Solubility of Liquid CO_2 in Synthetic Sea Water at Temperatures from 278 K to 293 K and Pressures from 6.44 MPa to 29.49 MPa, and Densities of the Corresponding Aqueous Solutions

Ho Teng*

Department of Mechanical Engineering, The Hong Kong University of Science and Technology,
Clear Water Bay, Kowloon, Hong Kong

Akihiro Yamasaki

National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba 305, Japan

Measurements are reported on the solubility of liquid CO_2 in synthetic sea water at temperatures from 278 to 293 K and pressures from 6.44 to 29.49 MPa and on the corresponding densities of the CO_2 aqueous solutions. On the basis of the experimental results, expressions for the solubility of CO_2 in sea water and density of the corresponding CO_2 aqueous solution as functions of temperature, pressure, and salinity were obtained. The resultant equations well represented experimental data: the average differences are 3% for solubility and less than 0.05% for density.

Introduction

The disposal and sequestration of captured anthropogenic CO_2 in the ocean has been considered as a means to mitigate global warming. The majority of disposal scenarios proposed to date call for discharge of liquefied CO_2 through submerged pipelines below the mixed layer of the ocean, typically between 500 and 3000 m. Modeling of dissolution of the CO_2 disposed of in the ocean requires information on the solubility of liquid CO_2 in the ocean. Although the solubility of CO_2 in sea water has been studied previously (e.g., Stewart and Munjal, 1970; Murray and Riley, 1971; Weiss, 1974), in most of the previous investigations CO_2 was in the gaseous state, and therefore, results of these studies do not apply to the conditions below depths of 500 m in the ocean, where CO_2 is in the liquid state. Owing to lack of accurate information on the solubility of CO_2 in high-pressure and low-temperature sea water, in many ocean disposal studies the solubility was treated as constant (e.g., Golomb et al., 1989; Liro et al., 1992), which may have led to over- or underestimation of the rate of dissolution of the disposed CO_2 in the ocean, and of the marine environmental impact induced by the ocean disposal. In this study, we present experimental results on the solubility of liquid CO_2 in sea water at temperatures and pressures corresponding to ocean depths between 500 and 3000 m. Dissolution of the disposed CO_2 induces a denser plume in the ocean. Modeling of this plume requires knowledge of the density of the CO_2 aqueous solution. Thus, measured densities of the CO_2-saturated sea water also are reported.

Experimental Section

Materials. Carbon dioxide with a minimum purity of 99.99% was supplied by the Nikko Oxygen Corporation. Since composition of natural sea water varies with location and ocean depth, sea water used in this study was prepared synthetically. Composition of the synthetic sea water is presented in Table 1. The synthetic sea water is similar to that used by Stewart and Munjal (1970) in their study of the solubility of CO_2 in sea water at temperatures between −5 and 25 °C and pressures up to 4.6 MPa.

Apparatus. A schematic diagram of the apparatus is shown in Figure 1. The apparatus consisted of a sapphire tube with 6 mm inside diameter, 260 mm in length, and 2 mm in wall thickness; a 90-mm i.d. acrylic cylinder (water jacket) through which the water from a thermal bath was circulated; a mercury reservoir; a piston pump; and a pressure control unit. The temperature of the system was controlled by the thermal bath with an accuracy of ±0.2 K. The temperature difference between the water jacket and the substances in the sapphire tube was determined by filling the tube with water at normal pressure, and the temperature was found to be within the accuracy of the thermal bath. The pressure of the system was controlled by the piston pump and the pressure control unit. The high-pressure side (pressurizing chamber) of the pump that connected with the mercury reservoir was filled with water, and the low-pressure side (control chamber) of the pump was filled with nitrogen gas, whose pressure was controlled by the pressure control unit. The pressure control unit consisted of a pressure transducer, two on/off magnetic valves that controlled the nitrogen pressure in the pressure control chamber, two needle valves that controlled the venting/filling rates of the magnetic valves, and a PID controller that controlled the actions of the magnetic valves according to the pressure difference between the set value and the value detected by the pressure transducer at the mercury reservoir. The system pressure could be controlled at an accuracy of ±0.01 MPa. The system was tested at 35 MPa by filling with water; no leakage was found over a period of 1 week.

Procedure. In the experiments, the sapphire tube was first filled with sea water, and then CO_2 gas at room

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* Author for correspondence. Fax: 852-2358-1543. E-mail: mehoteng@uxmail.ust.hk.

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Table 1. Composition of Synthetic Sea Water

component	concentration g/kg·sol	concentration g/L·sol[a]
NaCl	26.518	27.133
$MgCl_2$	2.447	2.504
$MgSO_4$	3.305	3.382
$CaCl_2$	1.141	1.167
KCl	0.725	0.742
$NaHCO_3$	0.202	0.207
NaBr	0.083	0.085
total salts	34.421	35.220
H_2O	965.579	964.780

[a] At standard pressure and temperature.

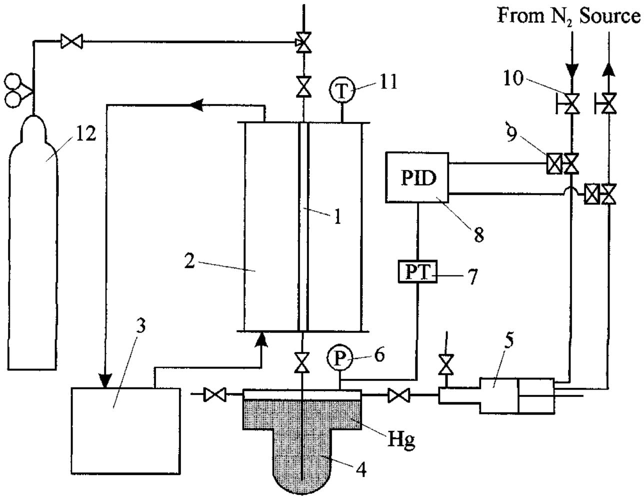

Figure 1. Schematic of experimental apparatus: 1, sapphire tube; 2, water jacket; 3, thermal bath; 4, mercury reservoir; 5, piston pump; 6, pressure gauge; 7, pressure transducer; 8, PID controller; 9, magnetic valve; 10, needle valve; 11, thermocouple; 12, CO_2 cylinder.

temperature was introduced from a high-pressure CO_2 cylinder into the system. At the required pressure and temperature ($p > 6$ MPa and $T \leq 293$ K) CO_2 was in the liquid state, so CO_2 became liquid when it entered the system. When the desired amount of liquid CO_2 was added, the filling valve was shut off. The sea water column in the tube was then in contact with a liquid CO_2 column at the top and with a mercury column (which connected with the mercury reservoir) at the bottom. The substances in the tube were pressurized by the mercury column. Changes in volume of the sea water column and of the liquid CO_2 column due to CO_2 dissolution could be determined with a scale attached to the sapphire tube in the water jacket. The scale could be read to an accuracy of ±0.2 mm using a magnifier. The behavior of the liquid CO_2−sea water interface could be viewed by a video camera and a monitor.

The density of liquid CO_2 varies considerably with temperature and pressure, while sea water density changes with temperature and pressure only slightly and may be treated as constant. To avoid an inversion of the sea water and liquid CO_2 columns at low temperatures and high pressures, each test was conducted with a starting pressure of 6.44 MPa. When equilibrium was reached, the pressure of the system was set to a higher value while the system temperature remained constant. Because the CO_2 aqueous solution is denser than sea water and a crystalline (if $T \leq 283$ K) or a quasi-crystalline (if $T > 283$ K) structure forms at the interface due to hydrate formation, no inversion was observed at temperatures from 278 to 293 K and pressures from 6.44 to 29.49 MPa. Since the mole fraction of CO_2 in the hydrate is much larger than the CO_2 solubility, the CO_2 hydrate ($CO_2 \cdot 5.75H_2O$) forms only at the interface where the sea water can be supersaturated with CO_2 (Teng et al., 1996). Because the hydrate interphase is very thin (Teng et al., 1995), the influence of hydrate formation on the measurement of the CO_2 solubility is small. Carbon dioxide hydrate is slightly denser than the CO_2 aqueous solution (Teng et al., 1996); however, owing probably to the small tube diameter and the wall effect, the thin hydrate phase (its thickness is of the order of 10^{-5} m) remained at the interface. As has been reported previously (Aya et al., 1993; Fujioka et al., 1994; Teng et al., 1995), formation of the hydrate at the interface at $T \leq 283$ K did not stop mass transfer from liquid CO_2 into sea water before saturation was reached.

During each test, the temperature and pressure of the system were maintained at set values. The temperature was measured by a thermocouple in the water jacket, and the system pressure was determined by the difference between the pressure at the mercury reservoir where the pressure transducer was installed and that due to the mass of the mercury column. An "agitation" was performed occasionally by setting the filling/venting rates so that pressure fluctuations were generated in the system. Since the system was filled with liquids, the pressure fluctuations induced pressure waves in the system and the CO_2−sea water interface was observed to "vibrate" around its equilibrium position when the system underwent a compression/expansion process. Although equilibrium can be obtained within 12 h, in each test the system was maintained at the set pressure and temperature for 24 h to ensure full saturation.

Results

Liquid CO_2 and water form an asymmetric system. At $T \leq 293$ K, the solubility of water in liquid CO_2 is smaller than that of liquid CO_2 in water by a factor of 10, and the lower the temperature, the smaller the value of the solubility of water in liquid CO_2 (Greenwood and Barnes, 1966; King et al., 1992). This behavior of the solubility of water in liquid CO_2 is significantly different from that of liquid CO_2 in water, which increases with decreasing temperature. Since liquid CO_2 is only slightly soluble in water, it is reasonable to treat the liquid CO_2−water system as a one-sided solubility system (Walas, 1985), with liquid CO_2 as the solute and water as the solvent. Because the solubility of liquid CO_2 in water forms a basis for the solubility of liquid CO_2 in sea water, the liquid CO_2−sea water system may also be treated as a one-sided solubility system. In the temperature and pressure range of the present study, values of the solubility of mercury in sea water are very small in comparison with that of CO_2 in sea water (Iwamoto et al., 1987). Therefore, the effect of dissolution of mercury in sea water on the CO_2 solubility is negligible.

The CO_2 solubility, C_s, may be defined as $C_s \equiv n_{CO_2}/V_{w,0}$, where n_{CO_2} is the number of moles of liquid CO_2 dissolved in water and $V_{w,0}$ is the volume of the sea water (CO_2 free) column at T and p. Since $n_{CO_2} = \rho_{CO_2}\Delta V_{CO_2}/M_{CO_2}$, C_s can be expressed as

$$C_s \equiv \frac{\rho_{CO_2}\Delta V_{CO_2}}{M_{CO_2}V_{w,0}} \qquad (1)$$

where ρ_{CO_2} is the density of liquid CO_2, ΔV_{CO_2} is the volume of the liquid CO_2 dissolved into sea water at T and p, and

Table 2. Measured and Calculated Solubilities x_{CO_2}

	$T = 278$ K		$T = 283$ K		$T = 288$ K		$T = 293$ K	
p/MPa	measd	calcd	measd	calcd	measd	calcd	measd	calcd
6.44	0.0277	0.0281	0.0236	0.0253	0.0218	0.0228	0.0196	0.0204
9.87	0.0290	0.0288	0.0258	0.0261	0.0240	0.0235	0.0217	0.0213
14.77	0.0309	0.0299	0.0273	0.0271	0.0255	0.0246	0.0232	0.0224
19.68	0.0317	0.0304	0.0286	0.0277	0.0263	0.0253	0.0239	0.0232
24.58	0.0322	0.0309	0.0295	0.0282	0.0269	0.0259	0.0246	0.0240
29.49	0.0327	0.0313	0.0302	0.0287	0.0276	0.0265	0.0252	0.0247

Table 3. Measured and Calculated Densities ρ_w/kg·m^{-3}

	$T = 278$ K		$T = 283$ K		$T = 288$ K		$T = 293$ K	
p/MPa	measd	calcd	measd	calcd	measd	calcd	measd	calcd
6.44	1048.57	1049.41	1043.28	1042.60	1040.03	1039.96	1036.66	1037.03
9.87	1051.67	1051.80	1046.69	1046.11	1043.39	1043.21	1039.76	1039.82
14.77	1054.19	1055.50	1049.24	1048.69	1045.81	1045.61	1041.32	1041.99
19.68	1056.20	1057.12	1051.93	1051.05	1046.91	1046.95	1042.80	1043.06
24.58	1057.43	1058.16	1053.06	1052.75	1048.07	1047.99	1043.94	1044.15
29.49	1058.68	1059.22	1054.26	1054.11	1049.69	1049.23	1045.12	1045.12

M_{CO_2} is the molar mass of CO_2, respectively. The solubility may be expressed alternatively in mole fraction as

$$x_{CO_2} = C_s/(C_s + \rho_{w,0}/M_{w,0}) \tag{2}$$

where x_{CO_2} is the CO_2 solubility in sea water in mole fraction and $\rho_{w,0}$ and $M_{w,0}$ are, respectively, the density and molar mass of sea water (CO_2 free). As was stated previously, sea water density may be treated as constant. In this study, the value of $\rho_{w,0}$ for the synthetic sea water was determined to be 1025.10 kg/m^3 by direct measurement at 288 K and 0.1 MPa. The density of the corresponding CO_2 aqueous solution, ρ_w, can be derived as

$$\rho_w = (\rho_{w,0} + C_s M_{CO_2})V_{w,0}/V_w \tag{3}$$

where V_w is the volume of the CO_2 aqueous solution at T and p. Since $\Delta V_{CO_2}/V_{w,0} = \Delta l_{CO_2}/l_{w,0}$ and $V_{w,0}/V_w = l_{w,0}/l_w$, where l is the length of the column for liquid CO_2 or sea water or the CO_2 aqueous solution, the inside diameter of the sapphire tube does not influence the measurement. An error analysis that considers all of the possible sources of error shows that the uncertainties of the measurements are 1.55% for the solubility and 1.87% for the density. The data obtained for solubilities of liquid CO_2 in sea water and the densities of the corresponding CO_2 aqueous solutions are presented in Tables 2 and 3.

Discussion

The solubility of liquid CO_2 in water may be expressed by the modified Henry's law (King, 1969) as

$$x^w_{CO_2} = f_{CO_2}/K_H \tag{4}$$

where $x^w_{CO_2}$ is the solubility of CO_2 in water and f_{CO_2} and K_H are, respectively, the fugacity of liquid CO_2 and the Henry's law constant at T and p. The values for f_{CO_2} at temperatures and pressures of common engineering applications have been given in the *International Thermodynamic Tables of the Fluid State: Carbon Dioxide* (Angus et al., 1976). In sea water, the solubility of CO_2 also depends on salinity. The effect of salinity on the solubility may be examined by considering the Setchenow equation (King, 1969)

$$\ln(x_{CO_2}/x^w_{CO_2}) = \alpha S‰ \tag{5}$$

where α is the salting-out coefficient and $S‰$ is the salinity. From eqs 4 and 5, the solubility of CO_2 in sea water can be derived as

$$x_{CO_2} = (f_{CO_2}/K_H)e^{\alpha S‰} \tag{6}$$

For the synthetic sea water investigated in this study, $S‰ = 34.421$. On the basis of the experimental data for solubilities of CO_2 in water (the CO_2 solubility in water will be reported elsewhere) and sea water, we have determined the dependence of the Henry's law constant and the salting-out coefficient on temperature and pressure as follows

$$K_H/\text{MPa} = a + b(p/\text{MPa}) + c(p/\text{MPa})^2 \tag{7}$$

with

$$a = 5.20 \times 10^3 - 39.2(T/\text{K}) + 0.075(T/\text{K})^2$$

$$b = -103 + 0.708(T/\text{K}) - 1.20 \times 10^{-3}(T/\text{K})^2$$

$$c = 0.022$$

$$\alpha = 0.543 - 3.54 \times 10^{-3}(T/\text{K}) + 5.69 \times 10^{-6}(T/\text{K})^2 \tag{8}$$

Comparison of values calculated from eqs 6, 7, and 8 with the experimental results is presented in Table 2. The average and maximum differences between the calculated and measured solubilities are 3.22% and 7.21%, respectively.

The density of a CO_2 aqueous solution is a function of the CO_2 concentration (Söhnel and Novotný, 1985). Thus, it is reasonable to assume that $\rho_w = \rho_w(\rho_{w,0},x_{CO_2})$. On the basis of the measured solubilities and densities presented in Tables 2 and 3, we have determined that

$$\rho_w/\text{kg·m}^{-3} = \rho_{w,0}/\text{kg·m}^{-3} - 42.2x_{CO_2} + 3.32 \times 10^4 x^2_{CO_2} \tag{9}$$

Comparison of calculations via eq 9 with the experimental results is presented in Table 3. Equation 9 represents the experimental data well exhibiting a maximum difference of 0.1%.

Experimental investigations of the density of the CO_2-saturated sea water at low temperatures and high pressures have not been reported previously. Although it has been predicted by Fujioka et al. (1995) that in the pressure range of this study ρ_w = 1050−1060 kg/m^3, which is consistent with the results of this study, it is evident in eq 9 that the value of ρ_w is influenced significantly by the reference density $\rho_{w,0}$, indicating that in the ocean ρ_w will vary with location and depth. Equation 9 will give a better prediction if the in situ measurement of the sea water density is used as the reference density $\rho_{w,0}$.

Conclusions

Experimental results on the solubility of liquid CO_2 in sea water at temperatures and pressures corresponding to ocean depths between 500 and 3000 m have been reported. The results of this study can be used as a basis for analyzing dissolution of liquid anthropogenic CO_2 disposed of in the ocean as a means to mitigate global warming. The solubility of CO_2 in sea water was calculated on the basis of the modified Henry's law, the Setchenow equation, and the resultant correlation equations for the Henry's law constant and salting-out coefficient. Good agreement was observed between the calculated solubilities and experimental data. The measured densities of the CO_2-saturated sea water also were reported. A relationship between the density of the CO_2 aqueous solution and the density of sea water as well as the CO_2 solubility was obtained, and the calculated densities via the resultant correlation equation agree well with the experimental data.

Literature Cited

Angus, S.; Armstrong, B.; de Reuck, K. M. *International Thermodynamic Tables of the Fluid State: Carbon Dioxide;* Pergamon Press: New York, 1976.

Aya, I.; Yamane, K.; Yamada, N. Effect of CO_2 Concentration in Water on the Dissolution Rate of Its Clathrate. *Proceedings of the International Symposium on CO_2 Fixation & Efficient Utilization of Energy*, Tokyo, 1993; pp 351−360.

Fujioka, Y.; Takeuchi, K.; Shindo, Y.; Komiyama, H. Shrinkage of Liquid CO_2 Droplet in Water. *Int. J. Energy Res.* **1994**, *18*, 765−769.

Fujioka, Y.; Ozaki, M.; Takeuchi, K.; Shindo, Y.; Yanagisawa, Y.; Komiyama, H. Ocean CO_2 Sequestration at Depths Larger Than 3700 m. *Energy Convers. Manage.* **1995**, *36*, 551−554.

Golomb, D.; Herzog, H.; Tester, J.; White, D.; Zemba, S. Feasibility, Modeling and Economics of Sequestering Power Plant CO_2 Emission in The Deep Ocean. MIT Energy Laboratory Report, MIT-EL 89-003; 1989.

Greenwood, H. J.; Barnes, H. L. *Handbook of Physical Constants*; Clark, S. P., Jr., Ed.; The Geological Society of America, Inc.: New York, 1966; Section 17.

Iwamoto, M.; Johnson, S. H.; Miyamoto, H. *Solubility Data Series*; Clever, H. L., Ed.; Pergamon Press: New York, 1987; Vol. 29.

King, M. B. *Phase Equilibrium in Mixtures;* Pergamon Press: London, 1969.

King, M. B.; Mubarak, A.; Kim, J. D.; Bott, T. R. The Mutual Solubilities of Water with Supercritical and Liquid Carbon Dioxide. *J. Supercrit. Fluids* **1992**, *5*, 296−302.

Liro, C. R.; Adams, E. E.; Herzog, H. J. Modeling the Release of CO_2 in the Deep Ocean. *Energy Convers. Manage.* **1992**, *33*, 667−674.

Murray, C. N.; Riley, J. P. The Solubility of Gases in Distilled Water and Sea Water−IV. Carbon Dioxide. *Deep-Sea Res.* **1971**, *18*, 533−541.

Söhnel, O.; Novotný, P. *Densities of Aqueous Solutions of Inorganic Substances*; Elsevier: New York, 1985.

Stewart, P. B.; Munjal, P. Solubility of Carbon Dioxide in Pure Water, Synthetic Sea Water and Sea Water Concentrates at −5 to 25 °C and 10 to 45 atm Pressure. *J. Chem. Eng. Data* **1970**, *15*, 67−71.

Teng, H.; Kinoshita, C. M.; Masutani, S. M. Hydrate Formation on the Surface of a CO_2 Droplet in High-pressure, Low-temperature Water. *Chem. Eng. Sci.* **1995**, *50*, 559−564.

Teng, H.; Yamasaki, A.; Shindo, Y. Stability of the Hydrate Layer Formed on the Surface of a CO_2 Droplet in High-pressure, Low-temperature Water. *Chem. Eng. Sci.* **1996**, *51*, 4979−4986.

Walas, S. M. *Phase Equilibrium in Chemical Engineering;* Butterworth Publishers: Boston, MA, 1985.

Weiss, R. F. Carbon Dioxide in Water and Sea Water: The Solubility of a Nonideal Gas. *Mar. Chem.* **1974**, *2*, 203−215.

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