-pressure vessel with three circular viewing windows, 20 mm in diameter and made of the sapphire glass. The volume capacity of the high-pressure vessel was about 30 cm^3. The vessel was designed to withstand safely 15 MPa of pressure. The pressure was measured by a pressure gauge (Kyowa, PVK-200KD) with a range of 0–20 MPa and with an accuracy of ±0.3% of the measured value. The measured gauge pressure was calibrated with a precise barometer, with a claimed accuracy of ±0.015 KPa (Tokyo Suzuki Seisakusyo, K.S.F model T60). The safety valve was set on, to work at 12 MPa.

Mixing the contents in the vessel was accomplished using a magnetic stirrer, which was coupled with a set of rotating magnets placed underneath the vessel. The magnets were driven by an electric motor with rpm control. The temperature in the high-pressure vessel was measured at two different positions by platinum (Pt100) resistance bulb thermometers of 1.6 mm in diameter, with an accuracy of ±0.05 K. All temperature sensors were calibrated with a standard thermometer certified by the Meteorology Institute of Japan. A nitrogen gas bomb, a vacuum pump, and two high-pressure pumps for supplying water and CO_2, were connected to the high-pressure vessel via two gas reservoirs, as

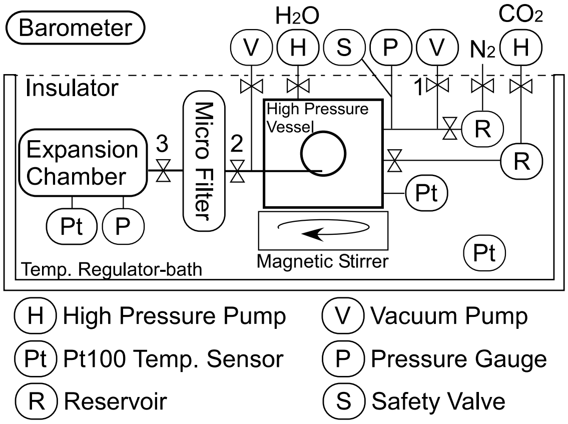

Fig. 1. Schematic diagram of the experimental apparatus.

shown in Fig. 1. The vacuum pump was used for degassing the distilled water and for deaerating the whole assembly. The whole assembly mentioned above, which was made of 316 stainless steel, was immersed in an insulated temperature regulator bath.

When a small amount of CO_2 solution was sampled from the high-pressure vessel for determining the CO_2 solubility, the sampled solution should not contain any hydrate crystals. A micro-filter of a sintered metal (Nupro, SS-2F-05) was used to separate the solution from the hydrate. The high-pressure filter assembly, which had a void size of 0.5 μm, could withstand 20.6 MPa of pressure. It functioned as a hydrate separator without flashing the dissolved CO_2 gas.

The whole experimental assembly was first evacuated to a pressure below 100 Pa, and then all valves were closed. The high-pressure vessel was filled with distilled water. CO_2 was supplied into the high-pressure vessel until the desired pressure was obtained. The system was maintained at the desired temperature for more than 36 h. When no pressure change was detected for more than 18 h, the condition was considered to be at equilibrium.

Then, valve 1 was opened to introduce nitrogen gas at the same pressure condition, to keep the pressure of the vessel constant during the sampling procedure. Then, valve 2 was immediately opened and a sample of the solution passed through the micro-filter to ensure that all hydrate crystals was separated from the aqueous solution. Valve 3 was then opened and the sample was collected in the evacuated expansion chamber, which could be removed from the system after it had been filled, by flashing the CO_2 solution into the chamber until the pressure reached approximately 0.1 MPa. The small amount of nitrogen gas, which was pumped in for pressurization, did not dissolve into the solution in the high-pressure vessel because the volume of added nitrogen gas was less than that in the tube from the N_2 reservoir to the vessel, and the time for the sampling procedure was only a few seconds. Expanding of the dissolved CO_2 never occurred in the high-pressure vessel because the pressure remained nearly constant during the extraction procedure. Therefore, the solution flowed into the chamber, keeping the relative amount of CO_2 and solution constant.

After sampling the CO_2 solution, the expansion chamber was disconnected from valve 3 and was cooled to 0.0 °C in another temperature regulator bath. The temperature in the chamber was monitored by a platinum resistance bulb thermometer and the pressure was monitored by a precise pressure gauge (Keyence Inc., AP-V41 with AP-44), with a range of ±101.3 KPa and an accuracy of ±0.041 KPa. Finally, when no pressure changes and no temperature changes were detected, the pressure, the temperature and the mass of the chamber were measured. An increase in the weight of the expansion chamber was measured using an analytical balance (Mettler Toledo Inc., AX504), with a claimed repeatability of 0.1 mg. The whole assembly of the evacuated expansion chamber weighs approximately 300 g including the thermometer, the pressure gauge and the valve. The volume capacity of the expansion chamber, made of aluminum, was 115.11 cm^3. The sampling procedure was carried out three times in parallel, i.e., three sets of expansion chambers were used. Only when the calculated solubility for each of the three samples was within ±0.00015 of mole fraction, their average was considered to be correct at the required *PT* condition.

The solubility was calculated as same as Bando et al., [14] did. The mass, W, of the saturated CO_2 solution in the expansion chamber can be expressed by Eq. (1). Here, M is the molecular weight, n is the amount of substance and the subscripts c and w correspond to CO_2 and water, respectively. Although most of the CO_2 in the expansion chamber was in the gas phase, the gas partially dissolved in the solution. The solubility of CO_2 in the solution can be estimated by Eqs. (2)–(6). Here, f_c is the fugacity of CO_2 at T_0 K (≈273.15 K) and P_m condition. T_0 and P_m are the measured temperature and the pressure in the expansion chamber. P_w is the vapor pressure of water at T_0 K. φ_c is the fugacity coefficient, which can be regarded as unity at low pressure. V_g is the volume of the gas phase in the expansion chamber, and V_0 is the volume of the expansion chamber itself. ρ_l is the density of the water at T_0 K. H is Henry's coefficient at T_0 K, R is the gas constant. Finally, the mole fraction of CO_2 in the solution, x_c, can be calculated.

$$W = n_c M_c + n_w M_w \tag{1}$$

$$f_c = \varphi_c P_c = \varphi_c (P_m - P_w) \approx (P_m - P_w) \tag{2}$$

$$V_g = V_0 - \frac{n_w M_w}{\rho_l} \tag{3}$$

$$n_c = \frac{f_c V_g}{R T_0} + n_w \frac{f_c}{H} \tag{4}$$

$$n_w = \frac{W - M_c \frac{P_c V_0}{R T_0}}{M_c \frac{P_c}{H} + M_w \left(1 - \frac{M_c P_c}{\rho_l R T_0}\right)} \tag{5}$$

$$x_c = n_c / (n_c + n_w) \tag{6}$$

3. Results

Fig. 2 shows the measured solubility, x_c, at 7, 10 and 12 MPa and at 9–20 °C. Some previously measured data [7,9] are also shown in Fig. 2.

Maximum value of the error, the accuracy for each x_c, was 2.5×10^{-5} of the mole fraction, estimated by

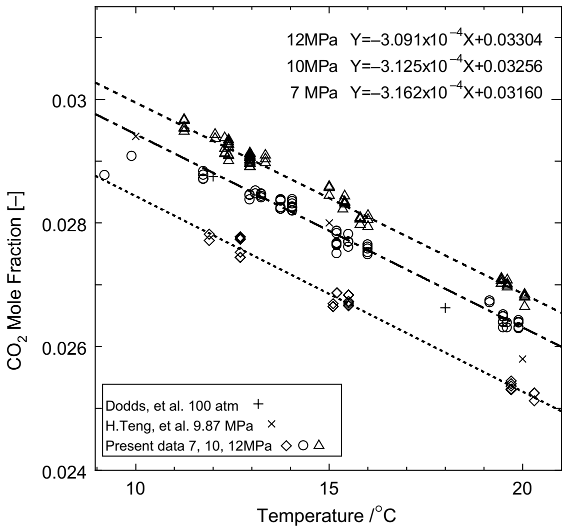

Fig. 2. The solubility of CO_2 into pure water at 9–21 °C.

the standard technique reported by the American Society of Mechanical Engineers [15]. The accuracy of each x_c was derived from the errors in P_m, W, T_0, V_0 and the measured atmospheric pressure for the calibration of the pressure gauge. This value was smaller than the repeatability errors (less than ±0.00015 of the mole fraction) at nearly equal PT conditions, although it was difficult to make experiments at exactly same temperature conditions due to the different room-temperatures at each measurement. The repeatability errors in Fig. 2 are smaller than the dispersion of other researchers' data [7,9], and our results seem to be consistent.

The solid lines in Fig. 2 were calculated using the least square method. The variance of the least square method for each line was less than 1.0×10^{-4} and the correlation coefficient was 0.993–0.994. This means the solid lines are well fitted and represent the solubility accurately enough.

As shown in Fig. 2, the measured solubility decreased at temperatures less than approximately 10 °C, due to the formation of the clathrate hydrate. In almost all experiments at low temperature conditions with the hydrate, the CO_2 solution under equilibrium conditions appeared as shown in Fig. 3a, i.e., the hydrate looked like frost.

In contrast, the calculated solubility became high when the solution with the hydrate appeared as shown in Fig. 3b or c. As soon as the first sampling procedure was complete, the features of the solution changed to those seen in Fig. 3a and the PT conditions also changed. This behavior means that the PT condition was not in equilibrium although the state was maintained for 18 h. Fig. 3b and c show that the liquid CO_2 was still inside of the hydrate film and the situation was similar to that reported by Teng et al. [7]. Therefore, the higher solubility at lower temperatures should be neglected. The results by Teng et al. [7] seemed not to show the solubility correctly, as had been pointed out by Ohmura and Mori [11].

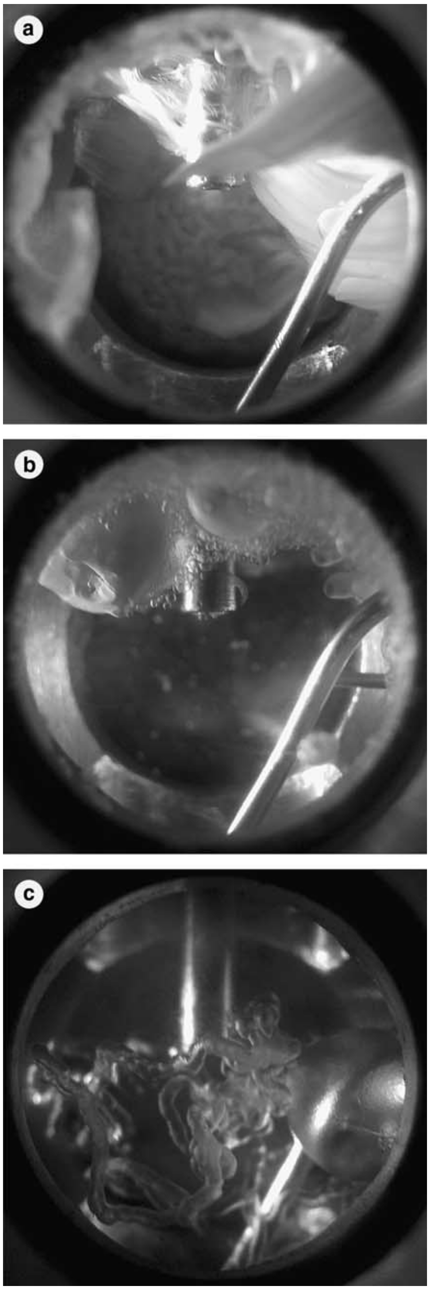

Fig. 3. Pictures of the clathrate hydrate features under equilibrium conditions (a) and under quasi-equilibrium condition (b) and (c).

Fig. 4 shows the measured solubility at 7, 10 and 12 MPa and at 2.5–10 °C, with previously reported data [12,13]. Fig. 4 also shows the results at 7.0 °C and 4 MPa.

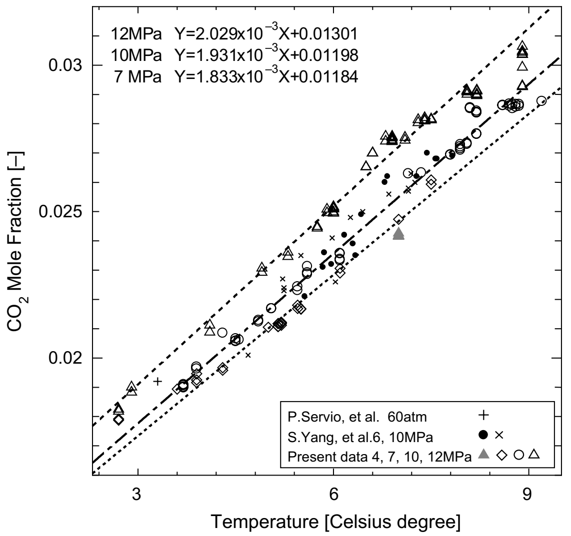

Fig. 4. The solubility of CO_2 into pure water with clathrate hydrate formation at 0–10 °C.

Yang et al. [12] explained theoretically that solubility at 7.0 °C decreased with increasing the pressure, while the few supporting experimental results were not accurate. Servio and Englezos [13] indicated that the effect of pressure on solubility was not strong. However, they did not take issue with Yang et al. [12], because the experimental data [13], shown in Fig. 4, dispersed a little.

Therefore, we tried to investigate this ambiguity in detail and concluded that the solubility was affected not only by the temperature but also by the pressure condition, i.e., the solubility with the hydrate decreased with decreasing temperature and pressure. We believe that there is no ambiguity now about the pressure effect on the CO_2 solubility, although the pressure effect is not clear in our data at temperature conditions below 4 °C.

4. Conclusions

The solubility of CO_2 into pure water with and without the clathrate hydrate formation was investigated accurately at pressure conditions of 7–12 MPa and temperature conditions of 2.5–20 °C. The present study clarified that solubility in the presence of the hydrate universally decreased with decreasing temperature and pressure.

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