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Experimental Study of Solubility of Natural Gas Components in Aqueous Solutions of Ethylene Glycol at Low-Temperature and High-Pressure Conditions

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A new experimental setup has been validated to measure gas solubility at low-temperature and high-pressure conditions. Solubility of natural gas components, for example, methane, nitrogen, and carbon dioxide, was measured in aqueous solutions of (40 and 60) mass % of ethylene glycol at (15.00 and 20.00) MPa and at temperatures of (−10.0, 0.0, and 10.0) °C.

Introduction

The marine transportation of compressed natural gas (CNG) is a new alternative to monetize stranded natural gas reserves.[1] Several technologies have been developed and are in commercialization stages.[2−4] The methods and apparatus for transporting compressed gas include a gas storage system having a plurality of pipes connected by a manifold whereby the gas storage system can be designed to operate in the pressure range of the minimum compressibility factor for a given gas composition. Diverse systems are proposed for ship-based transport of CNG. In general, marine CNG systems are based on uploading and unloading to ships under variable pressures; however, one of the systems is based on loading and offloading under isobaric conditions.[3] A displacement fluid [such as ethylene glycol (EG)] may be used to load or offload the gas from the gas storage system. It can also be used as an inhibitor to prevent hydrate formation in flow lines. Hydrocarbons and other natural gas components may be partially dissolved in EG, which can potentially reduce its effectiveness as a hydrate inhibitor or change its properties. It is therefore important to quantify the amount of natural gas components dissolved during the multiple use of EG for various process conditions: pressures, temperatures, and EG concentrations. For this purpose, extensive experimental work has been done to measure the solubility of natural gas components in aqueous EG solutions at various temperature and pressure conditions.[5−11] The experimental data were regressed to derive the corresponding binary interaction parameters for a reliable prediction of natural gas components dissolved in aqueous EG solutions.

Russel et al.[5] measured the solubility of natural gas in DEG at 38 °C. Khoroshilov et al.[6] measured the solubility of natural gas in DEG at temperatures between (15 and 25) °C and pressures up to 13.3 MPa. Borodina and Nam measured the solubility of natural gas in DEG at the temperature range of (20 to 60) °C and the pressure range of (0.1 to 10.0) MPa.[7] The solubility of methane in EG was measured by Jou et al.[8] and Yokoyama et al.;[9] however, their measurements were in the temperature range of (25 to 125 °C) and focused only on the solubility of methane in EG.

Natural gas contains mostly methane, but in some cases CO_2 and N_2 content can be significant, and it is of practical importance to study the solubility of natural gas and its major constituents. Zheng et al.[10] measured the solubility of natural gas and its components (CO_2 and N_2) in EG at temperatures between (50 and 125) °C and various pressures. However, there is still a lack of data on the solubility of high-pressure natural gas and its components in aqueous solutions of EG, especially in low temperatures. In this work we validated a new experimental setup for the measurement of gas solubility in liquids and measured the solubility of binary systems of aqueous EG−methane, aqueous EG−N_2, and aqueous EG−CO_2 at (−10.0, 0.0, and 10.0) °C and (15.00 and 20.00) MPa.

Materials and Experimental Setup

Methane (99 %), N_2 (ultrahigh purity, 99.999 %), and EG (99.99 %) used in this research work were purchased from Praxair Canada and Brenntag Canada Inc., respectively. The high-pressure cell (DBR series II phase behavior PVT apparatus) and gas measurement equipment were manufactured by Schlumberger Oilphase-DBR. A schematic flow diagram of the experimental system (PVT analysis equipment) is depicted in Figure 1.

The PVT equipment comprises three basic units: a positive displacement pump, a temperature chamber, and the equilibrium cell. The working temperature range and maximum pressure of this equilibrium cell are (−35 to 200) °C and 100 MPa, respectively. The PVT cell is equipped with a magnetic mixer that provides vigorous mixing and ensures gas−liquid phase equilibrium while reducing the total required experimental time. The PVT cell is placed in the constant-temperature chamber (air bath) to maintain the desired working temperature while the pressure in the cell is maintained by a precise positive displacement pump connected to the cell by a valve shown in Figure 1.

The gasometer supplied by Schlumberger Oilphase-DBR as a component of the PVT system was used to measure the

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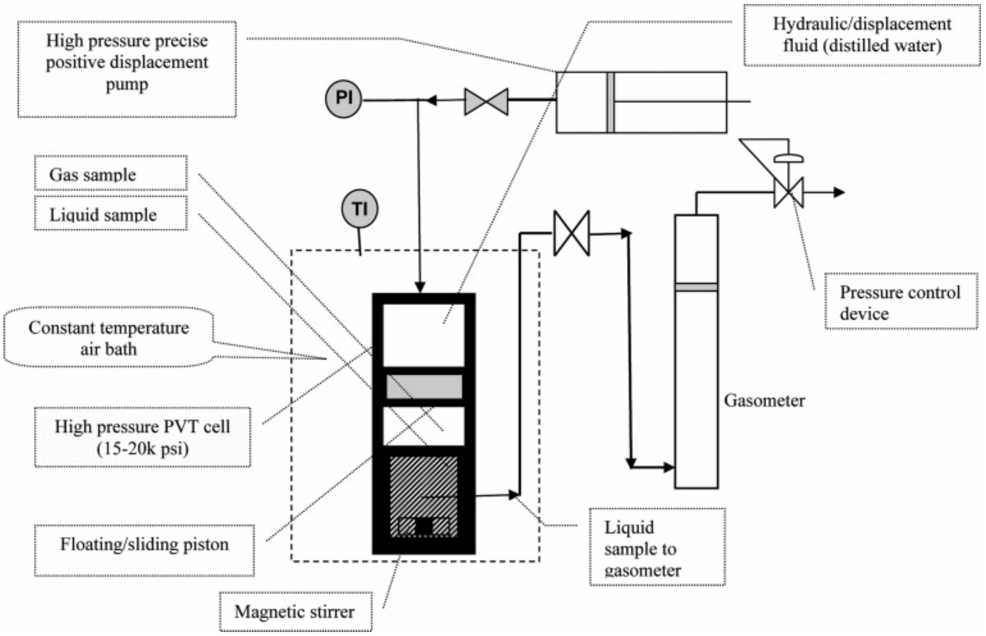

Figure 1. Schematic flow diagram of the experimental system.

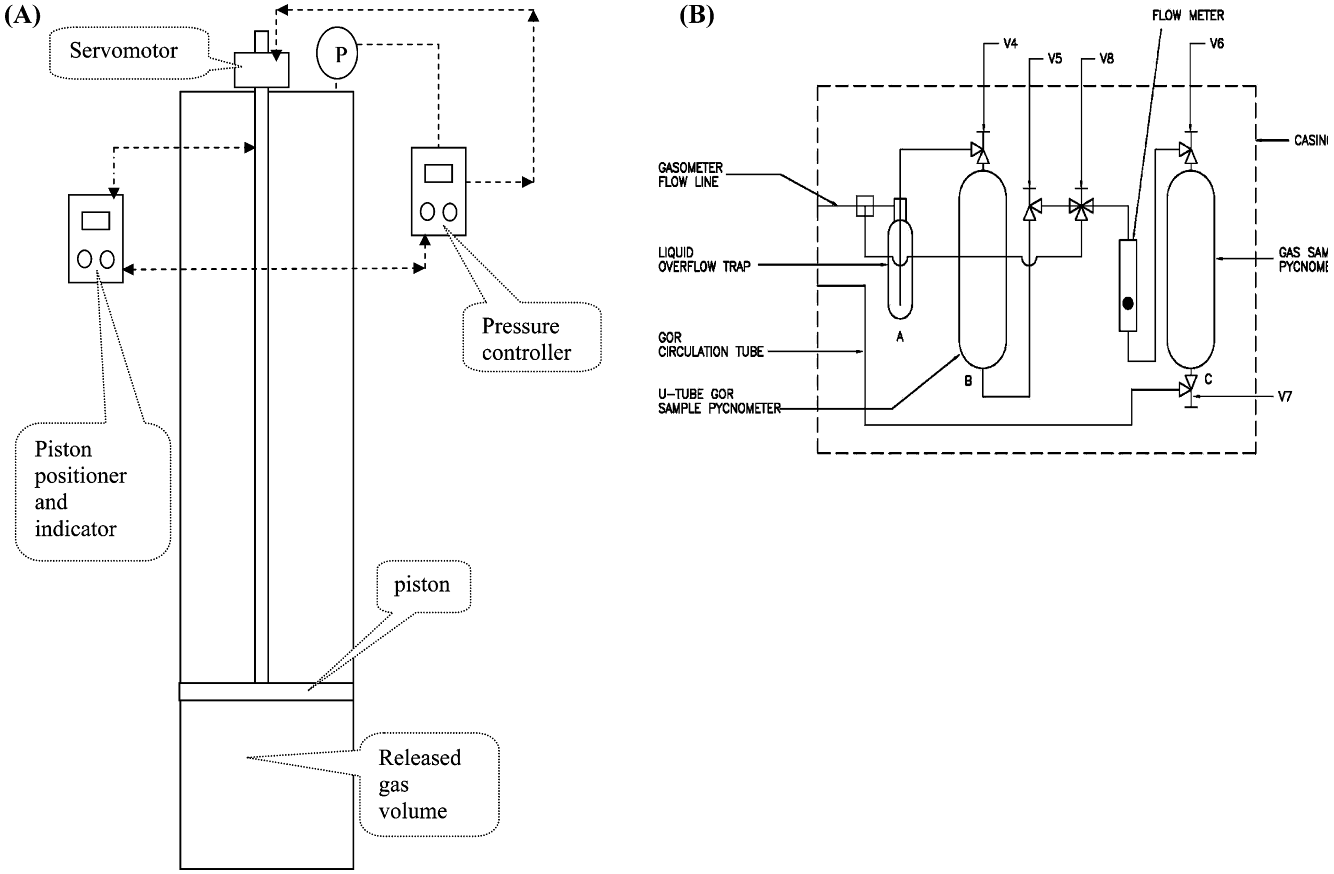

Figure 2. DBR gasometer assembly: A, motorized volume displacement gasometer; B, sampling vessel assembly.

solubility of natural gas components in ethylene glycol. The gasometer uses a motor-driven piston in a stationary cylinder to measure the exact volume of the released gas under atmospheric conditions. The piston displacement is monitored to determine the swept volume of the cylinder. The cylinder pressure is automatically held at 1 atm by a pressure controller. As the gas enters the gasometer, a pressure-sensing device responds to any pressure change and controls the motor to reposition the piston. This restores a null pressure reading in the gasometer. The piston motion is tracked by a linear encoder. This reading is converted to show the gas volume (liters) in the cylinder. The fluid sample is flushed at the atmospheric pressure, and the amount of gas released is measured using the gasometer. The gasometer device schematic is shown in Figure 2.

Experimental Procedure

To perform the solubility tests in the PVT equipment, first the PVT cell is cleaned and evacuated. The high-pressure cell

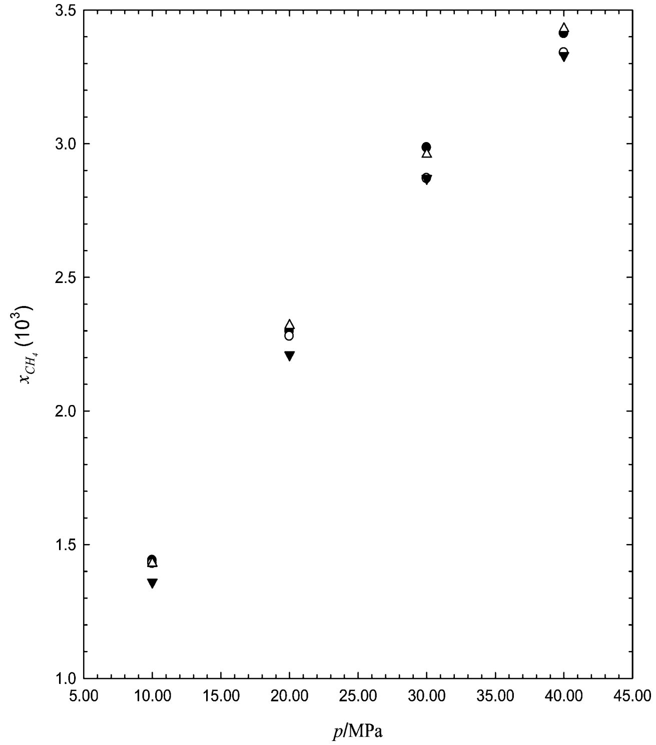

Figure 3. Solubility of methane in pure water at 51.0 °C: ●, this work; ○, O'Sullivan and Smith;[11] ▼, ROP data; [11] △, Ruska data.[11]

Table 1. Results of Solubility Tests for Validation Purposes: Methane−Water System at 51.0 °C

	methane mole fractions (10^3)			
p/MPa ± 0.04	this work	O'Sullivan and Smith[11]	ROP data[11]	RUSKA data[11]
10.00	1.441	1.43	1.36	1.43
20.00	2.298	2.28	2.21	2.32
30.00	2.985	2.87	2.87	2.96
40.00	3.412	3.34	3.33	3.43

Table 2. Results of Solubility Tests for Validation Purposes: Methane−Ethylene Glycol System at 25.0 °C

this work		Wang et al.[11]		Jou et al.[8]	
p/MPa ± 0.04	x_{CH_4} ± 0.1 (10^3)	p/MPa ± 0.04	x_{CH_4} ± 0.1 (10^3)	p/MPa ± 0.04	x_{CH_4} ± 0.1 (10^3)
20.35	17.3	20.04	15.9	20.35	18.2
15.53	14.5	15.05	13.5	15.53	15.3
10.74	11.0	10.05	10.3	10.74	12.1
5.94	6.5	5.00	5.7	5.94	7.6

Table 3. Results of Methane and Nitrogen Solubility Tests in 60 % Ethylene Glycol Solution

	x_{N_2} ± 0.1 (10^3)		x_{CH_4} ± 0.1 (10^3)	
t/°C ± 0.2	p/MPa = 15.00	p/MPa = 20.00	p/MPa = 15.00	p/MPa = 20.00
10.0	2.02	2.24	3.43	3.66
0.0	2.05	2.42	3.17	3.77
−10.0	2.42	2.72	3.51	4.26

Table 4. Results of Nitrogen Solubility in 40 % Ethylene Glycol Solution at (15.00 and 20.00) MPa

	x_{N_2} ± 0.1 (10^3)	
t/°C ± 0.2	p/MPa = 15.00	p/MPa = 20.00
10	1.69	1.87
0	1.83	1.91
−10	2.26	2.37

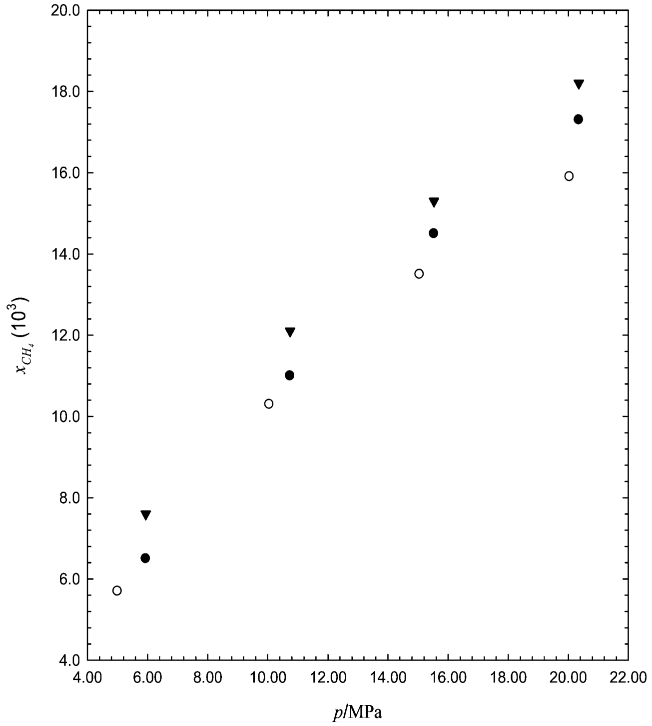

Figure 4. Solubility of methane in pure ethylene glycol: ●, this work; ○, Wang et al.;[11] ▼, Jou et al.[8]

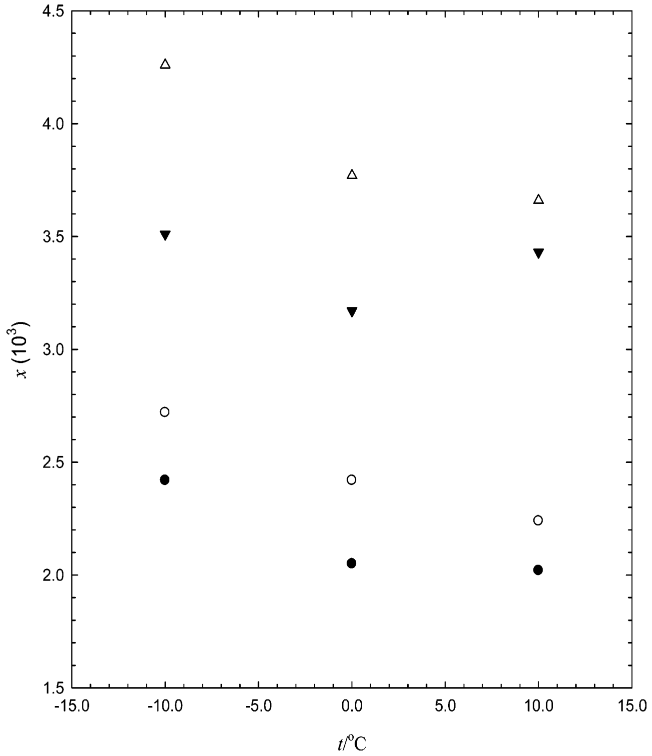

Figure 5. Effect of temperature on nitrogen and methane solubilities in 60 mass % ethylene glycol solution at (15.00 and 20.00) MPa: ▼, CH_4 at 15.00 MPa; △, CH_4 at 20.00 MPa; ●, N_2 at 15.00 MPa; ○, N_2 at 20.00 MPa.

is then charged with the gas and desired volume of the aqueous EG solution (~ 50 cm^3). The cell containing the EG solution and the gas is pressurized by the displacement pump to the desired pressure. The liquid−gas mixture is well agitated by the magnetic stirrer at the bottom of the cell in order to reach the equilibrium as quickly as possible. Ample time is provided until the two phases reach equilibrium (between 45 min and 60 min). When equilibrium at the desired temperature and pressure was established, a (7 to 10) mL sample is taken from the cell into a steel sample container. The steel sample container is

Table 5. Results of Methane Solubility in 40 % Ethylene Glycol Solution at (15.00 and 20.00) MPa

	$x_{CH_4} \pm 0.1\ (10^3)$		
t/°C ± 0.2	p/MPa = 15.00	p/MPa = 20.00	p/MPa = 30.00
0.0	4.11[a]	4.48[a]	4.54[a]
10.0	3.88	4.51	4.45

[a] Hydrate fog formed during the tests; data are presented to show the trend but might not be suitable for thermodynamic modeling.

Table 6. Results of Nitrogen Solubility Tests in 60 % and 40 % Ethylene Glycol Solutions

	60 mass % EG $x_{N_2} \pm 0.1\ (10^3)$		40 mass % EG $x_{N_2} \pm 0.1\ (10^3)$	
t/°C ± 0.2	p/MPa = 15.00	p/MPa = 20.00	p/MPa = 15.00	p/MPa = 20.00
10.0	2.02	2.24	1.69	1.87
0.0	2.05	2.42	1.83	1.91
−10.0	2.42	2.72	2.26	2.37

Table 7. Results of Carbon Dioxide Solubility in 60 % Ethylene Glycol Solution at (0.0 and 15.0) °C

	$x_{CO_2} \pm 0.1\ (10^3)$	
p/kPa ± 40	t/°C = 0.0	t/°C = 15.00
1034	0.1	0.8
2068	3.8	4.0
3446	3.6	4.3

Table 8. Results of Carbon Dioxide Solubility in 40 % Ethylene Glycol Solution at (0.0 and 30.0) °C

	$x_{CO_2} \pm 0.1\ (10^3)$	
p/kPa ± 40	t/°C = 0.0	t/°C = 30.00
1034	0.5	0.4
2068	1.3	1.7
3446	1.7	2.2

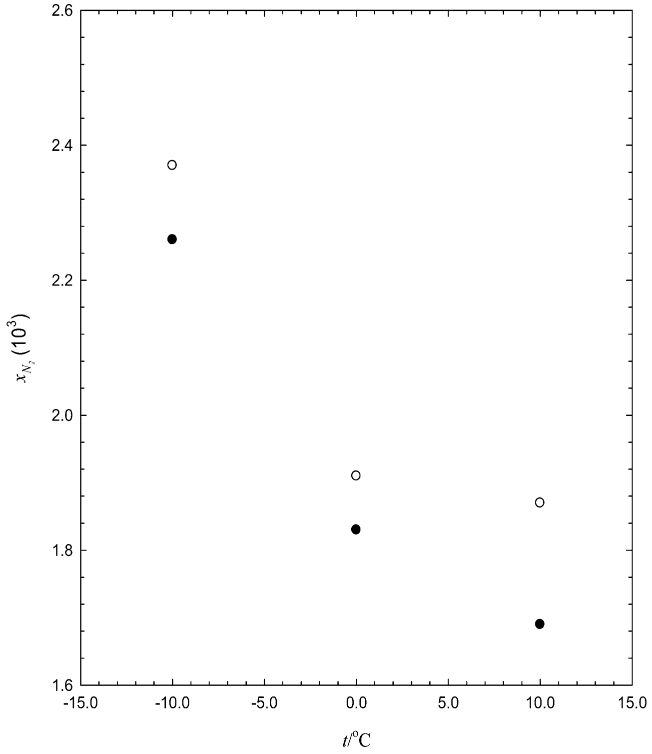

Figure 6. Effect of temperature on nitrogen solubility in 40 mass % ethylene glycol solution at (15.00 and 20.00) MPa: ●, N_2 at 15.00 MPa; ○, N_2 at 20.00 MPa.

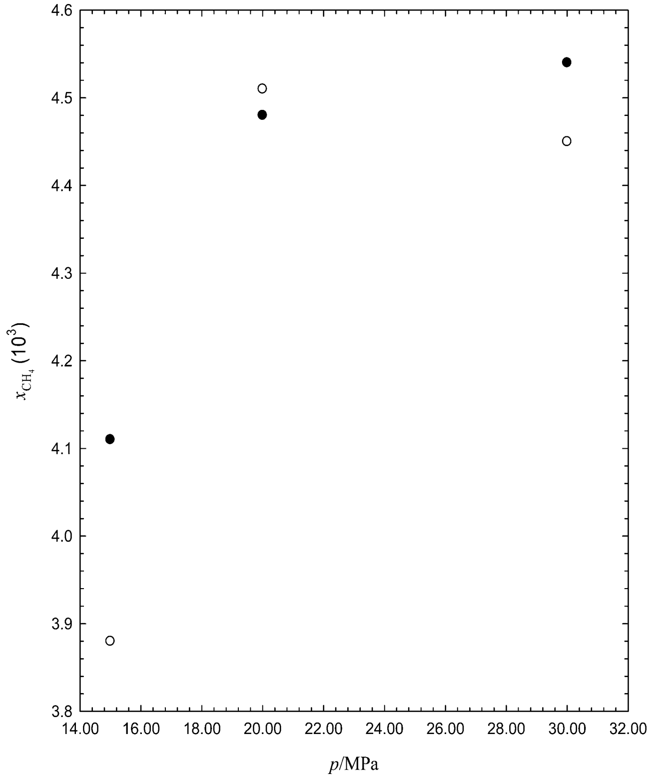

Figure 7. Effect of pressure on methane solubility of in 40 mass % ethylene glycol solution at (0.0 and 10.0) °C: ●, CH_4 at 0.0 °C; ○, CH_4 at 10.0 °C. Note that hydrate was formed at 0 °C.

purged with the same gas used in the solubility test before each sampling. By purging, we make sure that no contamination exists. The sampler is then equilibrated with the atmosphere so that when the sample is flashed into the sampler the pressure goes above atmospheric pressure to accommodate the positive pressure required for the released gas volume measurement. The sample containing the same gas that was dissolved in the liquid under the equilibrium condition remains in liquid phase until it is delivered to the sampler container, which is attached to the cell sampling port with a short steel tube. The weight of the sample cylinder is taken before and after the sample is taken. Sample is then gradually flashed at ambient temperature and pressure in the gasometer. The gasometer is also purged with the respective gas, the solubility of which is to be measured, prior to flashing the sample into it. This eliminates the presence of air or other gases in the gasometer. The amount of gas liberated from the sample is measured, and its volume is displayed on the gasometer. The sample container is again weighed after flashing the sample into the gasometer. The amount of gas evolved from the sample is recorded and plotted in terms of pressure versus mole fraction of the gas. The mole fractions were calculated by measuring the volume of gas evolved using the GOR apparatus. The GOR apparatus was calibrated by releasing known volumes of gases charged to a high-pressure picnometer. The weights of picnometers were measured, before and after the gas was charged and/or released, using a Sartorius balance with a resolution of 0.001 g. The average uncertainties of gas volume measurements and mole fractions were therefore calculated to be about ± 0.2 % and ± 0.0001 of the calculated average values, respectively. The resolution of pressure measurement is ± 0.1 kPa. The pressure sensors were calibrated against known pressures, and we had a maximum uncertainty of ± 40 kPa within the measured pressure range of (15.00 to 20.00) MPa. The temperature of the sample is maintained within the temperature-controlled chamber with an accuracy of ± 0.1 °C. The thermocouples were calibrated with deionized water (ice and boiling at known pressure), and

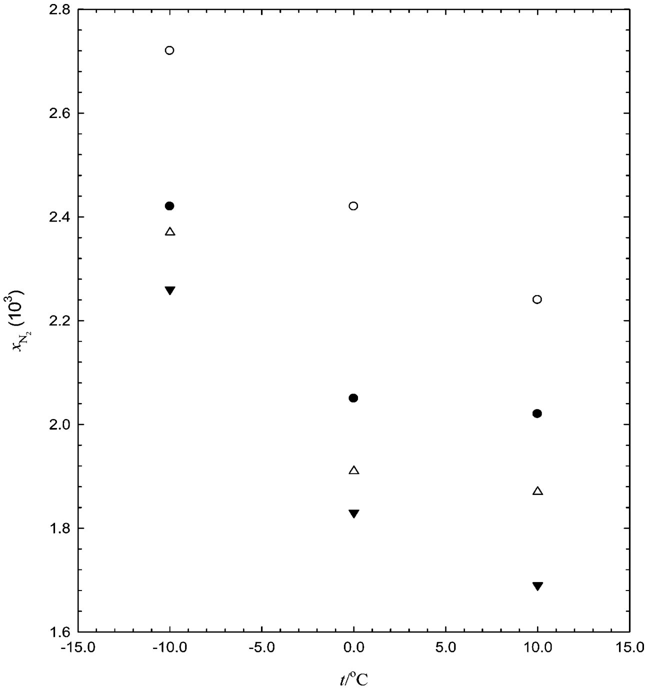

Figure 8. Effect of temperature on nitrogen solubility in (40 and 60) mass % ethylene glycol solutions at (15.00 and 20.00) MPa: ●, at 15.00 MPa and 40 mass % ethylene glycol; ○, at 20.00 MPa and 40 mass % ethylene glycol; ▼, at 15.00 MPa and 60 mass % ethylene glycol; △, at 20.00 MPa and 60 mass % ethylene glycol.

the maximum uncertainty was less than ± 0.2 °C. Some preliminary experiments have been conducted to prove the capability of the system for proposed solubility tests. The solubilites of methane in water measured at 51.0 °C and 100 % EG measured at 25.0 °C by the PVT equipment are shown in Figures 3 and 4. The data obtained by PVT equipment were compared with the results presented in previous research work.[8,11,12] The results are also summarized in Tables 1 and 2, and they are within a reasonable range with the measured data reported in the literature, which indicates that the experimental setup is capable of conducting gas−liquid solubility tests very efficiently.

Results and Discussion

Experimental data for the solubility of nitrogen, methane, and carbon dioxide in aqueous solutions of ethylene glycol were measured. Lower temperature ranges were intentionally selected as there were no experimental data available in the literature for near-zero temperature ranges. The results are summarized in Tables 3 to 8 and shown in Figures 5 to 10. The values of solubilities are given in mole fractions (x) in various concentrations of ethylene glycol solutions. As can be seen in the diagrams the impact of temperature on the solubility is very small compared to that of pressure. In most cases the solubility increased slightly with temperature, whereas the pressure effects remained significantly high. Given the very small changes in solubility and the accuracy of measurements, no clear trend (increasing or decreasing) could be concluded for the temperature ranges studied in this work. For temperatures below −10.0 °C, extensive hydrate formation prevented accurate measurements of the solubility for the glycol compositions under study. For the 40 mass % ethylene glycol−methane system, the hydrate formation temperatures were approximated from the data given in the literature.[12] We noticed the formation of hydrate in very small quantities at 0.0 °C and heavier accumulation at −10.0 °C. Due to relatively small supersaturations the nucleation occurs very slowly. Methane hydrate formation temperatures in the presence of pure water at (15.00 and 20.00) MPa were estimated using the data given in the literature[13] to be around (17.0 and 19.0) °C, respectively. On the basis of the data reported by Østergaard et al.,[12] the hydrate formation temperatures for 40 mass % EG solution at (15.00 and 20.00) MPa are estimated to be around (−1.0 and 2.0) °C, respectively. Therefore, the data presented in Figure 7 and Table 4 for temperatures below 0.0 °C should be looked at with the consideration that some hydrates were formed and therefore may result in poor

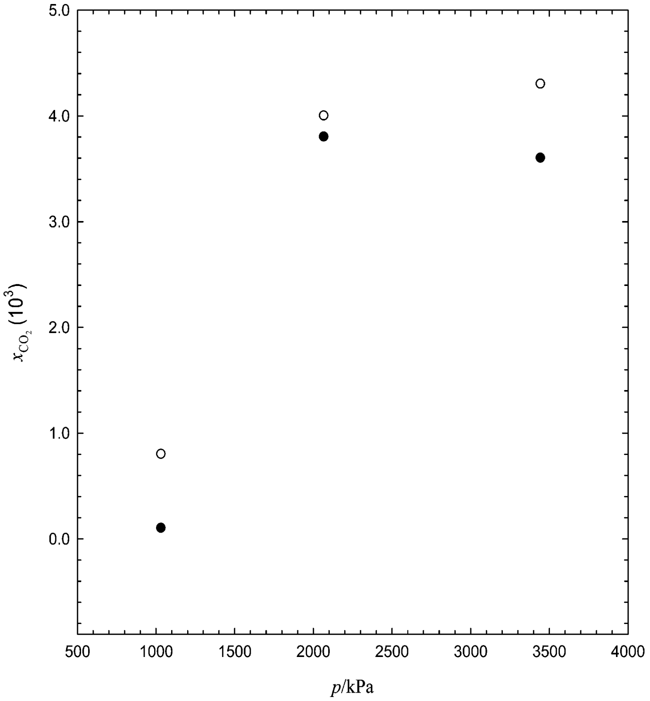

Figure 9. Effect of pressure on carbon dioxide solubility in 60 mass % ethylene glycol solutions at (0.0 and 15.0) °C: ●, CO_2 at 0.0 °C; ○, CO_2 at 15.0 °C.

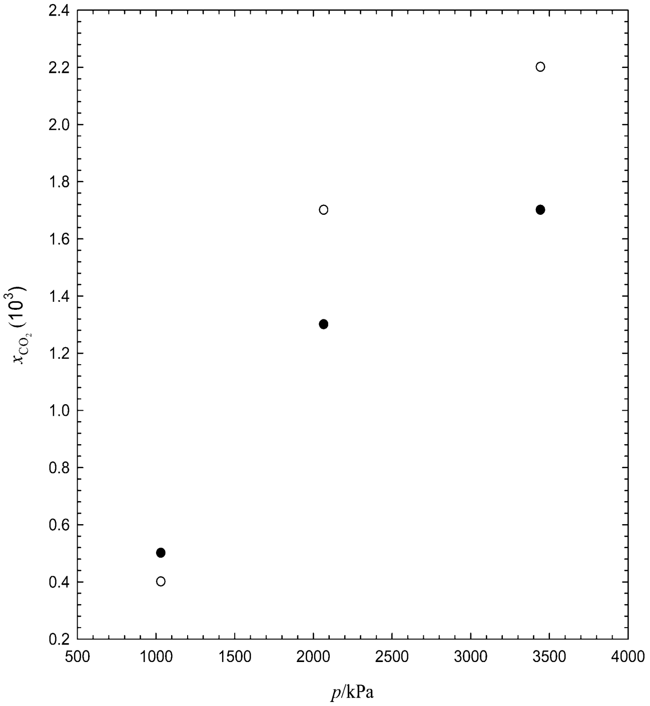

Figure 10. Effect of pressure on carbon dioxide solubility in 40 mass % ethylene glycol solutions at (0.0 and 30.0) °C: ○, CO_2 at 30.0 °C; ●, CO_2 at 0.0 °C.

consistencies in thermodynamic modeling. The data are presented here only to show the observed trends.

Figures 9 and 10 show the solubility of carbon dioxide in (60 and 40) mass % EG solutions. Looking at the carbon dioxide phase diagram,[13] we noticed that liquefaction can start at about (2.50 and 3.50) MPa for temperatures of (0.0 and 15.0) °C, respectively. As seen in Figure 9 the solubility approaches a plateau above 2.00 MPa as above this pressure, carbon dioxide liquefies and liquid−liquid solubility should be measured. At 15.0 °C, liquefaction starts at pressures above 3500 kPa.

Conclusions

Solubilities of nitrogen, methane, and carbon dioxide in different concentrations of ethylene glycol were measured. The calibration results confirmed the previous studies. The new PVT/GOR system used in our studies offers an experimental setup to measure gas solubilities at different temperatures and pressures and enables the study of natural gas hydrate formation. Our studies also showed that hydrate can be easily formed in temperatures below −10 °C even in the presence of a 60 mass % ethylene glycol mixture.

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