

Mass Transfer Coefficient and Solubility of CO₂ Drops and CO₂ Hydrates under Simulated Deep Ocean Situations

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INTRODUCTION

Nonatmospheric sequestration of carbon dioxide is the subject of great national and international concern (Carbon Sequestration, 1999). Large potential sinks include geologic formations, soils and vegetation, and the deep ocean. In both geologic and oceanic systems the CO₂ is often in contact with water, seawater or brines. Understanding the behavior and fate of CO₂ in aqueous systems is important for developing many of the potential options and for understanding the impacts of seepage or leakage of CO₂ into aqueous environments, such as unintentional release of CO₂ from a sub-oceanic storage reservoir.

The behavior of CO₂ in water and salt water has been addressed in previous work (Aya, et al.1996; Hirai, et al., 1996a, 1996b; Holder et al., 2001; Mori, et al, 1997; Teng, et al., 1996; Radhakrishnan, et al., 2003; Teng, et al., 1998b). An important issue that impacts research in cold aqueous systems under pressure is the possible formation of the ice-like CO₂ hydrate. The hydrate may be beneficial in that it could potentially seal any unintentional releases from sub-oceanic storage reservoirs as the CO₂ migrates through the cold ocean floor sediments. It could also influence the behavior of any CO₂ that enters the ocean environment at depths below about 500 m.

While the research mentioned above has greatly contributed to our understanding of the behavior of CO₂ in aqueous systems, there is still some uncertainty with respect to the rates of dissolution and mass transfer associated with a CO₂ drop in an under-saturated aqueous system and on the impact of hydrate on these processes. At the National Energy Technology Laboratory (NETL) a unique device has been built to study the behavior of CO₂ under simulated free rise or free sinking conditions (Warzinski et al., 2004). This device, the High-Pressure Water Tunnel Facility (HWTF), is currently being used to measure the rates of dissolution of CO₂ drops and the impact of hydrate at various conditions of temperature, pressure, salinity, and dissolved CO₂.

In this paper, the dissolution rates for CO₂ drops obtained in the HWTF are used to determine mass transfer coefficients for CO₂ drop dissolution in seawater both in the absence and presence of hydrate. By varying the background concentrations of dissolved CO₂, the solubility (or metastable solubility) of liquid CO₂ in seawater has also been determined. This is especially useful when hydrate formation occurs on the surface of a liquid CO₂ drop, which can

make the measurement of CO₂ solubility difficult, since the solid phase can be inadvertently mixed and sampled with the aqueous phase. There are limited data on the solubility of CO₂ in seawater (Teng, et al, 1998b; Stewart, et al, 1970) compared to the extensive studies on the solubility of CO₂ in water (Chapoy, et al., 2004; Diamond, et al, 2003; Anderson, 2002; Crovetto, 1991). The present study provides this information under conditions that attempt to simulate the natural behavior of CO₂ as it enters the deep ocean, either through unintentional releases or through an engineered system.

EXPERIMENTAL

The basic operation of the HWTF has been previously described (Warzinski, et al., 2004). It basically consists of a flow loop and visual observation section. It incorporates automated systems for controlling the position of an object (bubble, drop or solid particle) in the viewing windows using a countercurrent flow of water or seawater and for measuring and recording the size, shape and motion of the object. Pressures to 34.5 MPa are possible.

The data reported in this paper were obtained using SFC purity CO₂ and artificial 35-salinity seawater prepared following the recipe given by Millero, 1996.

RESULTS

Solubility and Mass Transfer Coefficients of Liquid CO₂ in Seawater

Figure 1 gives the rate of dissolution of liquid carbon dioxide in seawater at 15 MPa at different temperatures and levels of dissolved CO₂, as determined from observations in the HWTF. Error bars based on the standard deviation of the average are shown if they were larger than the symbol size. Using this data the solubility of CO₂ in seawater and the associated mass transfer coefficient at very high pressure can be determined.

The dissolution behavior of the liquid CO₂ droplet is described by Equation (1).

$$\frac{d(\rho_{co_2}V)}{dt} = -kA(C_s - C) \quad (1)$$

Where, ρ_{co_2} is the molar density of liquid CO₂; V and A are the volume and surface area of a liquid CO₂ droplet, respectively. k is the mass transfer coefficient in the boundary layer between the liquid CO₂ and seawater, or between the outer hydrate layer and seawater if hydrates form. C_s is the interfacial concentration of the CO₂, which is the solubility of CO₂ at the system pressure and temperature. When hydrates are not present, C_s is the two-phase solubility where the CO₂ phase can be either gas or liquid. When hydrates are present, C_s is the CO₂ solubility at three-phase equilibrium (VLH) and will be denoted by C_{sh} . C is the ambient concentration of CO₂ in seawater which is sometimes set at non-zero values in the experiments.

For the purposes of this paper, the equivalent spherical diameters of the drops are used in all calculations. Although drop non-sphericity can be an important factor in drop dissolution, in most experiments it was rather close to unity ($0.7 < E < 1$, where E = height/width). Equation (1) can then be converted into equation (2).

$$\rho_{CO_2} \frac{dR}{dt} = -k(C_s - C) \quad (2)$$

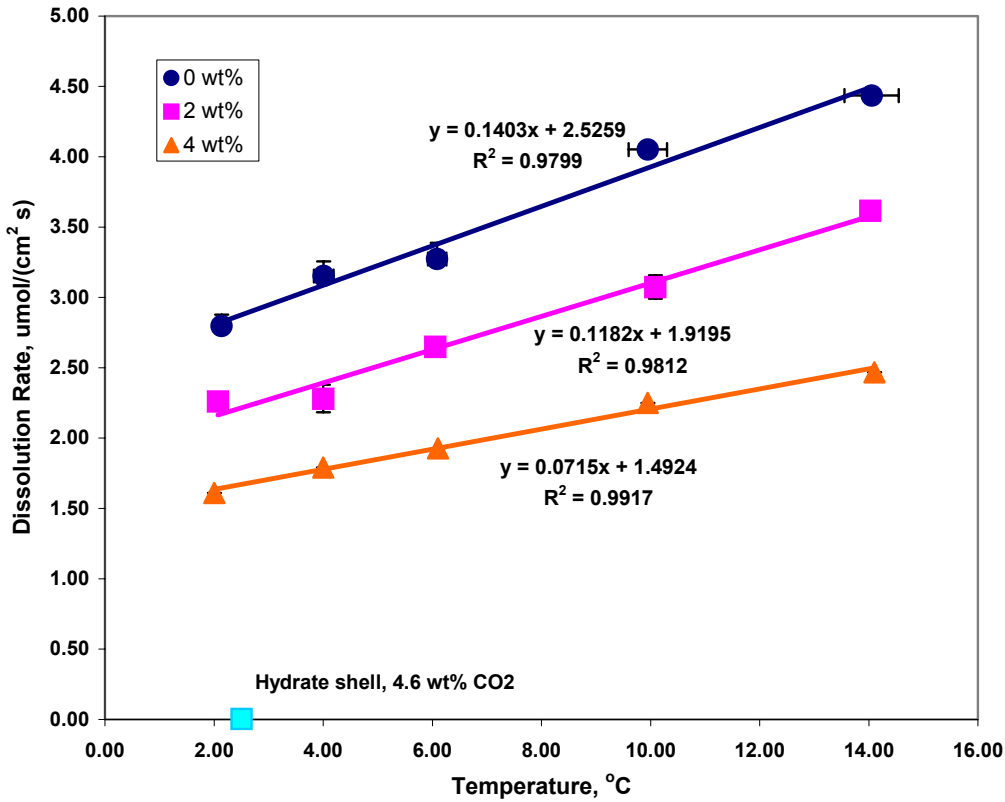


Figure 1. Dissolution rate, $\rho_{CO_2}(dR/dT)$, as a function of temperature at 15 MPa (1500 m depth) in 35 salinity artificial seawater at different levels of dissolved CO_2 . Hydrate-coated drop data collected at 29 MPa.

Hence, the rate of dissolution of a liquid CO_2 droplet can be obtained by measuring its shrinkage rate, dR/dt .

Solubility and Mass Transfer Coefficients of Liquid CO_2 Droplet without a Hydrate Shell

Equation (2) applies whether hydrates are present or not. Hydrate formation does induce a significant change in the rate of the interfacial mass transfer, as subsequent calculations will demonstrate. However, the lower rate of mass transfer is due to the lower solubility of CO_2 , C_{sh} , not to a reduction in the mass transfer coefficient as proposed by Teng, et al., 1998a. At a fixed temperature, the dissolution rate is a function of the ambient CO_2 concentration, C , in water, as shown in Equation (2). If we plot the dissolution rate vs. CO_2 concentration, C , at a fixed temperature, the absolute value of the slope should be the mass transfer coefficient k in the boundary layer as indicated in Equation (2). The solubility of CO_2 in water C_s can be calculated from the intercept, which is $-k \times C_s$.

Our experiments were conducted at 15 MPa in the temperature range of 2°C to 10°C. A seawater velocity in the range of 10 cm/s to 13 cm/s was required to stabilize the droplets in

the viewing section of the HWTF. Because we have data with different background concentrations of dissolved CO₂, we can use this data to determine mass transfer coefficients and CO₂ solubility in aqueous solutions by applying the just proposed method. Table 1 shows data calculated from the regression equations shown in Figure 1 with converted units.

Table 1. CO₂ Drop Dissolution and Shrinkage Rates in Artificial Seawater at Different Conditions Calculated from the Regression Equations Obtained from the Data in Figure 1.

Temperature, °C	Concentration of CO ₂ , C, wt%	Dissolution Rate, $\rho_{CO_2}(dR/dT)$, $\times 10^2$, mol/(m ² s)	Shrinkage Rate, dR/dT , $\times 10^6$, m/s
14.0	4	2.493	1.174
14.0	2	3.574	1.684
14.0	0	4.490	2.116
12.0	4	2.350	1.096
12.0	2	3.338	1.556
12.0	0	4.210	1.963
10.0	4	2.207	1.019
10.0	2	3.102	1.432
10.0	0	3.929	1.813
8.0	4	2.064	0.9435
8.0	2	2.865	1.310
8.0	0	3.648	1.667
6.0	4	1.921	0.8699
6.0	2	2.629	1.190
6.0	0	3.368	1.525
4.0	4	1.778	0.7977
4.0	2	2.392	1.073
4.0	0	3.087	1.385
2.0	4	1.635	0.7336
2.0	2	2.156	0.9671
2.0	0	2.806	1.259
2.5	4.6*	0.0033	0.00148

* Actual experimental data for a hydrate-covered drop at this condition, pressure was 29 MPa.

The data in this table, except for the hydrate-covered drop, represent the calculated dissolution rates of CO₂ drops at seven different fixed temperatures (14°C, 12°C, 10°C, 8°C, 6°C, 4°C, 2°C) and three different levels of dissolved CO₂ (0 wt%, 2 wt%, 4 wt%). These data can be compared with similar results found in the literature. As discussed previously, the dissolution rate is determined from the CO₂ droplet diameter shrinkage rate. In Radhakrishnan et al.'s (2003) paper, for pressures of 9.8 to 39.2 MPa, temperatures of 276 to 286K, and water

velocity of 1.5~7 cm/s, the diameter shrinks at a rate of $1.3\sim 3 \times 10^{-6}$ m/s, when hydrate is not present. The rate is $4\sim 19 \times 10^{-7}$ m/s when hydrate is present. It can be seen that our data fall in the same ranges and the presence of hydrate dramatically reduces the shrinkage rate, but not the mass transfer coefficient as subsequently proposed by Teng et al., 1998a.

Figure 2 gives dissolution rates as a function of concentration of CO₂ at different temperatures at 15 MPa. A straight line fit of the data is adequate. The correlation for each temperature is not displayed in this figure.

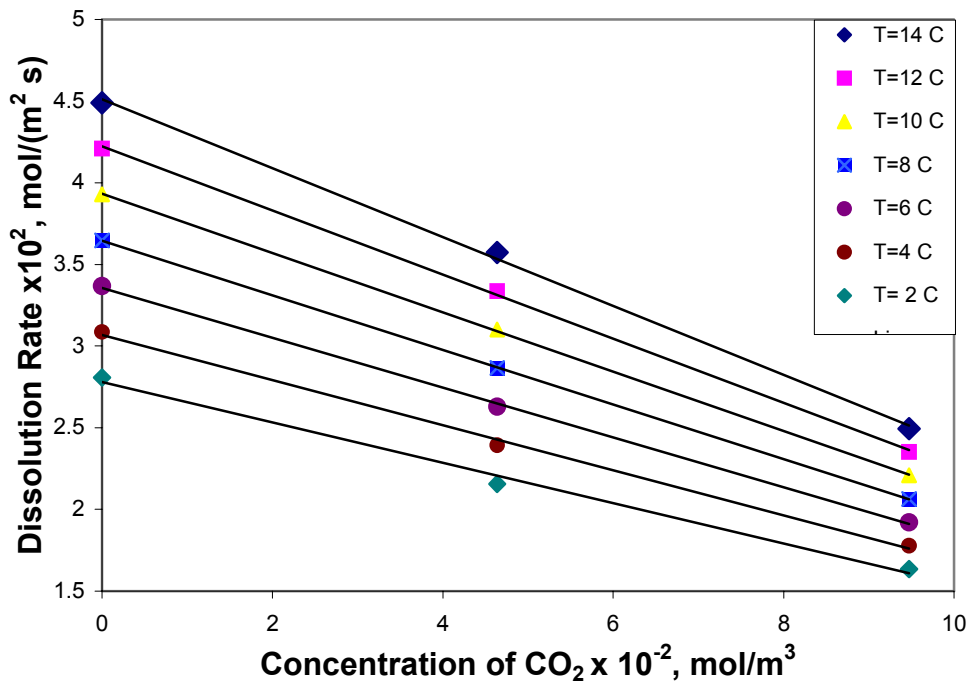


Figure 2. Dissolution rate, $\rho_{CO_2}(dR/dT)$, as a function of CO₂ concentration, C , at different temperatures at 15 MPa

The mass transfer coefficient and solubility of CO₂ in seawater at certain temperatures and pressures in the absence of hydrate were then easily obtained by using the method described above. The results are shown in Table 2. Also shown are calculated results for the solubility of CO₂, C_{sh} , and k when hydrates were present. These calculations will be discussed below. Note the presence of hydrate does not affect the systematic increase of k with increasing temperature.

The solubility and mass transfer coefficient results in Table 2 are plotted in Figure 3 and Figure 4, respectively. Note that some of the solubilities are the solubility of CO₂ in a metastable state since some temperatures and pressures were at conditions where hydrates can form but did not. In general, hydrates did not form because the bulk solution was undersaturated with CO₂. The only place where the reported solubilities actually exist is at or near the interface. As can be seen from the Figure 3, the presence of hydrate decreased the solubility of CO₂ in the surrounding seawater dramatically. This is an actual equilibrium solubility. Also note that the mass transfer coefficient when hydrate was present is also shown

in Figure 4 by the solid circle. The procedure for obtaining this value is described in the next section.

Table 2. Calculated Solubility and Mass Transfer Coefficient of CO₂ in Artificial Seawater as a Function of Temperature at 15 MPa

Temperature, °C	Solubility of CO ₂ in water, $C_s, \times 10^{-2}$, mol/ m ³	Mass Transfer Coefficient, $k, \times 10^5$, m/s
2.0	22.51	1.235
2.5*	10.99	1.262
4.0	22.22	1.381
6.0	21.99	1.527
8.0	21.81	1.672
10.0	21.64	1.818
12.0	21.51	1.963
14.0	21.39	2.109

*Hydrate formed at this temperature and 29 MPa.

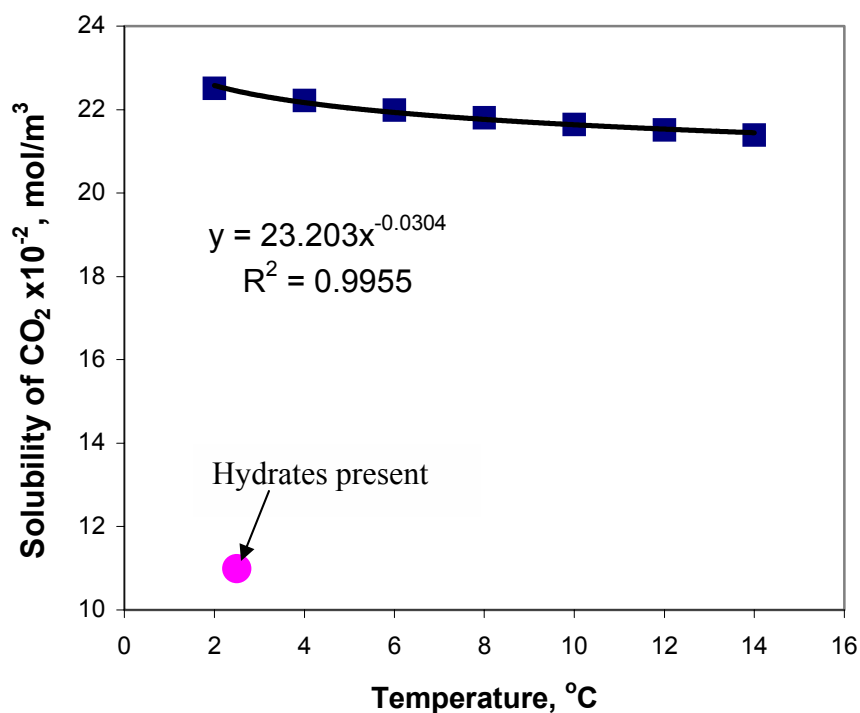


Figure 3. Solubility of CO₂, C_s or C_{sh} , in seawater as a function of temperature at 15 MPa

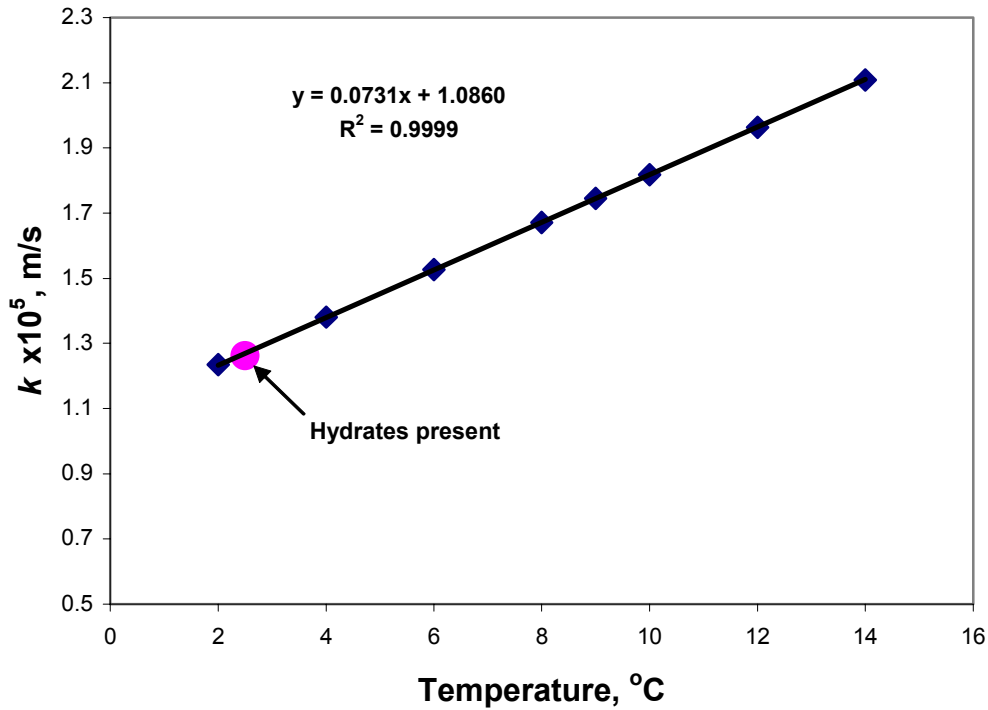


Figure 4. Mass transfer coefficient as a function of temperatures in seawater at 15 MPa

Solubility and Mass Transfer Coefficient of a Liquid CO₂ Drop with the Presence of Hydrate Shell

We can use the information obtained above to calculate the solubility of CO₂ when hydrates are present. This measurement is difficult to obtain experimentally. We assume that the water adjacent to the drop is saturated with carbon dioxide. When the hydrates are absent, this saturation is the (metastable) solubility of liquid carbon dioxide at the system pressure. When the hydrates are present, the solubility is the three-phase solubility. If the concentration were any higher, more hydrate would form from the supersaturated water. Thus the driving force is $C_{sh} - C$ when hydrates are present and $C_s - C$ when they are absent. However, the mass transfer is limited by the water phase and the mass transfer coefficient should be the same whether hydrates are present or not.

Based on this, the dissolution rate as a function of the driving force ($C_s - C$) when hydrates were absent at 2.5°C is plotted in Figure 5. A linear correlation is shown. Note that C_s was calculated by applying the correlation of CO₂ solubility developed in Figure 3. The slope of this correlation is the mass transfer coefficient, k , at this temperature with or without the presence of hydrate shell. Using this k and the experimentally measured dissolution rate in the presence of hydrate, C_{sh} is obtained from Equation (3) and shown by the solid circle in Figure 3.

$$\rho_{co2} \frac{dR}{dt} = -k(C_{sh} - C) \quad (3)$$

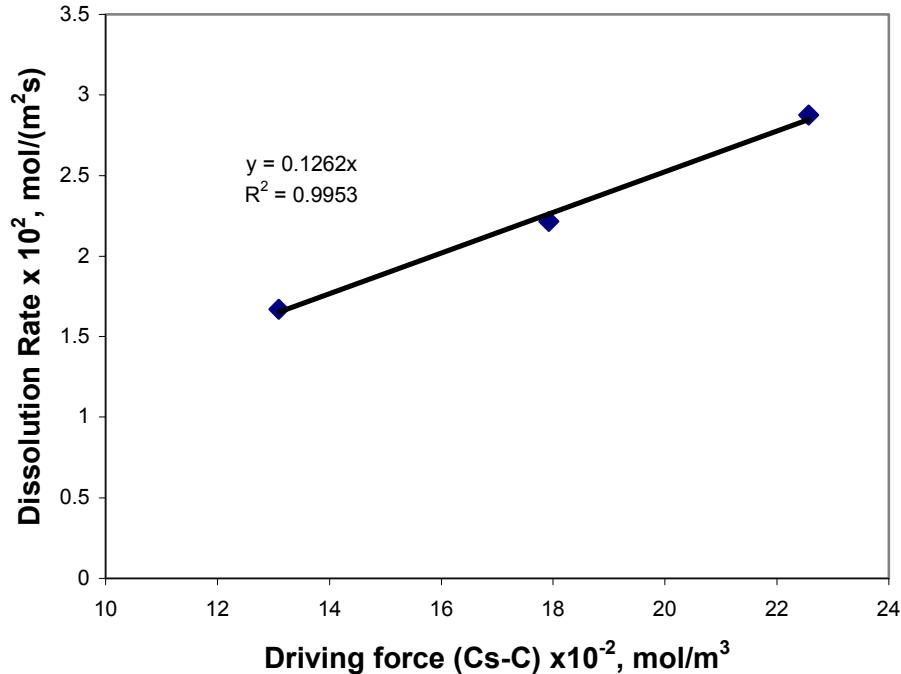


Figure 5. Rate of dissolution, $\rho_{CO_2}(dR/dT)$, as a function of driving force at 2.5°C at 15 MPa.

To test the validity of using the value of k obtained when hydrates were not present, we compared our solubility (1099 moles/m³) to that calculated using the method of Diamond and Akinfiev (2003) which gives a value of 1020 moles/m³. The excellent agreement supports the use of one value of k whether or not hydrates are present.

DISCUSSION

The mass transfer coefficients obtained from the data obtained in the simulated deep-ocean conditions in the HWTF are two orders of magnitude larger than those obtained in the static system used by Teng, et al., 1998a. It has previously been shown that even a small flow of 0.3 cm/s can cause a factor of 10 increase in the value of k (Radhakrishnan, et al., 2003). Also, in our experiments, a small (typically 1.5 cm diameter or less) CO₂ drop was injected into a large volume of circulating seawater (16.4 L). Under these conditions the ambient concentration of CO₂ was nearly constant as the drop dissolved. In contrast, the system used by Teng et al., 1998b had a volume of 0.07 L and the concentration of the CO₂ in water column changed as the CO₂ dissolved. In our previous work in a static 0.4 L cell, the observed dissolution rates were also lower (Warzinski et al., 1997). From a design perspective, the mass transfer coefficients reported here are those expected when CO₂ droplets move under their own buoyancy in a large volume of seawater.

Our results on mass transfer coefficients are also compared with published mass transfer correlations for fluid-fluid interfaces (Cussler, 1997) in Figure 6. The following equation was used in their study.

$$k = 0.42D_L / d(d^3 \Delta\rho g / \rho \nu^2)^{1/3} (\nu / D_L)^{0.5} \quad (4)$$

In this equation, D_L is the diffusion coefficient of CO_2 ; g is the acceleration due to gravity; k is the mass transfer coefficient; ν is the kinematic viscosity; d is bubble diameter, $\Delta\rho$ is the density difference between CO_2 bubbles and surrounding fluid; and ρ is the fluid density. Figure 6 shows good agreement between the calculated and experimental values.

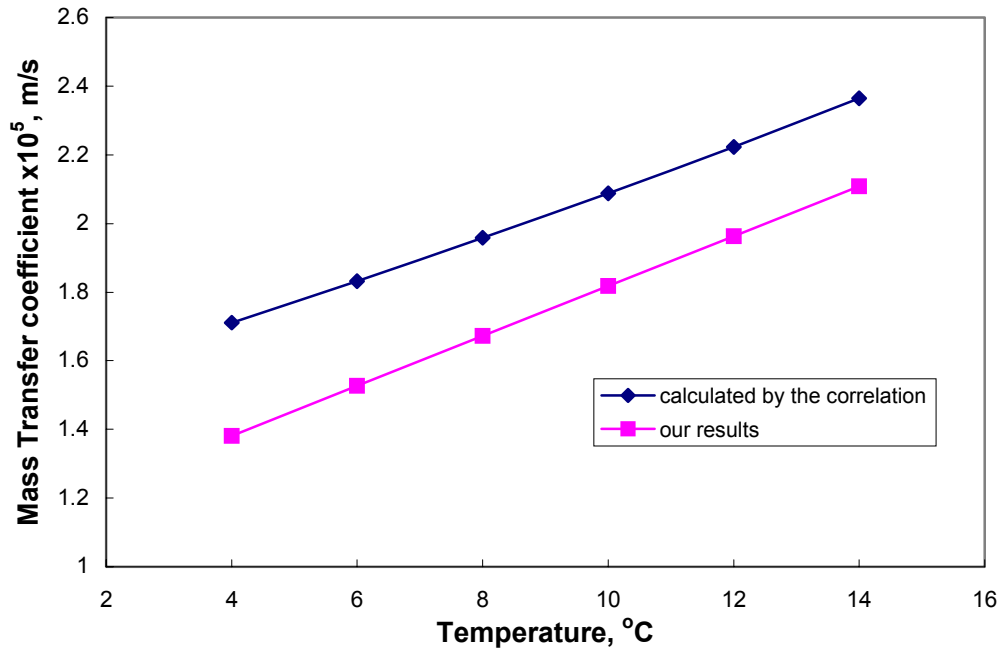


Figure 6. Comparison of our results and calculated results on mass transfer coefficient, k , of CO_2 in seawater at 15 MPa.

Finally, Figure 7 compares our solubility results with the values determined by Teng et al., 1998b. The disagreement is larger than would be expected. Ohmura and Mori(1999) suggest that Teng’s solubilities may be low which could explain some or all of the difference shown in Figure 7.

SUMMARY

The dissolution rate of CO_2 drops in seawater at different temperatures and levels of dissolved CO_2 has been used to provide information on the mass transfer coefficient of CO_2 in seawater, and on the solubility of CO_2 in both a metastable equilibrium state and the three-phase, VLH, equilibrium state. The results obtained under simulated free rise conditions can be useful to predict the fate of CO_2 drops in the ocean, whether released from natural sources, leaks from suboceanic storage sites or from deliberately engineered discharges.

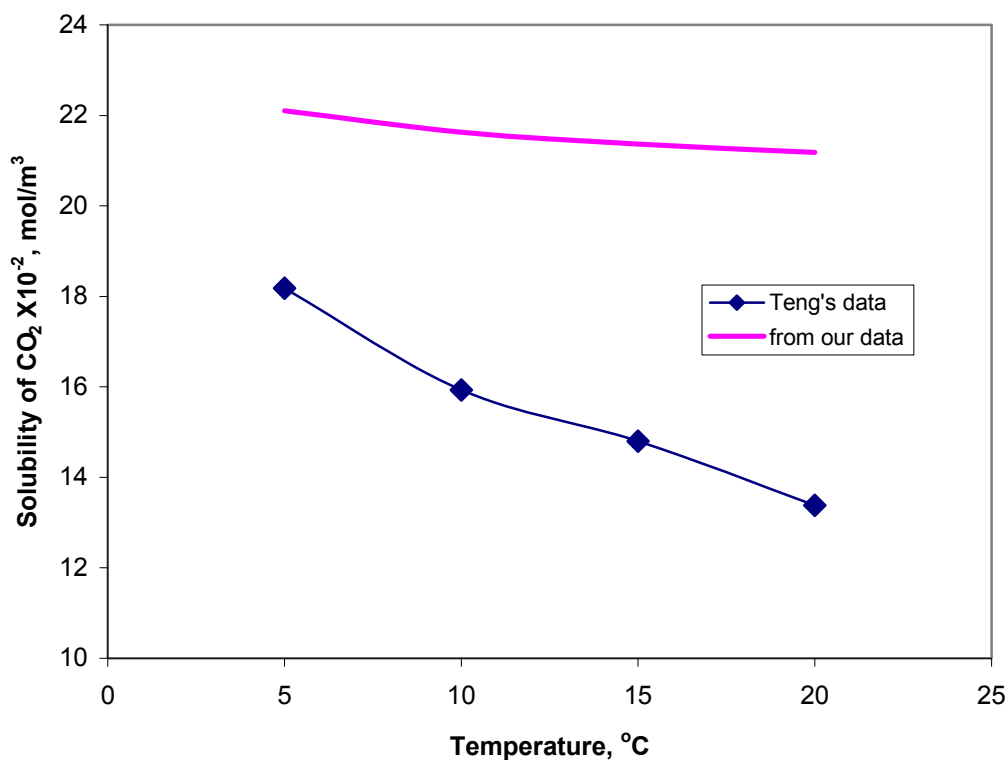


Figure 7. Comparison of our results with the data of Teng et al., (1998b), on the solubility of CO₂, C_s, in seawater at 15 MPa.

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