JOURNAL OF CHEMICAL & ENGINEERING DATA

ARTICLE

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Water Solubility Measurements of the CO_2-Rich Liquid Phase in Equilibrium with Gas Hydrates Using an Indirect Method

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ABSTRACT: The solubility of water in the CO_2-rich phase was measured in the presence of hydrate using an indirect method at the temperatures ranging from (274 to 294) K and pressures of (6.1 and 10.1) MPa. The experimental data set of Song and Kobayashi (*SPE Form. Eval.* **1987**, *2*, 500−508) was previously reported for this system, and a large pressure dependence was observed at the pressures of (6.21 and 10.34) MPa. The present solubility data were compared with published experimental data at the hydrate-free region. A weak pressure dependence was observed compared with the data of Song and Kobayashi in the present measurements.

INTRODUCTION

The flow of liquid CO_2 streams from flue gas as in carbon dioxide sequestration through the ocean environment is likely to be at gas-hydrate forming conditions depending on the content of water. For such applications, the water contents need to be kept below the hydrate-forming solubility limit to suppress solid accumulation and pipe plugging. The only data set available for the composition of the liquid CO_2-rich phase (L_{CO_2}) in equilibrium with the gas hydrate phase (H) is from Song and Kobayashi.[1] When the L_{CO_2}-H equilibrium curve shifts to the L_{CO_2}-L_W (liquid CO_2 with liquid water) curve at constant pressure witha temperature rise, the water content of L_{CO_2} in L_{CO_2}-H and L_{CO_2}-L_W equilibria is expected to be identical at the three-phase equilibrium conditions. Thus L_{CO_2}-L_W data of Wiebe and Gaddy,[2] Gillespie and Wilson,[3] and King et al.[4] may appear to extrapolate to Song and Kobayashi data at hydrate forming conditions. The composition of the L_{CO_2} phase in L_{CO_2}-H equilibria appears to smoothly extrapolate to L_{CO_2}-L_W data sets of previously reported data at 10.34 MPa, but the other data (6.21 and 13.79 MPa) deviate significantly from the L_{CO_2}-L_W data sets.

The data set from Song and Kobayashi[1] also presented difficulties in modeling due to large deviations in compositions and their pressure dependence.[5,6] Yang and co-workers[5] reported that their model prediction agrees with other L_{CO_2}-L_W data but not with the L_{CO_2}-H data of Song and Kobayashi. Li et al.[6] reported large deviations in solubility prediction with the experimental L_{CO_2}-H equilibrium data from Song and Kobayashi and commented on the need to verify their experimental results. The calculation result from CSMGem software[8] also shows a similar trend.

Kim and co-workers[7] used an indirect method to measure CO_2 contents in a water-rich liquid in equilibrium with hydrate by determining the temperature at which hydrates disappear. Considering the typical water contents in the CO_2-rich phase (about 0.002 in mole fraction), an indirect method without composition analysis may be considered advantageous for improved uncertainty in composition determination compared with a typical gas chromatography analysis with TCD detectors. In this study, the indirect method of Kim is modified to measure a very small amount of water introduced into a large amount of carbon dioxide, and temperatures were monitored at constant pressure when the formed hydrates disappear. The measured data may provide a solution to the inconsistency between L_{CO_2}-H data of Song and Kobayashi and previously reported L_{CO_2}-L_W data.[2−4]

EXPERIMENTS

Materials. High-purity CO_2 ($w > 0.99999$, assay GC) from PS Chemical Co. (Korea) was used without further purification. Triple-distilled water was prepared by purifier from Human Co., Ltd. (Korea) and used after degassing by ultrasonication for 30 min.

Apparatus and Procedures. The same apparatus used in Kim et al.[7] for water-rich phase measurements was modified for the CO_2-rich phase as shown in Figure 1. In this method, temperatures at which two-phase L_{CO_2}-H mixtures become a single liquid phase were visually determined at constant pressures for predetermined amounts of CO_2 and water. The variable volume view cell (1) was connected to a Rheodyne injection valve (2) that was designed to inject small amount of water into the view cell. Volumes of two sampling loops were calibrated by filling the loop with acetone, flushing with predetermined amount of ethanol, and determining acetone composition using a gas chromatography (Agilent 7890A) with a flame-ionization detector. The calibrated volumes were found to be (69.35 ± 0.20) mm^3 and (27.00 ± 0.21) mm^3, respectively.

The calibrated sampling loop was first filled with purified water from a water reservoir (3) using a metering pump (4). A detachable gas buret (5) was used to measure the amount of CO_2 introduced into the system. The gas buret was evacuated using a vacuum pump (6) and filled with liquefied CO_2 from the CO_2 cylinder (7) through a 50 μm pore gas filter. The pressurized CO_2 in the gas buret was expanded to inject water from the injection valve into the view cell. The mass of the detached gas

Received: February 2, 2011
Accepted: March 30, 2011
Published: April 04, 2011

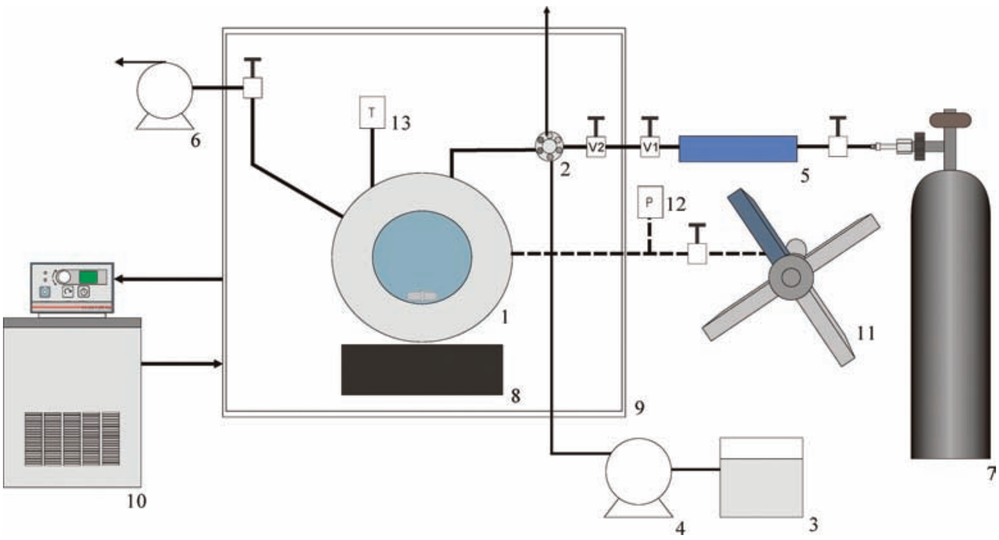

Figure 1. Experimental apparatus; 1, variable-volume view cell; 2, Rheodyne injection valve; 3, water reservoir; 4, metering pump; 5, CO_2 detachable gas buret; 6, vacuum pump; 7, CO_2 cylinder; 8, magnetic stirrer; 9, water bath; 10, constant temperature circulator; 11, pressure generator; 12, pressure transducer; 13, RTD.

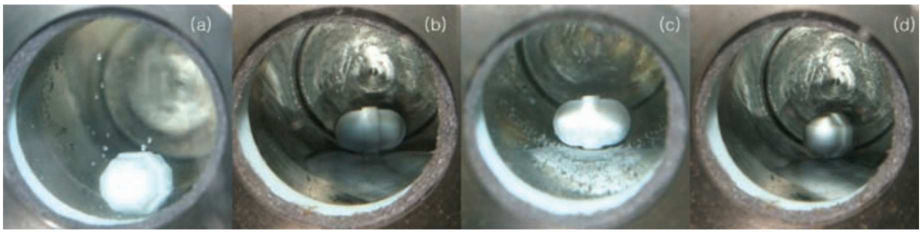

Figure 2. Experimental procedure; (a) L_{CO_2}-L_W mixture not in equilibrium after injection, (b) single phase L_{CO_2} on raising temperature, (c) L_{CO_2}-H mixture in equilibrium on lowering temperature, (d) single phase L_{CO_2} after hydrates dissolved.

buret was determined before and after expansion using an Ohaus balance with an uncertainty of 0.014 g, and the difference of masses was taken as the amount of CO_2 charged into the system. The total mass of the gas buret was approximately 1200 g, and the injected mass of CO_2 ranged from (50 to 90) g. The combined expanded uncertainties of composition analysis were estimated to be $\pm 3 \cdot 10^{-5}$ (coverage factor, $k = 2$).

The mixture with a predetermined composition was agitated using a magnetic stirrer (8). The equilibrium cell was immersed in the water bath (9), of which the temperature was controlled by a Polyscience circulator (10) which can maintain temperature within ± 0.01 K. A pressure generator (11) was used to adjust pressure. A Valcom pressure transducer readable to 0.1 MPa (12) was used to measure the system pressure. A Hart Scientific RTD thermometer with resolution of 0.001 K (13) was placed near the equilibrium cell and used to measure the system temperature. The combined expanded uncertainties of calibrated pressure and temperature gauges were 0.1 MPa and 0.02 K, respectively. The former was determined by Korea Testing Laboratory, and the latter was the suggested value from the manufacturer.

Water and CO_2 form two-phase mixtures (L_{CO_2}-L_W) when injected into the cell as shown in Figure 2a, which become single liquid phase when raising temperature (Figure 2b). Then the temperature was lowered to approximately 275 K to form a L_{CO_2}-H two-phase mixture (Figure 2c). Constant temperature and pressure were maintained for more than 6 h to equilibrate the system. For measurements in hydrate-free conditions, the temperature of initial two-phase mixtures was lowered to approximately 283.15 K and maintained over 6 h to reach the equilibrium L_{CO_2}-L_W mixture. The system temperature was raised at a rate of $0.5 \text{ K} \cdot \text{h}^{-1}$ initially, which become 0.1 K and subsequently 0.05 K near complete dissolution. The equilibrium dissolution temperature was visually determined (Figure 2d) with an estimated uncertainty of 0.1 K.

■ RESULTS AND DISCUSSION

The measured solubility data of water in the CO_2-rich phase in equilibrium with hydrate or liquid water are listed in Table 1. The measured solubility and previous experimental data available in the literature (Song and Kobayashi,[1] Wiebe and Gaddy,[2] Gillespie and Wilson,[3] and King et al.[4]) are plotted together in Figure 3. The vertical line represents L_W-H-L_{CO_2} three-phase equilibrium and divides the plane into two; the hydrate-forming region on the left and hydrate-free region on the right.

Around 10 MPa, data from Song and Kobayashi[1] (10.34 MPa) and our data (10.1 MPa) approximately extrapolate to the literature data of Wiebe and Gaddy,[2] Gillespie and Wilson,[3] and King et al.[4] However, data of Song and Kobayashi at 6.21 MPa deviate significantly from the trend of L_{CO_2}-L_W data of King et al. at 5.88 MPa. Also, the extrapolation of the data of

Table 1. Solubility of Water (x_{water}) in Liquid CO_2 at (6.1 and 10.1) MPa from (274.3 to 294.5) K

T/K	p/MPa	x_{water}	phase
274.3	10.1	0.00183	L_{CO_2}-H
276.1	10.1	0.00199	L_{CO_2}-H
277.1	10.1	0.00206	L_{CO_2}-H
277.8	10.1	0.00208	L_{CO_2}-H
277.9	10.1	0.00207	L_{CO_2}-H
279.0	10.1	0.00217	L_{CO_2}-H
279.5	10.1	0.00221	L_{CO_2}-H
279.8	10.1	0.00223	L_{CO_2}-H
280.7	10.1	0.00234	L_{CO_2}-H
281.5	10.1	0.00235	L_{CO_2}-H
281.5	10.1	0.00239	L_{CO_2}-H
283.4	10.1	0.00249	L_{CO_2}-L_W
286.7	10.1	0.00277	L_{CO_2}-L_W
291.0	10.1	0.00304	L_{CO_2}-L_W
274.9	6.1	0.00183	L_{CO_2}-H
277.1	6.1	0.00199	L_{CO_2}-H
277.7	6.1	0.00206	L_{CO_2}-H
278.1	6.1	0.00207	L_{CO_2}-H
278.9	6.1	0.00208	L_{CO_2}-H
280.5	6.1	0.00221	L_{CO_2}-H
280.6	6.1	0.00223	L_{CO_2}-H
281.9	6.1	0.00235	L_{CO_2}-H
282.3	6.1	0.00239	L_{CO_2}-H
285.7	6.1	0.00256	L_{CO_2}-L_W
287.5	6.1	0.00263	L_{CO_2}-L_W
288.4	6.1	0.00273	L_{CO_2}-L_W
290.6	6.1	0.00280	L_{CO_2}-L_W
294.5	6.1	0.00289	L_{CO_2}-L_W

Song and Kobayashi at 13.79 MPa seems to cross that of Wiebe and Gaddy, Gillespie and Wilson, and King et al. at near 20.2 MPa. However, the transition from hydrate-forming region and hydrate-free region of this study seems quite reasonable.

It should be noted that the pressure dependence of solubility hydrate-forming conditions is quite different from that of Song and Kobayashi. In this study, the pressure dependence of solubility at hydrate-forming conditions at two different pressures [(6.1 and 10.1) MPa] was very small. The data from Song and Kobayashi shows strong pressure dependence at [(6.21 and 10.34) MPa]. Yang and co-workers[5] showed discrepancies in the data from Song and Kobayashi with other data. Li et al.[6] also pointed out that pressure has less effect on the calculated L_{CO_2}-H equilibrium curve.

■ CONCLUSION

The water content of liquid CO_2 in equilibrium with gas hydrates was measured from (274 to 294) K at pressures of (6.1 and 10.1) MPa by determining the temperature at which hydrates dissolved completely with predetermined compositions. The uncertainties in the measurements were ± 0.1 K in temperature, ± 0.1 MPa in pressure, and $\pm 3 \cdot 10^{-5}$ in composition, respectively. The reliability of the present data was substantiated by comparisons with other data sets. The measured solubility was smaller at 10.1 MPa but larger at 6.1 MPa than previous experimental results and showed weak pressure dependence.

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Funding Sources

The authors are grateful for financial support from the Korea Ocean Research and Development Institute.

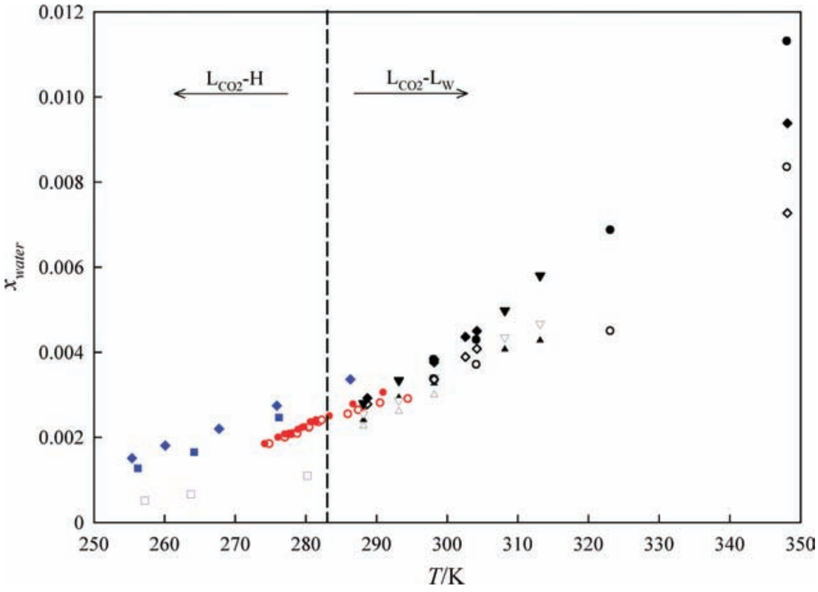

Figure 3. Comparison of experimental data for the solubility of water in liquid CO_2 for the L_{CO_2}-H and L_{CO_2}-L_W phase. ○, this work, 6.1 MPa; ●, this work, 10.1 MPa; □, Song and Kobyashi, 6.21 MPa; ■, Song and Kobyashi, 10.34 MPa; blue ◆, Song and Kobyashi, 13.79 MPa; black ▼, Wiebe and Gaddy, 10.13 MPa; gray ▼, Wiebe and Gaddy, 20.27 MPa; black ◆, Gillespie and Wilson, 10.13 MPa; gray ◆, Gillespie and Wilson, 20.27 MPa; △, King, 5.88 MPa; black ▲, King, 10.13 MPa; light gray ▲, King, 12.67 MPa; dark gray ▲, King, 20.27 MPa.

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