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# Solubilities of Carbon Dioxide, Methane, and Ethane in Sodium Chloride Solution Containing Gas Hydrate

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Studies on two-phase equilibria between the water-rich phase ($L_W$) and the gas hydrate phase (H) are important in understanding gas behavior in water at hydrate forming conditions for processes such as carbon dioxide sequestration and natural gas recovery. A new indirect method was developed in this study and applied for measurements of gas solubilities of carbon dioxide, methane, and ethane in aqueous solutions containing gas hydrates with and without sodium chloride. Effects of temperature, pressure, and salt concentrations on the solubility of these gases in the aqueous phase in equilibrium with the hydrate phase were investigated for $P$ = (10 to 20) MPa. Solubilities for these gases were found to increase as temperature increases. Methane and ethane were found to show a salting-out effect, whereas carbon dioxide showed a salting-in effect in hydrate forming conditions. Solubilities of methane and ethane decreased with pressure, but those of carbon dioxide showed very weak pressure dependence.

## Introduction

Gas hydrates are water crystal structures stabilized by guest molecules such as carbon dioxide, methane, and ethane. Phase equilibria involving gas hydrates are of importance in natural gas recovery and carbon dioxide sequestration. Studies on gas hydrates are comprehensively reviewed in Sloan's book.[1] Various three-phase equilibria involving gas hydrates and the inhibition effects of alcohols and electrolytes on the formation of gas hydrates have been extensively studied. However, studies on two-phase equilibria involving gas hydrates are relatively limited. Two-phase equilibrium data for guest-rich and water-rich phases in equilibrium with the hydrate phase (H) are listed in the book. Experimental studies for the water-rich liquid phase ($L_W$) are reported on systems of carbon dioxide,[2–4] methane,[5,6] and ethane.[7] For carbon dioxide in the water-rich phase, liquid samples were expanded to determine the amount of dissolved gas in water in equilibrium with gas hydrates.[2–4] The expansion method is not accurate enough for small solubility measurements of methane and ethane systems, and Kim et al.[7] used an indirect method to measure small solubilities of methane, ethane, and propane, in which equilibrium temperatures were measured for predetermined liquid phase compositions. Recently, Zhang et al.[8] reported $L_W$−H equilibrium data using an indirect method for carbon dioxide in simulated seawater. Experimental solubilities of carbon dioxide by different investigators show general agreements in their magnitudes and temperature dependence considering experimental uncertainties. The pressure dependence of the solubility is generally considered very weak, but Someya et al.[4] reported the increase of solubility with pressure. Other than by Zhang et al.,[8] studies have not been reported on the effects of inhibitors such as sodium chloride on hydrate-containing two-phase equilibria.

In the present study, the indirect method of Kim et al.[7] is improved, and hydrate-containing, two-phase equilibria are measured for carbon dioxide, methane, and ethane in the presence of sodium chloride. These measurements are hoped to be helpful in understanding the effects of pressure and salts on the solubility of these gases in hydrate-containing aqueous solutions.

## Experiments

High-purity carbon dioxide (99.99 %) from Sung-Kang Gas (Korea), ultra purity grade methane (> 99.99 %) from Air Product, research purity grade ethane (99.99 %) from Matheson, and sodium chloride (99.5 %) from Junsei Chemical (Japan) were used without further treatments. Triple-distilled water was prepared in the Barnstead MegaPure system and used.

The indirect method of Kim et al.[7] is modified and used for the solubility measurement of carbon dioxide, methane, and ethane in aqueous solutions with and without sodium chloride. The present apparatus shown in Figure 1 was equipped with a variable-volume view cell (1) and was different from the Kim et al.[7] apparatus in that a volume-calibrated gas reservoir (2) was used instead of a high-pressure syringe pump for the determination of the amount of gaseous species introduced into the equilibration system. The volume of the gas reservoir was determined by measuring the mass of water that filled the reservoir using a Mettler H80 balance readable to 0.1 mg. The solution in the equilibrium cell was mixed using a magnetic stirrer (3). The equilibration system was immersed in a water bath (4) with an external circulator (5) and connected to a vacuum pump (6). The pressure in the gas reservoir was measured using pressure transducers (7), Valcom VPRQ-50bar with 0.01 MPa accuracy for carbon dioxide and methane, and Sensys PHSH0010KAAA with 0.001 MPa accuracy for ethane. For the pressure measurement in the equilibrium cell, Valcom VPRQ-50 MPa (8) was used. Bath temperature was measured close to the equilbrium cell using Ertco Hart model 850C (9) with an accuracy of 0.05 K. The maximum temperature variation in the bath was found to be 0.05 K. The gas reservoir (2) was connected to a check valve (10) that was connected to the gas cylinder (11). Gas reservoirs with different volumes were used depending on gas species. The variable-volume view cell (1) was connected to a pressure generator (12) for pressure adjustment.

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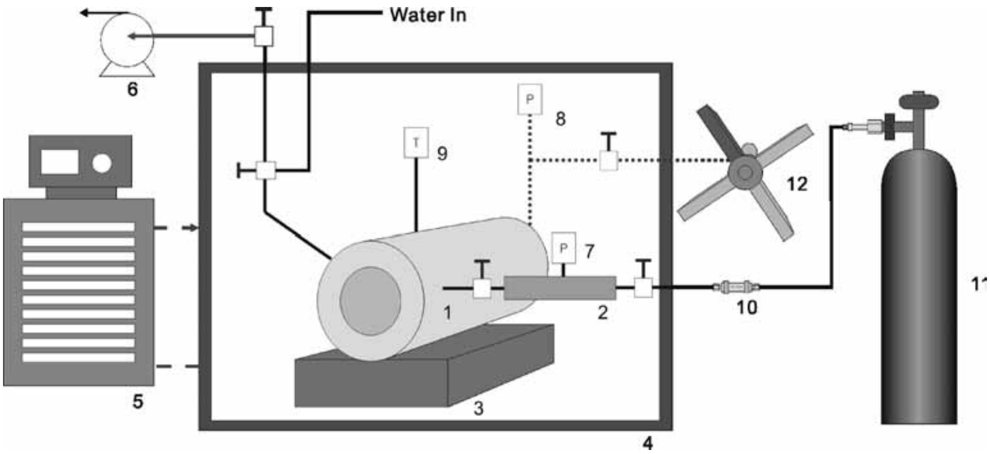

**Figure 1.** Schematic diagram of experimental apparatus. 1, variable-volume view cell; 2, calibrated gas reservoir; 3, magnetic stirrer; 4, constant temperature bath; 5, constant temperature circulator; 6, vacuum pump; 7, pressure gauge; 8, pressure gauge; 9, temperature indicator; 10, check valve; 11, gas cylinder; 12, pressure generator.

After a preliminary cleansing and leak test with 6 MPa carbon dioxide, the whole system was flushed two or three times with the gas species whose solubility was to be measured and then evacuated. A preweighed amount of about 40 g of solution was introduced through the solution inlet into the equilibrium cell (1) and evacuated for 30 min to remove gases in the solution and system with the valve to the closed gas reservoir. After evacuation, the valve to the solution inlet was closed, and the equilibrium cell was isolated in a vacuum. A gas species was introduced to the gas reservoir (2), which was isolated subsequently by closing the connecting valve to the gas cylinder (11), and the reservoir pressure was recorded. The gas species in the reservoir was introduced into the equilibrium cell by opening the reservoir valve to the equilibrium cell. Then, the valve was closed and the reservoir pressure was recorded again. The amount of the gas species in the gas reservoir was determined using *PVT* correlations of NIST[9] from the calibrated reservoir volume, bath temperature, and measured reservoir pressure. The difference in the amounts before and after introducing a gas component into the equilibrium cell was taken as the amount of gas in the equilibration system. Masses of water and gas in the equilibrium cell should be fairly accurate when determined by the present method. The uncertainty of compositions is primarily dependent on the uncertainty of the mass of the gas introduced and conservatively estimated to be 1 %.

The mixture of a gas and aqueous solution in the equilibration system was initially in the $L_W-V$ two-phase state and made to be in the $L_W-H$ two-phase state by pressurization and temperature adjustments. The mixture should be close to the solubility limit in the $L_W-H$ two-phase region at temperatures a few degrees below the expected equilibrium temperature. At the same time, hydrates in the mixture should be completely dissolved before reaching the three-phase equilibrium temperature when heated. The composition of the mixture was found by trial and error to meet these conditions. For the measurements of equilibrium temperature, the $L_W-H$ mixture with hydrates was heated very slowly until hydrates were visually disappeared keeping pressure constant at a selected value. The typical rate of temperature rise was 0.1 K in 8 h, and it took a couple of days for a data point. For the measurement at other pressures but with the same composition, the temperature was lowered to form hydrates, and a different pressure was selected and the procedure was repeated. The measured temperature minus 0.1 K was taken as the equilibrium temperature. Considering the equipment accuracy of 0.05 K, the uncertainty in temperature measurements was assumed to be 0.1 K.

**Table 1. Measured Solubilities in Mole Fractions $x_{CO_2}$ on a Salt-Free Basis for Carbon Dioxide in $H-L_W$ Equilibria Containing Sodium Chloride at Molality *M* at Different Temperature *T* and Pressure *P***

| *M* | *P*/MPa | *T*/K | $x_{CO_2}$ |
|---|---|---|---|
| 0 M | 10.1 | 279.1 | 0.0231 |
| | 10.1 | 280.4 | 0.0251 |
| | 10.1 | 281.1 | 0.0271 |
| | 12.1 | 279.7 | 0.0230 |
| | 12.1 | 280.8 | 0.0251 |
| | 15.1 | 279.7 | 0.0231 |
| | 15.1 | 280.8 | 0.0251 |
| | 15.1 | 281.5 | 0.0271 |
| | 20.1 | 279.5 | 0.0227 |
| | 20.1 | 280.4 | 0.0251 |
| 1 M | 10.1 | 278.9 | 0.0231 |
| | 10.1 | 280.0 | 0.0249 |
| | 15.1 | 279.3 | 0.0231 |
| | 15.1 | 280.4 | 0.0249 |
| | 20.1 | 278.8 | 0.0231 |
| | 20.1 | 279.8 | 0.0249 |

**Table 2. Measured Solubilities in Mole Fractions $x_{CH_4}$ on a Salt-Free Basis for Methane in $H-L_W$ Equilibria Containing Sodium Chloride at Molality *M* at Different Temperature *T* and Pressure *P***

| *M* | *P*/MPa | *T*/K | $x_{CH_4}$ |
|---|---|---|---|
| 0 M | 10.1 | 280.3 | 0.00178 |
| | 12.7 | 280.5 | 0.00178 |
| | 14.3 | 280.8 | 0.00178 |
| 1 M | 10.1 | 277.8 | 0.00122 |
| | 10.1 | 279.6 | 0.00141 |
| | 10.1 | 281.6 | 0.00162 |
| | 10.1 | 283.2 | 0.00178 |
| | 15.1 | 278.5 | 0.00122 |
| | 15.1 | 280.0 | 0.00141 |
| | 15.1 | 282.1 | 0.00162 |
| | 15.1 | 283.7 | 0.00178 |

Pressure measurements are relatively accurate, and their effects are relatively small. From the information given above and solubility data in Tables 1 to 3, the expanded combined uncertainties[10] were estimated to be 0.3 K for temperature and 3 % for composition. The sum of inlet tube volumes for the introduction of solution and gas was less than 1 % of the total volume of the equilibration system. However, the fluid in the volume is not readily mixed by stirring and may become inhomogeneous if gas is trapped before the pressurization. To minimize the uncertainty due to the incomplete mixing, pressurization and depressurization were repeated to expel trapped gas as much as possible after introducing a gas component, and the equilibrium cell was tilted during

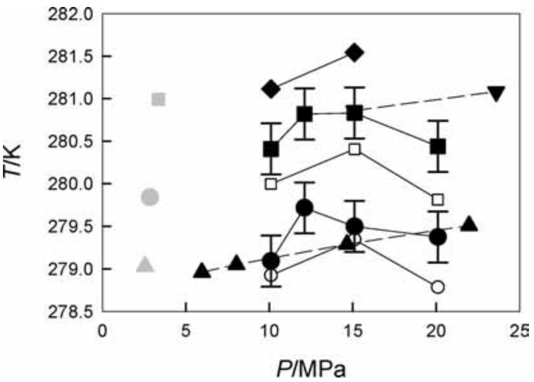

**Figure 2.** Measured $L_w$−H equilibrium temperature $T$ as a function of pressure $P$ for different carbon dioxide mole fractions $x_{CO_2}$ on a salt-free basis and molalities of sodium chloride $M$. ●, $M = 0$, $x = 0.0231$; ■, $M = 0$, $x = 0.0251$; ♦, $M = 0$, $x = 0.0271$; ○, $M = 1$, $x = 0.0231$; □, $M = 1$, $x = 0.0249$; gray-filled triangle, ref 1, $M = 0$, $x = 0.0218$; gray-filled circle, ref 1, $M = 0$, $x = 0.0231$; gray-filled box, ref 1, $M = 0$, $x = 0.0251$; ▲, ref 8, $M = 0$, $x = 0.0218$; ▼, ref 8, $M = 0$, $x = 0.0242$.

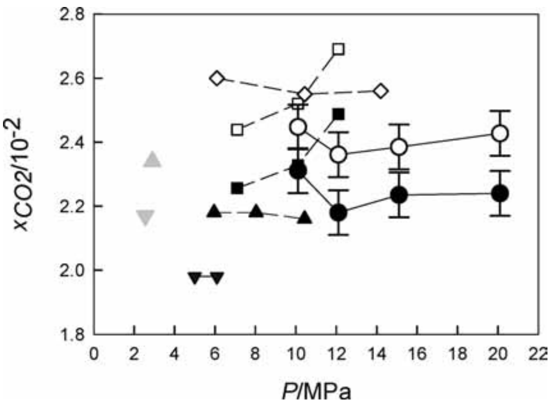

**Figure 3.** Comparisons of interpolated experimental mole fraction of carbon dioxide, $x_{CO_2}$, in salt-free $L_w$−H equilibria with literature data as a function of pressure $P$ for different temperatures $T$. ●, present data, 279 K; ○, present data, 280 K; ▼, ref 3, 278 K; gray-filled down triangle, ref 1, 279 K; ■, ref 4, 279 K; ▲, ref 8, 279 K; gray-filled up triangle, ref 1, 280 K; ◇, ref 2, 280 K; □, ref 4, 280 K.

pressurization to prevent the gas component from re-entering into the connecting tubes. The present solubility data appeared relatively free from scattering, and the extra error due to gas trapping was judged negligible. Solubility data in solute mole fractions on a salt-free basis are collected in Tables 1 to 3.

## Results and Discussions

Constant solubility lines of carbon dioxide are shown as functions of pressure and temperature in Figure 2. The figure shows that solubilities increase as temperature increases with or without sodium chloride in solution, and therefore $(\partial x/\partial T)_{P,m}$ is positive. The temperature effect is in agreement with the previous studies for salt-free systems in hydrate-forming conditions.[2–4,8] Constant solubility lines of Zhang et al.[8] are also shown at slightly different compositions in the figure. If compositions of their data are approximately corrected to the solubility values of present data, their temperatures are found within the present uncertainty bounds. Three-phase equilibrium points that correspond to the compositions of Zhang et al. (0.0218) and present data (0.0231, 0.0251) are obtained using CSMGem[1] and shown in the figure. Both sets of data are seen to extrapolate to the calculated three-phase equilibrium points. However, the second point of the present data sets at 12.1 MPa is probably too low in temperature.

The figure also shows that the equilibrium temperature decreases at constant pressure and mole fractions on a salt-free basis with the addition of the salt whose concentration is denoted by molality $m$. Therefore, $(\partial T/\partial m)_{P,x}$ is negative. The salt effect on the solubility of carbon dioxide can be seen by a form of the triple product rule at constant pressure.[11]

$$\left(\frac{\partial x}{\partial m}\right)_{T,P} = -\left(\frac{\partial x}{\partial T}\right)_{P,m}\left(\frac{\partial T}{\partial m}\right)_{P,x} \tag{1}$$

The sign of the first derivative on the right-hand side is positive, and that of the second is negative. Therefore, the sign of the derivative on the left-hand side is positive, indicating a salting-in effect. The salt effect is contrary to those of the hydrate-free carbon dioxide−water system that is known to show salting-out behavior.[12] If present equilibrium temperatures for salt-containing systems are estimated on an overall mole fraction basis instead of a salt-free basis, however, the temperatures are found to be similar or slightly higher than those of salt-free systems. Zhang et al.[8] reported higher temperatures for salt-containing systems.

To compare with literature data, solubility isotherms are obtained by interpolating data in Table 1 and represented in Figure 3 at (279 and 280) K. Since equilibrium temperatures were determined for different pressures at constant composition in the present study, the effect of pressure on the solubility at constant temperature can be seen using the triple product rule at constant salt molality.[11]

$$\left(\frac{\partial x}{\partial P}\right)_{T,m} = -\left(\frac{\partial x}{\partial T}\right)_{P,m}\left(\frac{\partial T}{\partial P}\right)_{x,m} \tag{2}$$

The first derivative on the right-hand side is positive as seen from the temperature effect. Figure 2 shows that the second derivative is positive at around 10 MPa, reaches a maximum at around (12 to 15) MPa, and then decreases. This behavior corresponds to solubility that decreases initially, reaches a minimum, and then increases. Isothermal $P$−$x$ plots in Figure 3 show such pressure effect on solubility.

Interpolated data of Yang et al.[2] at 280 K are found larger than the present solubility by about 10 % and show that solubility decreases slightly with pressure. Data of Servio and Englezos[3] at 278 K agree with the present data if temperature correction is made to 279 K and show negligible pressure dependence. Zhang et al.[8] data are in general agreement with present data, extrapolate smoothly to the three-phase equilibrium point at 279 K obtained using CSMGem,[1] and show that solubility decreases slightly with pressure. Considering that the deviations of each data point from constant mean values are less than the present uncertainty of 3 %, the observed solubility minimum is uncertain. The present data are considered accurate in the mean, and the pressure dependence is expected to be very small. This pressure dependence is different from those of Someya et al.[4] who showed that solubility increases with pressure.

As shown by Figure 4, the present solubilities in Table 2 for methane in salt-free solution are confirmed to agree with those of Kim et al.[7] and Yang[13] but estimated to be larger than those of Servio and Englezos[6] when the pressure is approximately extrapolated to the present value. Kim et al.[7] employed an indirect method and found large deviations from Yang et al. data,[5] for which solution was sampled and expanded. In their method, a minute amount of unfiltered hydrate crystal in the solution sample was suspected responsible for the large deviations in determining the small solubility of methane. The figure shows that solubilities for methane increase with temperature

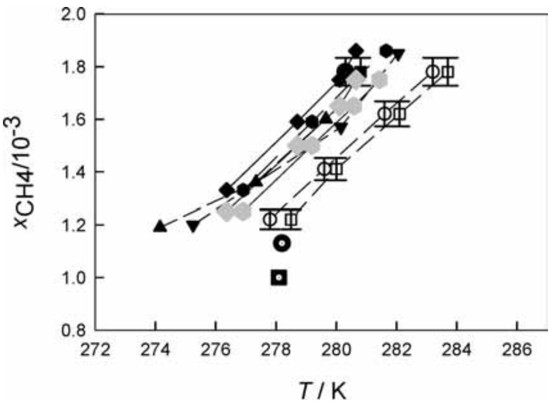

**Figure 4.** Comparisons of the salt-free mole fraction of methane, $x_{CH_4}$, in $L_w$−H equilibria with literature data as a function of temperature $T$ for different pressures $P$ and NaCl molalities $M$. ●, present data, $M = 0$, $P$/MPa = 10.1; ■, present data, $M = 0$, $P$/MPa = 14.3; ○, present data, $M = 1$, $P$/MPa = 10.1; □, present data, $M = 1$, $P$/MPa = 15.1; solid circle with hollow center, ref 1, $M = 0$, $P$/MPa = 10.4; solid square with hollow center, ref 1, $M = 0$, $P$/MPa = 16.0; ♦, ref 7, $M = 0$, $P$/MPa = 10.1; ⬢, ref 7, $M = 0$, $P$/MPa = 14.3; ▲, ref 6, $M = 0$, $P$/MPa = 5.0; ▼, ref 6, $M = 0$, $P$/MPa = 6.5; gray-filled diamond, ref 13, $M = 0$, $P$/MPa = 10.1; gray-filled hexagon, ref 13, $M = 0$, $P$/MPa = 14.3.

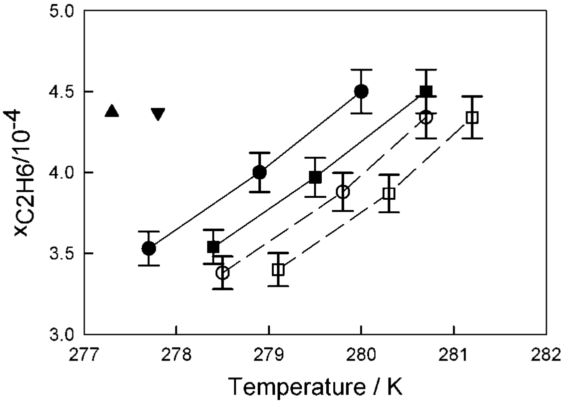

**Figure 5.** Comparisons of salt-free mole fraction for ethane, $x_{C_2H_6}$, in $L_w$−H equilibria with literature data as a function of temperature $T$ for different pressures $P$ and NaCl molalities $M$. ●, present data, $M = 0$, $P$/MPa = 10.1; ■, present data, $M = 0$, $P$/MPa = 15.1; ○, present data, $M = 1$, $P$/MPa = 10.1; □, present data, $M = 1$, $P$/MPa = 15.1; ▲, ref 7, $M = 0$, $P$/MPa = 10.1; ▼ref 7, $M = 0$, $P$/MPa = 15.1.

**Table 3. Measured Solubilities in Mole Fractions $x_{C_2H_6}$ on a Salt-Free Basis for Ethane in H−$L_W$ Equilibria Containing Sodium Chloride at Molality $M$ at Different Temperature $T$ and Pressure $P$**

| $M$ | $P$/MPa | $T$/K | $x_{C_2H_6}$ |
|---|---|---|---|
| 0 M | 10.1 | 277.7 | 0.000353 |
| | | 278.9 | 0.000400 |
| | | 280.0 | 0.000450 |
| | 15.1 | 278.4 | 0.000354 |
| | | 279.5 | 0.000397 |
| | | 280.7 | 0.000452 |
| 1 M | 10.1 | 278.5 | 0.000338 |
| | | 279.8 | 0.000388 |
| | | 280.7 | 0.000434 |
| | 15.1 | 279.1 | 0.000334 |
| | | 280.3 | 0.000387 |
| | | 281.2 | 0.000434 |

and decrease with the addition of salt in hydrate-forming conditions. Thus, the system shows a salting-out effect unlike the behavior of carbon dioxide. The solubilities decrease with pressure, but the pressure effect is small. Kim et al. data extrapolate to the calculated $L_W$−H−V equilibrium temperature 286.1 K and mole fraction 0.0022 at 10 MPa that are obtained using CSMGem.[1]

Solubilities of ethane in Table 3 are an order of magnitude smaller than those of methane and increase with temperature. When compared with the previous data of Kim et al. in salt-free conditions,[7] the present solubilities are about 20 % smaller. The present method of determining composition using calibrated volumes is considered more accurate than the previous method that uses a high-pressure syringe pump in determining small solubilities of ethane. The effects of temperature, pressure, and salts are similar to those for methane. The solubility of ethane increases with temperature and decreases with pressure and the addition of salt.

## Conclusions

A new indirect method was developed for the measurement of gas solubility in aqueous solutions in the presence of gas hydrates and applied to H−$L_W$ equilibria of carbon dioxide, methane, and ethane with aqueous solution with and without sodium chloride. The method was found reliable. Solubilities of gases were found to increase generally with temperature. Carbon dioxide showed a salting-in effect, while methane and ethane showed a salting-out effect. Solubilities of methane and ethane decreased with pressure, but those of carbon dioxide showed a weak maximum around $P$ = (12 to 15) MPa.

## Literature Cited

(1) Sloan, E. D.; Koh, C. *Clathrate Hydrates of Natural Gases*, 3rd ed.; Taylor and Francis: Boca Raton, FL, 2007.
(2) Yang, S. O.; Yang, I. M.; Kim, Y. S.; Lee, C. S. Measurement and Prediction of Phase Equilibria for Water+CO2 in Hydrate Forming Conditions. *Fluid Phase Equilib.* **2000**, *175*, 75–89.
(3) Servio, P.; Englezos, P. Effect of Temperature and Pressure on the Solubility of Carbon Dioxide in Water in the Presence of Gas Hydrate. *Fluid Phase Equilib.* **2001**, *190*, 127–134.
(4) Someya, S.; Bando, S.; Chen, B.; Song, Y.; Nishio, M. Measurement of CO2 Solubility in Pure Water and the Pressure Effect on It in the Presence of Clathrate Hydrate. *Int. J. Heat Mass Transfer* **2005**, *48*, 2503–2507.
(5) Yang, S. O.; Cho, S. H.; Lee, C. S. Measurement and Prediction of Phase Equilibria for Water+Methane in Hydrate Forming Conditions. *Fluid Phase Equilib.* **2001**, *185*, 53–63.
(6) Servio, P.; Englezos, P. Measurement of Dissolved Methane in Water in Equilibrium with Its Hydrate. *J. Chem. Eng. Data* **2002**, *47*, 87–90.
(7) Kim, Y. S.; Ryu, S. K.; Yang, S. O.; Lee, C. S. Liquid Water−Hydrate Equilibrium Measurements and Unified Predictions of Hydrate-containing Phase Equilibria for Methane, Ethane, Propane, and Their Mixtures. *Ind. Eng. Chem. Res.* **2003**, *42*, 2409–2414.
(8) Zhang, Y.; Holder, G. D.; Warzinski, R. P. Phase equilibrium in Two-Phase, Water-Rich-Liquid, Hydrate Syems: Experiment and Theory. *Ind. Eng. Chem. Res.* **2008**, *47*, 459–469.
(9) http://webbook.nist.gov/chemistry/fluid/.
(10) Chirico, R. D.; Frenkel, M.; Dicky, V. V.; Marsh, K. N.; Wilhoit, R. C. ThermoML-An XML-Based Approach for Storage and Exchange of Experimental and Critically Evaluated Thermophysical and Thermochemical Property Data. 2. Uncertainties. *J. Chem. Eng. Data* **2003**, *48*, 1344–1359.
(11) Sandler, S. I. *Chemical and Engineering Thermodynamics*, 3rd ed.; Wiley: New York, 1999.
(12) Bando, S.; Takemura, F.; Nishio, E.; Hihara, E.; Akai, M. Solubility of $CO_2$ in Aqueous Solutions of NaCl at (30 to 60) °C and (10 to 20) MPa. *J. Chem. Eng. Data* **2003**, *48*, 576–579.
(13) Yang, S. O. Measurements and Predictions of Phase Equilibria for Water+Natural gas Components in Hydrate-Forming Conditions, Dissertation, Korea University, Seoul, 2000.

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