Experimental study on solution and diffusion process of single carbon dioxide bubble in seawater

Qiusheng LIU*, Hirohiko ENDO*, Katsuya FUKUDA*, Makoto SHIBAHARA* and Peng ZHANG**
* Graduate School of Maritime Sciences, Kobe University
5-1-1, Fukae Minamimachi, Higashinada, Kobe 658-0022, Japan
E-mail: qsiiu@maritime.kobe-u.ac.jp
** Institute of Refrigeration and Cryogenics,
Shanghai Jiao Tong University, Shanghai 200240, China

Received 2 May 2016

Abstract
Solution and diffusion process of carbon dioxide (CO₂) in seawater is important in the research and development of CO₂ ocean sequestration technology to mitigate global warming. In this study, solution and diffusion process of single CO₂ bubble in seawater and pure water were experimentally studied under various pressures and temperatures to evaluate the transport process of CO₂ in seawater. The solution process was conducted in a test vessel. CO₂ bubble was generated by a CO₂ bubble generator installed at the bottom of the vessel. The diameter of CO₂ bubble was recorded using a high speed video camera. The pressure and temperature of liquids were measured by using a pressure transducer and thermocouples. Experimental conditions for the temperature ranged from 277 K to 297 K, and the pressure ranged from around 101 kPa up to 400 kPa. It was obtained that the complete solution time decreases with the increase in pressure due to its higher solubility at a higher pressure. It decreases with an increase in temperature arising from a higher diffusivity at a high temperature. It was clarified that the complete solution time for CO₂ in seawater is longer than that in pure water due to its relatively lower solubility compared with pure water.

Key words : Solution and diffusion process, Carbon dioxide, Bubble, Seawater, Solution time, Solubility, Diffusion coefficient

1. Introduction

Every year more than 27 billion tons of carbon dioxide (CO₂) is emitted from the industrial works and power plants, and disposed into the atmosphere due to the consumption of fossil fuel by human beings. The increasing concentration of carbon dioxide in the atmosphere is one of the causes of greenhouse effect. In order to control the concentration of CO₂ in the atmosphere, technologies such as effective use of fossil fuel and conversion to clean energy are important. On the other hand, the technology of recovering the emitted CO₂ and isolating from the atmosphere is also considered to be effective (Aya et al.,2000).

There are several isolating methods: one is utilization of ocean, the others are utilization of underground such as aquifer, drilled gas filed and drilled oil field. CO₂ ocean sequestration technology is considered to be promising due to its larger capacity compared with CCS (CO₂ capture and storage) through underground (Bergman, 2000). Figure 1 illustrates the CO₂ ocean sequestration technology (Liu et al., 2011). As shown in Fig.1, after separating and collecting the CO₂ gas produced from thermal power plant by the chemistry absorbing method or the physical adsorbing method, it then can be disposed into the ocean. One of the methods is to put carbon dioxide directly into the deep sea, and it is stored in the ocean by dissolving in it. It is considered that the carbon dioxide gas supplied to the deep sea is isolated from the atmosphere over about 1000 years. In order to absorb and dispose the CO₂ in the ocean, it is required to dissolve it into seawater, and it is necessary to investigate the solubility of CO₂ in seawater at various pressures and temperatures. Furthermore, in order to analyze global-scale circulation of CO₂ gas, the detailed fundamental data of solubility and diffusion coefficient are required.
Many researches (Uematsu et al., 1983, Maruzen, 2004) were reported about the solubility of the CO$_2$ gas in pure water. However, the data of the solubility in seawater is seldom reported and not completely understood. Stewart and Munjal (1970) reported their results of solubility of CO$_2$ in distilled water, artificial seawater in the temperature ranged from –5 °C to 25 °C under the pressures ranged from 10 to 45 atm. The solubility decreased with an increase in salt concentration in seawater. However, the temperature is limited and the correlation for solubility was not obtained. Weiss (1974) obtained the solubility at the temperatures ranged from -1 °C to 40 °C, the effect of pressure was not reported. Nighswander et al. (1989) obtained the experimental data of solubility for CO$_2$ in water and 1wt% NaCl solution. However, the data for general seawater was not reported.

Liu et al. (2011) measured the solubilities of CO$_2$ in seawater and synthetic seawater by a change in pressure due to absorption at temperatures ranged from 277 K to 333 K near atmospheric pressures, and ranged from 277 K to 298 K at pressures of 1 MPa, 2 MPa, and 3 MPa. They obtained that the solubilities of CO$_2$ increase with an increase in pressure, but decrease with an increase in temperature. The solubility of CO$_2$ in synthetic seawater decreases with an increase in salt concentration. An empirical correlation for solubility of CO$_2$ in seawater at various temperatures and pressures was obtained based on the experimental data. In the theoretical analysis for the solution of single CO$_2$ bubble in seawater, Liu et al. (2011) assumed a simple model that the single CO$_2$ bubble was stationary and surrounded by infinite liquid seawater. They reported that the rate of solution of bubble in liquid is affected strongly by various parameters, such as solubility, diffusion coefficient, bubble radius, and temperature. However, there are not sufficient experimental data to validate the analytical solutions.

In this study, to clarify the solution process of single CO$_2$ bubble in seawater, the solution and diffusion processes in pure water and seawater were experimentally studied under various pressures, temperatures, and initial bubble diameters. The experimental data for bubble diameter and solution time were measured. The effects of temperature, pressure, and initial bubble diameter on the complete solution time were clarified.

![Fig.1 CO$_2$ ocean sequestration technology (Liu et al., 2011).](image)

**Nomenclature**

- $D$: diameter of CO$_2$ bubble [mm]
- $D_0$: initial diameter of CO$_2$ bubble [mm]
- $D_{if}$: diffusion coefficient [$m^2/s$]
- $H$: Henry’s law constant [Pa]
- $P$: pressure [Pa]
- $P_{CO2}$: partial pressure of CO$_2$ [Pa]
- $T$: temperature [K]
- $t$: time [s]
- $\alpha$: constant in Eq.(2)
- $\beta$: constant in Eq.(2)
- $\eta$: viscosity of seawater [Pa·s]
2. Solubility and diffusivity of CO₂ in seawater

In this study, synthetic seawater with 3.5% concentration of sodium chloride (NaCl) was used. The dissolution theory for gas in liquid is fundamentally based on Henry’s law. It states that at a constant temperature, the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid. For CO₂ gas in seawater, the equation can be expressed as follows,

\[ x_{CO_2} = \frac{P_{CO_2}}{H} \]  

(1)

Where, \( x_{CO_2} \) is the solubility of CO₂ gas, \( P_{CO_2} \) is the partial pressure of CO₂, and \( H \) is a constant with the dimension of pressure. The constant, known as the Henry's law constant, depends on the solute, the solvent and the temperature (Houghton et al., 1962). The Henry’s law constant is also dependent on the pressure at higher pressures as reported by Liu et al. (2011).

Diffusion is the net movement of a substance such as an atom, ion or molecule, from a region of high concentration to a region of low concentration (Greet et al., 1988). This is also referred to as the movement of a substance along a concentration gradient. Diffusion coefficient, \( D_f \), for CO₂ in seawater can be obtained by the following equation (Funazukuri and Nishio, 1995).

\[ D_f = T \alpha \eta^\beta \]  

(2)

Where, \( T \) is temperature with the degree of Kelvin, \( \eta \) is viscosity of seawater, \( \alpha \) and \( \beta \) are constant values given by 1.013 \times 10^{-14} \text{ and } -0.9222, \text{ respectively (Funazukuri and Nishio, 1995).}

3. Experimental apparatus and method

3.1 Experimental apparatus

The solution and diffusion processes of CO₂ bubble in pure water and seawater (3.5% NaCl solution) were conducted in a pressure vessel. Figure 2 shows the pressure vessel for the measurement of CO₂ bubble solution in seawater. It is designed similar to a previous apparatus (Liu et al., 1996, Liu, 1998). It consisted of a solution container (pressure vessel), a test section (stainless block), a CO₂ bubble generator, and an agitator. The pressure vessel was the same with that used in the measurement of solubilities (Liu et al., 2011). The pressure vessel was made of stainless steel with a diameter of 60 mm, and a height of 190 mm. Pyrex glass windows were installed for the observation, and the measurement of the gas bubble diameter was conducted by a CCD camera. The pressure and temperature were measured by using a pressure transducer and thermocouples. The temperature of the liquid was regulated by a cooling coil installed in the vessel. The temperature was well controlled with a precision of within \( \pm 0.5 \text{ K} \). A CO₂ gas generator was installed at the bottom of the vessel. The CO₂ gas was led to the test section by regulating the pressure difference between the CO₂ gas generator and the test section within several kilopascals. The introduction of CO₂ gas into test section was conducted using a magnetic coil and an iron rod with a rubber at the end of it.

A stainless steel foil was installed on the upper of CO₂ gas generator. At the center part of the foil, a small hole with a diameter of 30–50 \( \mu \text{m} \) was made to generate small single bubble. At the end of shaft of the agitator, a stainless block with a diameter of 20 mm was installed. The distance between the downward wall of block and the foil of bubble generator was 10 mm. The generated single bubble was attached to the stainless block wall and kept stationary. It will become smaller with the passage of time and finally disappears as the solution and diffusion process progresses. The diameter of CO₂ bubble was recorded using a CCD camera (K-II, Katokoken) through the observation window. The shutter speed was 5 ms.

Figure 3 shows the overall schematic diagram of the experimental apparatus. There are three main pipelines which are degassing line, pressurizer line and CO₂ line, all are connected to the pressure vessel. As shown in Fig.3, degassing line is connected to the vessel and CO₂ line, and is connected to a vacuum pump. Pressurizer line is connected to the vessel and carbon dioxide line through differential pressure gauge. CO₂ line is connected to the vessel, pressurizer line and degassing line.

[DOI: 10.1299/mej.16-00269] © 2016 The Japan Society of Mechanical Engineers
3.2 Experimental method

The experimental procedure was carried out as follows. First, pure water or seawater was degassed, and the temperature was regulated to a desired level. The pressurization was conducted by nitrogen gas through a pressurizer chamber. CO$_2$ gas was led to test section using CO$_2$ bubble generator. When CO$_2$ was generated and attached to the stainless block surface stationary, then measure the pressure, temperature and record the solution and diffusion process of gas bubble in the test section. The diameter of CO$_2$ gas decreased with the passage of time as the solution and diffusion processes progressed. The data of bubble diameter with the time were obtained using Image-J software.

4. Experimental results and discussion

The measurements of CO$_2$ bubble diameter and the solution time were carried out for various initial diameters ranging from 0.14 mm to 2.4 mm at temperatures ranged from 277 K to 297 K under system pressures ranged from 101 kPa to 400 kPa.

Figure 4 shows a typical recorded photographs of the CO$_2$ bubble in solution process under 0.4 MPa and 293 K. It shows that the bubble diameter decreases with the passage of time, and disappears finally due to the solution and diffusion process of CO$_2$ in seawater. Figure 5 shows calibration method for measurement of the diameter of CO$_2$.
bubble. A screw with a diameter of 3.9 mm was installed on the generator.

![CO₂ bubble diameter with the passage of time.](image)

**Fig. 4 CO₂ bubble diameter with the passage of time.**

![Diameter measurement of CO₂ bubble.](image)

**Fig. 5 Diameter measurement of CO₂ bubble.**

![CO₂ bubble solution process in pure water at 278 K.](image)

**Fig. 6 CO₂ bubble solution process in pure water at 278 K.**

Figure 6 shows typical experimental data of CO₂ bubble diameter versus time at a pressure of 401.9 kPa and a temperature of 278 K. The initial diameter of bubble was 1.5 mm. The solvent is pure water. As shown in this figure, the solution process can be divided into three regions: the bubble decreases rapidly at first, then decreases slowly at the intermediate region (100~1600 s), and finally, it shows again rapid decrease before it disappears into the water. Hereafter results and discussions are focused on the effects of pressure, temperature, and initial diameter on the solution process.

### 4.1 Effect of the pressure

Figure 7 indicates CO₂ bubble diameter versus time at various pressures. The temperature was around 277 K, and the initial diameter was near 0.507 mm. It can be seen from the figure that the higher the pressure is, the shorter the
complete solution time becomes. This is because that the solubilities are higher for higher pressures as reported by authors in a previous work (Liu et al., 2011). According to Eq.(1), the solubility is proportional to the pressure of the gas. When the pressure increases, the concentration of dissolved CO$_2$ at the gas-liquid interface increases. Therefore, the time for the bubble to completely dissolve in seawater decreases. The same dependence of complete solution time on pressure can be found at the initial diameter of 0.15 mm as well.

Figure 8 shows experimental results for single CO$_2$ bubble solution in pure water at various pressures. The experimental data were indicated by non-dimensional diameter. The non-dimensional diameter is the diameter, $D$, divided by initial diameter, $D_0$. The initial diameter of bubble was 1.5 mm. The temperature was 278 K. They show the same dependence of complete solution time on pressure: the solution time is shorter for a higher pressure.

4.2 Effect of the temperature

Figure 9 shows CO$_2$ bubble diameter versus time at various temperatures. The initial diameter of bubble was 0.35 mm. As indicated in the figure, the complete solution time decreases as the temperature in the vessel increases. According to Eq.(2), the diffusion coefficient is proportional to the temperature, it increases as the temperature increases. As the diffusion coefficient increases, the rate of mass flux for dissolved CO$_2$ surrounding the bubble increases. As the result, the speed of dissolution becomes to increase. It was verified that the dependence of complete solution time on temperature is the same at the initial diameter of 0.15 mm.

Based on the discussion of Figs. 7 and 9, we can derive that diffusion coefficient affects the complete solution time more than solubility. As reported in previous work (Liu et al., 2011), we know that as the pressure increases, the solubility increases but the solubility decreases as the temperature increases. However, as the temperature increases the diffusion coefficient increases (Funazukuri and Nishio, 1995). Therefore, based on the experimental data, we can
conclude that the diffusion coefficient affects the complete solution time more than the solubility.

![Fig. 9 Diameter of CO₂ bubble at various temperatures.](image)

![Fig. 10 Solution process of CO₂ bubble in seawater and pure water.](image)

We can also derive from these figures that the CO₂ gas dissolved very quickly at the beginning of the dissolution process. Since there was no dissolved CO₂ gas at the beginning of the dissolution process, CO₂ gas dissolved easily and quickly. However, at the intermediate region, it can be seen that the speed of dissolution were almost constant. This is because after some time of dissolution, the concentration of the dissolved CO₂ gas becomes high in the surrounding liquid, thus the solution process is in rate-determining process. At nearly the end of the process, we can see that the gradient of the curve becomes steep again. This is considered that as the CO₂ gas dissolves in the liquid, the pressure of the CO₂ bubble will become higher because of surface tension for a smaller bubble. As a result, the dissolution rate becomes rapid as the bubble reduces to a very small one.

### 4.3 Comparison between seawater and pure water

Figure 10 shows solution process for single bubble of CO₂ in seawater at a constant pressure of 0.4 MPa and a temperature of 293 K. It indicates that the complete solution time taken for the single bubble of CO₂ decreases as the salinity decreases. In other words, CO₂ gas diffuses in pure water easier than the 3.5% NaCl seawater because the differences in the solubility and diffusivity. As shown in authors’ previous paper Liu et al. (2011), the solubility is dependent on the salt concentration. It is lower for a higher salt concentration, then the complete solution time in seawater is longer than that in pure water. On the other hand, as can be obtained by Eq.(2) (Greet et al., 1988, Funazukuri and Nishio, 1995), pure water has a higher diffusion coefficient \((1.72 \times 10^{-9} \text{ m}^2/\text{s})\) than that of seawater \((1.64 \times 10^{-9} \text{ m}^2/\text{s})\), CO₂ gas diffuses and spreads easier in pure water. Therefore, the CO₂ bubble needed a shorter time to dissolve completely in pure water than in seawater.

### 4.4 Effect of the initial diameter

Figure 11 shows solution process for single bubble of CO₂ in seawater at various initial diameters. The pressure is
0.4 MPa and temperature is 277 K. It is understood that the complete solution time is shorter for a smaller initial bubble, and it can be seen that a very small bubble with an initial diameter of 0.141 mm may dissolve rapidly without the intermediate region.

![Graph showing solution process of CO₂ bubble in seawater at various initial diameters.](image)

**Fig. 11** Solution process of CO₂ bubble in seawater at various initial diameters.

### 5. Conclusions

Solution and diffusion processes of CO₂ single bubbles in pure water and seawater were experimentally studied under various pressures, temperatures, and initial diameters. Effects of parameters such as pressure, temperature, salinity and initial diameter of CO₂ bubble were investigated. Their effects were evaluated and discussed using published correlations and data for solubility and diffusivity. Following conclusions were obtained:

1. The complete solution time decreases with the increase in pressure due to its higher solubility at a higher pressure.
2. The complete solution time decreases with an increase in temperature arising from a higher diffusivity at a high temperature.
3. The complete solution time for CO₂ in seawater is longer than that in pure water due to its relatively lower solubility and diffusivity compared with pure water.
4. The rate of solution of bubble in liquid is affected strongly by various parameters, such as solubility, diffusion coefficient, pressure, and especially temperature.
5. For a large bubble, the solution process at the beginning and near end, the rate of dissolution is high. However, at the intermediate region of the process, the rate decreases significantly.

### Acknowledgments

The authors would like to express our deep appreciations to NKKK (Nihon Kaiji Kentei Kyokai) for the grants-in-aid for scientific research awarded to this research.

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