Solubility of CO_2 in Aqueous Solutions of NaCl at (30 to 60) °C and (10 to 20) MPa

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The solubility of CO_2 in NaCl solutions with mass fractions of 0.01 to 0.03 was measured at (30 to 60) °C and (10 to 20) MPa. The CO_2 was dissolved in NaCl solution in a pressurized vessel, and a sample of the saturated solution was removed from the vessel. The solubility was then estimated by measuring the mass of the sample and the pressure of the dissolved gas. On the basis of this experimental data, an equation for predicting the CO_2 mole fraction x_1 in NaCl solution as a function of temperature $t = (30$ to $60)$ °C, pressure $P = (10$ to $20)$ MPa, and mass fraction, S, of NaCl = (0.01 to 0.03) was determined. $H(P,T,S)/\text{MPa} = 36.1P/\text{MPa} + 3.87T/\text{K} - 1097.1 + (196P/\text{MPa} + 26.9T/\text{K} - 8810)S$, where H is Henry's coefficient, $H = P_c/x_1$, P_c is the partial pressure of carbon dioxide, T is the absolute temperature, and S is the mass fraction of NaCl in the aqueous solution.

Introduction

Geological storage of CO_2 has been investigated as an option for reducing the concentration of carbon dioxide in the atmosphere.[1] The storage of CO_2 in deep saline aquifers is technically feasible, as demonstrated at the Sleipner gas field in the Norwegian North Sea. Since 1996, 1 million metric tons of CO_2 have been injected annually into saltwater saturated sands at depths below 800 m.[1] When the possibility of such a geological storage technique is discussed, the critical parameter is the CO_2 storage capacity of saltwater. Estimation of the total amount of stored CO_2 requires information about the thermophysical properties of saltwater, such as solubility.

Measurement of the solubility of CO_2 in pure water[2−12] has been extensively studied, whereas that in solutions that include an electrolyte such as NaCl has not.[9] In the low-pressure regime (i.e., near atmospheric pressure), the solubility can be theoretically estimated by considering the ionic strength and the salting-out parameter.[13,14] However, in the high-pressure regime (i.e., above 1 MPa), the correlation of activity coefficients in aqueous solutions should be determined by regressing the experimental data.[15,16] To determine the CO_2 storage capacity at depths below (1000 to 2000) m, where many saline aquifers exist, we measured the solubility of CO_2 in NaCl solution at (30 to 60) °C and at (10 to 20) MPa and NaCl mass fractions of 0.01 to 0.03 . On the basis of the results, a prediction equation for the solubility as a function of temperature, pressure, and mass fraction of NaCl has been derived.

Materials and Methods

Figure 1 shows a schematic of the experimental apparatus used to determine the CO_2 solubility. The apparatus consisted of a high-pressure vessel, an agitator, a pressure transducer for the range (0 to 25) MPa (TEAC, TP-AP 20 MPa), another pressure transducer for the range (0 to 0.2) MPa (Validyne, DP15-46), an amplifier (TEAC, SA-59), a temperature bath, a pump for pressurizing the water (GL Science, PU610-0X), a CO_2 gas cylinder, and a 50 cm^3 sample cylinder. The mass of the sample was measured by using a gravimetric balance (Sartorius, LP1200S).

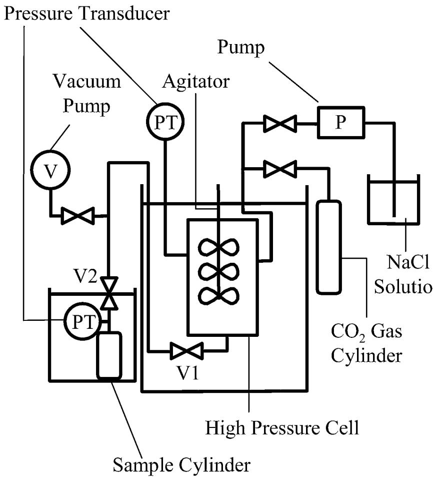

Figure 1. Schematic of apparatus for determining the solubility of CO_2 in NaCl solution.

The pressurized vessel had a 45 mm inner diameter and was 260 mm long, and its maximum pressure was 70 MPa. The vessel, all of the tubes, and sample cylinder were made of stainless steel. The water used to prepare the NaCl solution was filtered by using a water purification system (Yamato Science, Co. Ltd., WA33). The purity of the CO_2 was 99.99%.

The solubility measurements were as follows for different temperatures (30 °C, 40 °C, 50 °C, and 60 °C), pressures

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(10 MPa, 15 MPa, and 20 MPa), and NaCl mass fractions (0, 0.0099, 0.02, and 0.03). The vessel and sample cylinder were first evacuated to a pressure below 100 Pa, and then valves 1 and 2 were closed. CO_2 was introduced into the vessel to around 1 MPa. Then the aqueous solution of NaCl or the purified water was pumped in with mixing by the agitator for 1 h and left in the vessel for 2 h until the pressure and the temperature were stable. This procedure was done repeatedly until the experimental conditions were reached. Keeping the pressure of the vessel constant by pumping the solution of NaCl, valve 1 was then opened. Valve 2 was opened, thus flashing the solution dissolved CO_2 into the sample cylinder until the pressure of the cylinder reached about 0.1 MPa. Here no solution pumped for the pressurization flows into the vessel because the volume of the added solution is less than that of the tube from the storage tank of the NaCl solution to the vessel. And also degassing of the dissolved gas never appears behind valve 2 because the pressure of the vessel remains nearly constant during this extracting procedure. Therefore, the solution flows into the cylinder keeping the relative amount of CO_2 and the solution constant. The sample cylinder was disconnected from valve 2 and then cooled to 0 °C by placing it in ice. Finally, the pressure and mass of the cylinder were measured, and then used to calculate the solubility. Each set of experimental conditions was repeated three times and the average was calculated, resulting in a total of 48 data points (Tables 1 and 2).

The solubility was calculated as follows. The mass, W/kg, of the saturated solution of CO_2 in the sample cylinder and the mass fraction, S, of NaCl can be expressed as

$$W = n_c M_c + n_w M_w + n_s M_s, \quad S = \frac{n_s M_s}{n_w M_w + n_s M_s} \quad (1)$$

Here, M is the molecular weight, n is the amount of substance, and the subscripts c, w, and s correspond to CO_2, water, and salt, respectively. Although most of the CO_2 in the sample cylinder is in the gas phase, the gas partially dissolves in the solution. The solubility of CO_2 in the solution at 0 °C and the measured pressure, P_s/MPa, of the sample cylinder can be estimated by considering the ionic strength, I, and the salting-out parameter, $k_s/(\mathrm{l \cdot mol^{-1}})$. The total amount of CO_2 in the sample cylinder was

$$n_c = \frac{f_c V_g}{R T_0} + n_w \frac{f_c}{H} \times 10^{-k_s I} \quad (2)$$

where f_c is the fugacity of CO_2 at T_0 and P_s conditions, H is Henry's coefficient at 0 °C, V_g is the volume of the gas phase in the sample cylinder, and I is the ionic strength. f_c is calculated by following eq 3.

$$f_c = \varphi_c p_c = \varphi_c (P_s - P_w) \quad (3)$$

Here, P_w is the vapor pressure of water at 0 °C, and φ is the fugacity coefficient, which can be regarded as unity at low pressure.[13] For our measurements, $H = 73.8$ MPa[14] and $k_s = 0.112$ l/mol.[17] Here, V_g is calculated as

$$V_g = V_0 - \frac{n_w M_w}{\rho_l} \frac{1}{1 - S} \quad (4)$$

where V_0 is the volume of the sample cylinder and ρ_l is the

Table 1. CO_2 Solubility, x_1, in Water at Various T/°C and P/MPa

	$T = 30$			$T = 40$			$T = 50$			$T = 60$		
	$P = 10$	$P = 15$	$P = 20$	$P = 10$	$P = 15$	$P = 20$	$P = 10$	$P = 15$	$P = 20$	$P = 10$	$P = 15$	$P = 20$
$100x_1$	2.38 ± 0.07	2.48 ± 0.06	2.57 ± 0.03	2.07 ± 0.02	2.23 ± 0.01	2.34 ± 0.07	1.97 ± 0.06	2.09 ± 0.04	2.29 ± 0.01	1.85 ± 0.05	2.04 ± 0.02	2.25 ± 0.06
lit.	2.39[8]		2.59[8]	2.20[11]	2.30[11]	2.50[11]	1.98[6] 2.00[12]	2.10[6] 2.19[10]	2.30[10] 2.29[12]			

Table 2. CO$_2$ Solubility x_1 in NaCl Solution at (0.01, 0.02, and 0.03) Mass Fractions of NaCl at Various T/°C and P/MPa

	100x_1											
	$T = 30$			$T = 40$			$T = 50$			$T = 60$		
S of NaCl	$P = 10$	$P = 15$	$P = 20$	$P = 10$	$P = 15$	$P = 20$	$P = 10$	$P = 15$	$P = 20$	$P = 10$	$P = 15$	$P = 20$
0.0099	2.27 ± 0.07	2.35 ± 0.02	2.46 ± 0.05	2.03 ± 0.02	2.16 ± 0.03	2.27 ± 0.04	1.88 ± 0.05	2.01 ± 0.06	2.18 ± 0.05	1.78 ± 0.05	1.97 ± 0.03	2.11 ± 0.05
0.02	2.15 ± 0.04	2.23 ± 0.03	2.32 ± 0.03	2.01 ± 0.05	2.12 ± 0.05	2.19 ± 0.04	1.82 ± 0.02	1.96 ± 0.03	2.12 ± 0.05	1.66 ± 0.03	1.91 ± 0.02	2.03 ± 0.02
0.03	2.09 ± 0.04	2.20 ± 0.03	2.27 ± 0.03	1.92 ± 0.01	2.04 ± 0.02	2.14 ± 0.03	1.77 ± 0.01	1.91 ± 0.02	2.03 ± 0.04	1.65 ± 0.04	1.83 ± 0.03	1.91 ± 0.05

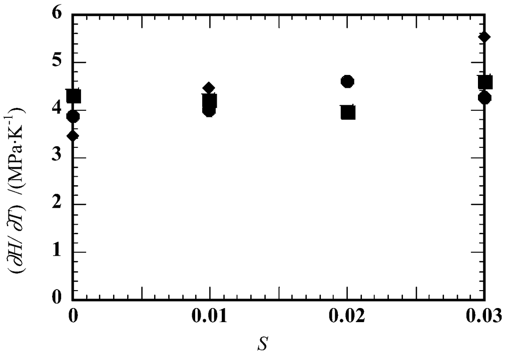

Figure 2. Partial derivative of Henry's coefficients to temperature as a function of mass fraction of NaCl, S: ●, 10 MPa; ■, 15 MPa; ◆, 20 MPa.

density of the solution at 0 °C.[18] From eqs 1, 2, and 4, n_w can be expressed as

$$n_w = \frac{W - M_c \dfrac{P_c V_0}{RT}}{M_c \dfrac{P_c}{H} \times 10^{-k_s I} + \dfrac{M_w}{1 - S}\left(1 - \dfrac{M_c P_c}{\rho_l R T_0}\right)} \tag{5}$$

where W is the mass of the sample and R is the gas constant. Finally, n_c can then be calculated by using eq 2, yielding the mole fraction of CO$_2$ in the solution, x_1, defined as $x_1 = n_c/(n_c + n_w + n_s)$.

Uncertainty in x_1 (i.e., δx_1) is derived from the errors in the measured pressure, P_s, the measured sample mass, W, the temperature, T, and the mass fraction, S, of NaCl. Those errors were estimated, and then δx_1 values were estimated by using a standard technique.[19]

Results and Discussion

Table 1 shows the measured x_1 for water only and previously reported data as a reference. The measured x_1 agrees well with the earlier investigation's data, indicating good reliability of the results obtained by the experimental method used here.

Table 2 shows the measured x_1 for 0.0099 to 0.03 mass fractions of NaCl. For the same temperature and mass fraction of NaCl conditions, the measured x_1 increased as pressure increased. However, x_1 was not proportional to pressure between (10 and 20) MPa, although the solubility was proportional to pressure near atmospheric pressure. The solubility x_1 decreased with increasing temperature but decreased with increasing mass fraction of NaCl. The solubility at 0.03 mass fraction of NaCl decreased to about 85% of that of water. This decrease is due to salting-out.

By regressing the experimental data, a prediction equation for the CO$_2$ solubility in NaCl solution for the pressure range (10 to 20) MPa, the temperature range (30 to 60) °C, and the NaCl mass fraction range 0 to 0.03 was obtained. In this regression, Henry's coefficient, H ($H = P_c/x_1$) was used, which is commonly used to express the solubility of gas in liquid. Because Henry's coefficient is affected by pressure, temperature, and mass fraction of NaCl, the dependency of this coefficient on those three parameters was investigated.

Figure 2 shows partial derivatives of Henry's coefficient to temperature ($\partial H/\partial T$) as a function of mass fraction of NaCl. The derivatives were calculated from the values of H at four different temperatures under the same pressure

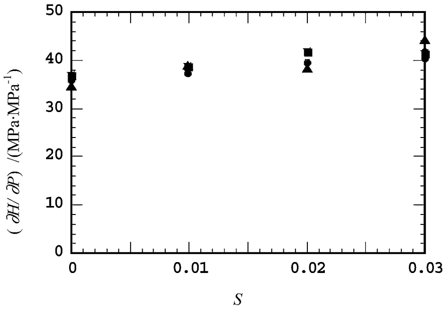

Figure 3. Partial derivative of Henry's coefficients to pressure as a function of mass fraction of NaCl, S: ●, 303.2 K; ■, 313.2 K; ◆, 323.2 K; ▲, 333.2 K.

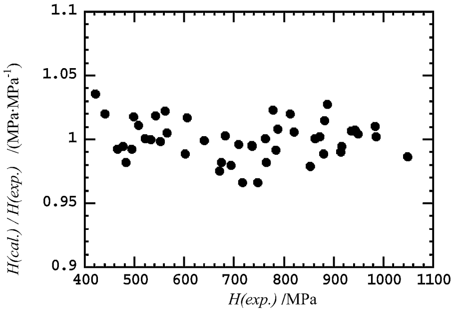

Figure 4. H(cal)/H(exp) as a function of measured H: ●, H(cal)/H(exp).

and same mass fraction of NaCl conditions. Figure 2 shows that $\partial H/\partial T$ is independent of pressure and can be expressed as a linear function of mass fraction of NaCl. Regression of the data yields

$$\left(\frac{\partial H}{\partial T}\right)/\mathrm{MPa{\cdot}K^{-1}} = 26.9S + 3.87 \tag{6}$$

Figure 3 shows partial derivatives of Henry's coefficient to pressure ($\partial H/\partial P$) as a function of mass fraction of NaCl. The derivatives were calculated from the values of H at three different pressures under the same temperature and same mass fraction of NaCl conditions. Figure 3 shows that $\partial H/\partial P$ is independent of temperature and can be expressed as a linear function of mass fraction of NaCl. Regression of the data yields

$$\left(\frac{\partial H}{\partial P}\right)/\mathrm{MPa{\cdot}MPa^{-1}} = 196S + 36.1 \tag{7}$$

Combining eqs 6 and 7, Henry's coefficient can be expressed as

$$H(P,T,S)/\mathrm{MPa} = (196S + 36.1)P/\mathrm{MPa} + (26.9S + 3.87)T/\mathrm{K} + A(S) \tag{8}$$

$A(S)$ for all 48 data points shown in Tables 1 and 2 was calculated, and then $A(S)$ was regressed by using a linear function, thus yielding the following prediction equation for Henry's coefficient:

$$H(P,T,S)/\mathrm{MPa} = 36.1P/\mathrm{MPa} + 3.87T/\mathrm{K} - 1097.1 + (196P/\mathrm{MPa} + 26.9T/\mathrm{K} - 8810)S \tag{9}$$

Figure 4 shows the Henry's coefficient calculated from this prediction equation. In this figure, the calculated values are normalized by the corresponding experimental values. These results show that Henry's coefficient can be predicted within 3.6% of the experimental values.

Conclusion

The CO_2 solubility in saline aquifers at depths below (1000 to 2000) m can be determined by using the experimentally determined correlation equation for the solubility of CO_2 in NaCl solution as a function of mass fractions of NaCl for (0.0099 to 0.03), temperatures for (30 to 60) °C, and pressures for (10 to 20) MPa.

Literature Cited

(1) The commission of the European communities. *The Underground Disposal of CO_2*; JOULE2 Project No. CT92-0031 Final Report: 1996.
(2) Weber, L. A. Mesurements of virial-coefficient and equation of state of carbon-dioxide + ethan system in the supercritical region. *Int. J. Thermophys.* **1992**, *13*, 1011−1032.
(3) Teng, H.; Yamasaki, A.; Chun, M. K.; Lee, H. Solubility of liquid CO2 in 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. *J. Chem. Thermodyn.* **1997**, *29*, 1301−1310.
(4) King, M. B.; Mubarak, A.; Kim, J. D.; Botto, T. R. The mutual solubilities of water with supercritical and liquid carbon dioxide. *J. Supercrit. Fluids* **1992**, *5*, 296.
(5) Nighswander, J. A.; Kalogerakis, N.; Mehrotra, A. K. Solubilities of carbon dioxide in water and 1 wt-percent NaCl solution at pressures up to 10-MPa and temperatures from 80 °C to 200 °C. *J. Chem. Eng. Data* **1989**, *34*, 355.
(6) D'Souza, R.; Patrick, J. R.; Teja, A. S. High-pressure phase-equilibria in the carbon-dioxide normal-hexadecane and carbon-dioxide water-systems. *Can. J. Chem. Eng.* **1988**, *66*, 319−323.
(7) Briones, J. A.; Mullins, J. C.; Thies, M. C.; Kim, B. U. Ternary phase-equilibria for acetic acid−water mixtures with supercritical carbon-dioxide. *Fluid Phase Equilib.* **1987**, *36*, 235−246.
(8) Gillespie, P. C.; Wilson, G. M. Vapor-Liquid and Liquid−Liquid Equilibria. *Gas Processors Association Research Report* **1982**, *1*, 73.
(9) Teng, H.; Masutani, S. M.; Kinoshita, C. M.; Nihous, G. C. Solubility of CO_2 in the ocean and its effect on CO2 dissolution. *Energy Convers. Manage.* **1996**, *37*, 1029−1038.
(10) Wiebe, R.; Gaddy, V. L. The solubility in water of carbon dioxide at 50, 75 and 100 °C, at pressures to 700 atm. *J. Am. Chem. Soc.* **1939**, *61*, 315−318.
(11) Wiebe, R.; Gaddy, V. L. The solubility of carbon dioxide in water at various temperature from 12 to 40 °C and at pressures to 500 atm. *J. Am. Chem. Soc.* **1940**, *62*, 815−817.
(12) IUPAC. *Carbon Dioxide in Water and Aqueous Electrolyte Solutions, Solubility data series vol. 62*; IUPAC: 1996; p 60.
(13) Hougen, O. A.; Kenneth, M. W.; Ronald, A. R. *Themodynamics*, 2nd ed., *Chem. Process Principles*; Wiley: New York, 1959.
(14) Perry, J. H. *Chemical Engineers' Handbook*, 4th ed.; McGraw-Hill: New York, 1963; pp 14-3 to 14-6.
(15) Pitzer, K. S.; Perper, J. C.; Busey, R. H. Thermodynamic properties of aqueous sodium chloride solutions. *J. Phys. Chem. Ref. Data* **1984**, *13*, 1−103.
(16) Pitzer, K. S. *Activity Coefficients in Electrolyte Solutions*, 2nd ed.; CRC Press: Boca Raton, FL, 1991.
(17) Danckwerts, P. V. *Gas−Liquid Reactions*; McGraw-Hill: 1970.
(18) JSME Data Book: *Thermophysical Property of Fluid*; The Jpn. Soc. Mech. Eng.: 1983.
(19) ASME: *Measurement Uncertainty*; ANSI/ASME PTC 19-1; 1985.

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