1246 *J. Chem. Eng. Data* **2008,** *53,* 1246–1249

Experimental Measurements of Vapor–Liquid Equilibria of the H_2O + CO_2 + CH_4 Ternary System

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Reported are the experimental measurements on vapor–liquid equilibria in the $H_2O + CO_2 + CH_4$ ternary system at temperatures from (324 to 375) K and pressures from (10 to 50) MPa. The results indicate that the CH_4 solubility in the ternary mixture is about 10 % to 40 % more than that calculated by interpolation from the Henry's law constants of the binary system, $H_2O + CH_4$, and the solubility of CO_2 is 6 % to 20 % more than what is calculated by the interpolation from the Henry's law constants of the binary mixture, $H_2O + CO_2$.

Introduction

The solubility of carbon dioxide in water or methane in water has been extensively studied, and the models based on these experimental data have been well established.[1,2] These models can not only accurately reproduce the experimental data but also extrapolate beyond the experimental range, thus finding wide applications in fluid inclusions study, CO_2 sequestration, and the investigation of the formation conditions of methane hydrate. However, natural fluids are often more complicated than binary mixtures. In many cases, natural fluids are composed of the ternary system $H_2O + CO_2 + CH_4$, which is widely found in fluid inclusions[3–5] and geopressured−geothermal reservoirs (e.g., Gulf of Mexico[6] and Hungary[7]). Methane is often dissolved in formation brine, which can be a potentially important sink for CO_2 sequestration. Now a series of questions arise: How do you calculate the solubility of the CO_2 and CH_4 in the ternary? How do you calculate the internal pressure of fluid inclusions at the homogenization temperature? Is CH_4 saturated in CO_2-bearing geopressured reservoirs and expelled from dissolved gas to form free-gas? In the geological sequestration of CO_2, is it possible to recover CH_4 from brine by injecting CO_2? All these questions cannot be answered with confidence if the liquid–vapor phase equilibrium of the $H_2O + CO_2 + CH_4$ system is not known quantitatively.

Surprisingly, there is very little experimental data reported for the $H_2O + CO_2 + CH_4$ ternary system. Dhima et al.[8] reported nine data points on the solubility data of methane and carbon dioxide in pure water at 345 K and pressures from (10 to 100) MPa. However, the solubility of gases or the liquid–vapor phase behavior changes dramatically with temperature and pressure. The data at the single temperature are not sufficient to draw conclusions about the phase behavior of the ternary system.

In this study, we measure the distribution of methane and carbon dioxide between liquid and vapor (or mutual solubilities) in the ternary system, $H_2O + CO_2 + CH_4$, at (324 and 375) K at pressures from (10 to 50) MPa, with the reaction cell used for hydrothermal solution studies at U.S. Geological Survey (Menlo Park). Based on the experimental data, some important conclusions about multicomponent-gas solubility are drawn.

Table 1. Vapor–Liquid Equilibria in the H_2O (1) + CO_2 (2) System

T / K	P / MPa	x_2 / (new data)	model[a]	y_2 / model[a]
375.0	49.9	0.0275	0.0285	0.9639
375.5	40.3	0.0256	0.0265	0.9663
375.8	30.4	0.0234	0.0241	0.9691
375.3	20.3	0.0208	0.0208	0.9726
375.2	10.6	0.0153	0.0148	0.9749
324.1	49.6	0.0302	0.0298	0.9918
323.6	30.1	0.0247	0.0263	0.9927

[a] Calculated from Duan and Sun.[2] x_2 is the mole fraction of CO_2 in liquid, and y_2 is the mole fraction of CO_2 in the vapor of the binary H_2O (1) + CO_2 (2) system.

Experimental

Apparatus. The experiments were conducted in the water−rock interaction laboratory of the U.S. Geological Survey (Menlo Park, CA). The reaction cell from the hydrothermal solution equipment similar to that described by Seyfried et al.[9] was previously used to measure the solubility of carbon dioxide[10] or methane[11] in pure water. All the solubility experiments were conducted in a custom designed reaction cell manufactured to our specifications by Newport Scientific and modified by Coretest Inc. This apparatus featured a titanium-lined autoclave with a 200 cm^3 capacity. The solid titanium closure contains three 1.59 mm compression fittings to accommodate two titanium sampling tubes and one thermocouple. Special microbore titanium valves are secured to each sampling tube. The total dead volume, including a fitting to attach a gastight syringe, was 0.535 cm^3. A second thermocouple was fitted to the base of the autoclave. The stock flat gasket was modified to accept a more reliable delta gasket. The entire assembly was secured to a furnace that rotates through 180° and could be sampled in either an upright or inverted position.

Temperature was maintained by a dual set point proportionating controller (Omega). Temperature was measured with two type K thermocouples calibrated with a Platinum RTD cerified

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10.1021/je700473e CCC: $40.75

Table 2. Vapor–Liquid Equilibria in the H_2O (1) + CH_4 (3) System

T	P	x_3		y_3
K	MPa	(new data)	model[a]	model[a]
375.8	49.9	0.0041	0.0041	0.9948
375.8	40.2	0.0035	0.0036	0.9943
375.6	30.2	0.0030	0.0030	0.9934
376.1	20.6	0.0023	0.0023	0.9916
375.7	10.9	0.0014	0.0014	0.9869
324.4	49.5	0.0039	0.0038	0.9992
324.2	30.1	0.0030	0.0030	0.9990

[a] Calculated from Duan and Mao.[1] x_3 is the mole fraction of CH_4 in liquid, and y_3 is the mole fraction of CH_4 in vapor of the binary H_2O (1) + CH_4 (3) system.

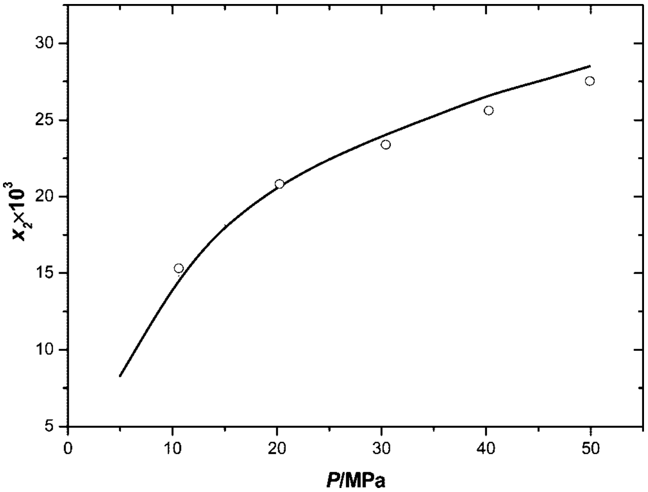

Figure 1. Solubility of CO_2, x_2, in pure water at 375 K. The solid curve is calculated using Duan and Sun (2003), and the measurements of this work are shown by circles.

by Yellow Springs Inc. Pressure was measured with a Heise gauge and a Heise 901B transducer and readout device calibrated by dead weights to an uncertainty of ± 0.1 MPa. Pressure was also measured by a transducer built into a syringe pump used for injecting fluids into the reaction cell.

First, the air present in the equilibrium cell was removed by drawing a vacuum, and then the cell was filled with CH_4 and a vacuum drawn again. This procedure was repeated two or three times. CO_2 and CH_4 were obtained from a zero-grade compressed-gas cylinder with a tube individually. For the first series of experiments, CO_2 and CH_4 were injected into the reaction cell via a titanium separator. Later experiments utilized a modified syringe pump manufactured by ISCO Inc., model 100 DX.

Materials. Research purity (purity given as 99.99 %) carbon dioxide and methane from the Matheson Co. Inc. were used. Water was prepared with distilled–deionized water.

Sampling and Analysis. In general, gases and water were continuously mixed (via rotation, 6 times per min) and allowed to equilibrate for (8 to 36) h depending on temperature and pressure. Previous to sampling the liquid phase, the furnace rotation was stopped and then kept in an inverted position for approximately (30 to 60) min to ensure complete separation of the liquid phase from the vapor phase. Samples of the liquid phase were obtained via a gastight syringe with an integral valve (vacuumed, total dead volume of 0.01 cm^3) containing (1 to 2) cm^3 of 17 % sodium hydroxide aqueous solution to fix the dissolved CO_2 as carbonate and bicarbonate. Typically, triplicate samples were taken at each sampling period, and the first part of flow was discarded because it was normally contaminated by residual material in the capillary tubes and sampling block. The volume of the lines and blocks was approximately 0.6 cm^3, thus triplicate samples of approximately 1 g each were taken after an initial (0.5 to 0.7) g was discarded with each sampling. Pressure was kept at or a little above the experimental pressure to prevent CO_2 and CH_4 from evolving from solutions. During the sampling process, the pressure was maintained by using the modified syringe pump manufactured by ISCO Inc., model 100 DX. The temperature drop during sampling was normally less than 1 K.

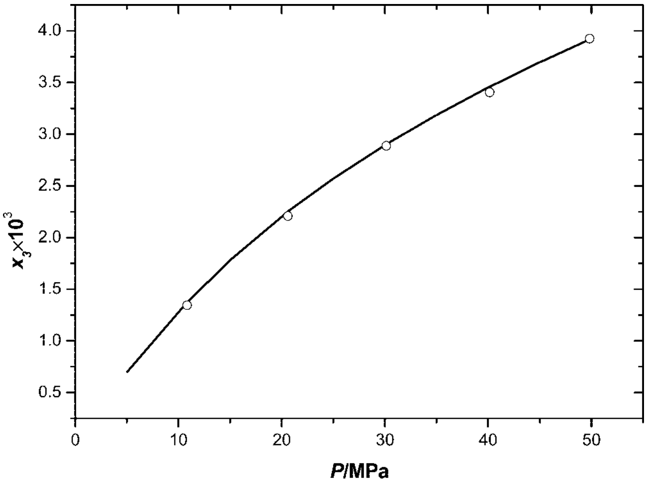

Figure 2. Solubility of CH_4, x_3, in pure water at 375 K. The solid curve is calculated using Duan and Mao (2006), and the measurements of this work are shown by circles.

Once the sampling of the liquid phase was completed, the furnace was rotated to the upright position and kept at this position for (30 to 60) min. Samples of the vapor phase were also obtained via a gastight syringe with an integral valve containing 2 cm^3 of the sodium hydroxide solution. Approximately 0.03 g of sample was taken for the determination of the vapor phase after an initial (0.5 to 0.7) g was discarded with each sampling.

A simple but efficient method was used to analyze dissolved CH_4 in the sampling syringe. The bottom of a glass tube (minimum scale 0.02 cm^3) filled with water and with an open bottom and sealed top was immerged vertically in a 2 L beaker filled with water. When analyzing, the dissolved CH_4 in the sampling syringe was injected into the glass tube via a plastic capillary tube at room temperature and about 1 bar, and the volume of CH_4 was measured by this method. The ideal gas law was used to calculate the total number of moles of CH_4 evolving from the sampled solution.

The dissolved CO_2 was completely converted to HCO_3^- and CO_3^{2-} by adding an excess of NaOH, thus eliminating $CO_2(aq)$. Dissolved CO_2 was analyzed by coulometric titration on a UIC Coulometrics model CM5012 standardized by calcium carbonate solutions. Replicate analyses are precise typically within (1 to 2) %.

In the H_2O (1) + CO_2 (2) + CH_4 (3) ternary system, the composition of H_2O in the vapor phase was estimated by binary systems. Since the maximum temperature of our measurements is only a little above 373 K, the partial pressure of H_2O is not much different from 1 bar, which is relatively small compared with the pressure of our experiment. Since our real interest is the distribution of CO_2 and CH_4 between liquid and vapor, the ratio of CO_2 to CH_4 is the most important. The uncertainty of the small amount of H_2O in the vapor does not significantly

Table 3. Vapor–Liquid Equilibria Measurements for the Ternary System H_2O (1) + CO_2 (2) + CH_4 (3)

T/K	P/MPa	x_2	x_3	y_2	y_3	y_1	$x_2{}^a$	$x_3{}^a$
375.5	49.9	0.01971	0.00152	0.70305	0.27019	0.02676	0.01935	0.00110
375.5	40.2	0.01882	0.00127	0.70550	0.26930	0.02520	0.01806	0.00095
375.6	30.4	0.01801	0.00104	0.71203	0.26480	0.02317	0.01664	0.00079
375.6	20.6	0.01524	0.00077	0.72455	0.25429	0.02296	0.01508	0.00058
375.9	10.7	0.01065	0.00038	0.72812	0.25108	0.02080	0.01115	0.00035
376.2	49.8	0.01549	0.00215	0.51698	0.46103	0.02199	0.01423	0.00188
375.2	40.3	0.01414	0.00199	0.51593	0.46484	0.01923	0.01321	0.00164
375.3	30.5	0.01369	0.00166	0.53282	0.44813	0.01905	0.01245	0.00126
375.6	20.7	0.01186	0.00127	0.51552	0.46683	0.01765	0.01073	0.00106
375.8	11.0	0.00855	0.00074	0.56551	0.41544	0.01906	0.00866	0.00057
375.7	50.6	0.01179	0.00258	0.39828	0.58351	0.01821	0.01096	0.00238
375.6	40.2	0.01172	0.00222	0.40332	0.57973	0.01695	0.01033	0.00205
375.4	30.2	0.01074	0.00188	0.41424	0.56895	0.01681	0.00968	0.00170
375.4	20.2	0.00940	0.00136	0.41846	0.56573	0.01581	0.00872	0.00129
374.8	10.5	0.00627	0.00084	0.43726	0.54527	0.01747	0.00669	0.00075
324.8	49.3	0.02231	0.00125	0.74103	0.25265	0.00632	0.02241	0.00097
324.8	30.6	0.01966	0.00092	0.76440	0.22968	0.00592	0.01891	0.00069
324.6	50.3	0.01817	0.00186	0.59844	0.39639	0.00517	0.01810	0.00153
324.0	30.8	0.01645	0.00144	0.58432	0.41092	0.00476	0.01446	0.00123
324.2	49.9	0.01131	0.00258	0.32466	0.67206	0.00328	0.00982	0.00219
324.3	30.4	0.01055	0.00196	0.33229	0.66459	0.00312	0.00822	0.00189

[a] x_2 and x_3 are the measured CO_2 and CH_4 mole fractions in the liquid, respectively. y_1, y_2, and y_3 are H_2O, CO_2, and CH_4 mole fractions in vapor, respectively, and y_1 is calculated from binary data, according to eq 1, where $x_2{}^a = y_2 \cdot x_2(H_2O + CO_2)$ and $x_3{}^a = y_3 \cdot x_3(H_2O + CH_4)$.

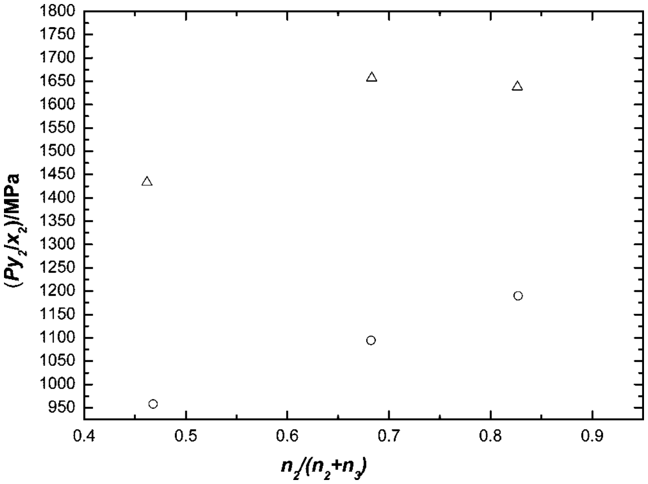

Figure 3. Py_2/x_2 as a function of the ratio of $n_2/(n_2 + n_3)$ in the H_2O (1) + CO_2 (2) + CH_4 (3) system at 324 K. The rectangle is at 49.9 MPa, and the circle is at 30.6 MPa, where n stands for the number of moles in the reaction cell.

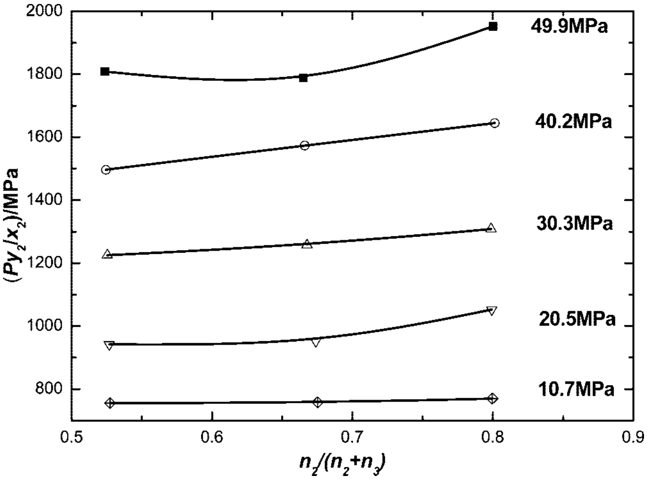

Figure 4. Py_2/x_2 as a function of the ratio of $n_2/(n_2 + n_3)$ in the H_2O (1) + CO_2 (2) + CH_4 (3) system at 375 K, where n stands for the total number of moles in the reaction cell.

affect the results. So we can approximately estimate the H_2O mole fraction in the vapor phase

$$y_1(\text{ternary}) = y_1(H_2O + CO_2 \text{ binary}) \cdot y_2(\text{ternary}) + y_1(H_2O + CH_4 \text{ binary}) \cdot y_3(\text{ternary}) \quad (1)$$

where y stands for mole fraction of the vapor phase.

The temperature measurement uncertainty was estimated to be ± 1 K with the aforementioned thermocouple, and the pressure was regulated and maintained constant during the sample with an uncertainty of ± 0.1 MPa. Subsequently, we estimate an overall experimental uncertainty of ± 3 % in the gas solubility.

Results and Discussion

System Validation. The solubility of CO_2 or CH_4 in pure water is well-known and was used to test the reliability of our experimental design and sampling protocol. The solubility data of CO_2 or CH_4 in pure water, determined in this study (Tables 1 and 2), are consistent with the models of Duan and Sun[2] and Duan and Mao,[1] which have been validated by a large number of experimental data.

Figure 1 shows our measured solubility data of CO_2 at 375 K, compared with the calculated results from the model of Duan and Sun,[2] indicating that our measured solubility is slightly lower than that of the model, with a maximum deviation of less than 4 %. Figure 2 shows our measured solubility of CH_4 at 375 K, compared with that of Duan and Mao,[1] showing that our measured data are almost in exact agreement with the model of Duan and Mao.[1] The agreement between our new measurements with the well-established models suggests that our measurements are reliable.

Liquid–Vapor Phase Equilibrium of the Ternary Mixtures. Results from the present experimental study of the liquid–vapor phase equilibria of the H_2O (1) + CO_2 (2) + CH_4 (3) mixtures are listed in Table 3. These data include measurements at different ratios of CO_2 to CH_4 at (324.3 and 375.7) K from (10 to 50) MPa. The amount of H_2O in the vapor phase is too small to be measured accurately by our method. Consequently, the compositions of H_2O in the vapor phase listed in Table 3 are estimated by Duan's model.[1,2] Uncertainties by this method should be less than ± 1 % for $(y_2 + y_3)/(y_1 + y_2 + y_3)$.

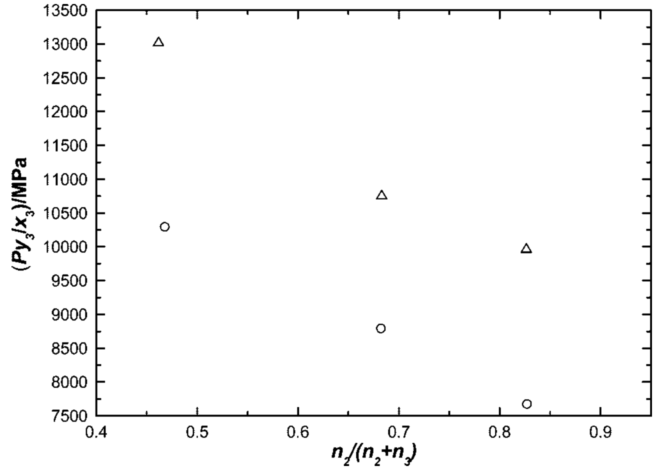

Figure 5. Py_3/x_3 as a function of the ratio of $n_2/(n_2 + n_3)$ in the H_2O (1) + CO_2 (2) + CH_4 (3) system at 324 K. The rectangle is at 49.9 MPa, and the circle is at 30.6 MPa, where *n* stands for the total number of moles in the reaction cell.

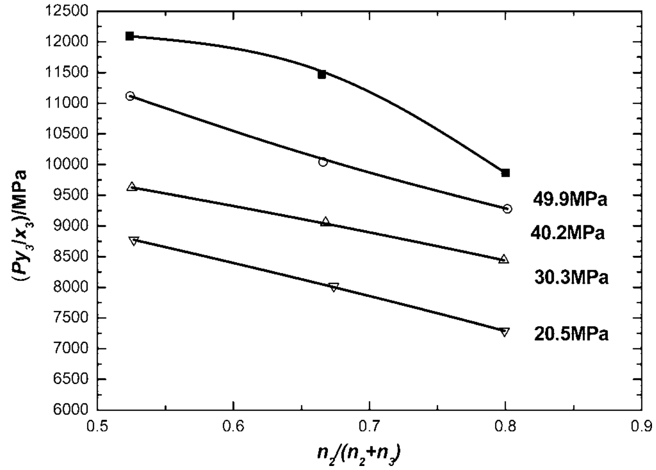

Figure 6. Py_3/x_3 as a function of the ratio of $n_2/(n_2 + n_3)$ in the H_2O (1) + CO_2 (2) + CH_4 (3) system at 375 K, where *n* stands for the total number of moles in the reaction cell.

To compare the solubility of CO_2 and CH_4 in the liquid phase in the ternary system as compared with that in the binary system, we define the apparent Henry's law constant, Py_i/x_i, where *i* stands for CO_2 or CH_4 and *x* stands for the mole fraction in the liquid phase. This constant represents the distribution of a gas between the vapor phase and liquid phase. A larger Henry's law constant represents a smaller solubility of the gas in the liquid.

Figures 3 and 4 show that with the increase of the ratio of CO_2 to CH_4 in the system the apparent Henry's law constant of CO_2 increases appreciably. That means that the more CH_4 is in the system, the smaller the Henry's law constant is. In other words, CO_2 becomes more soluble in the presence of CH_4, and the solubility of CO_2 in the ternary system is (6 to 20) % more than what is calculated from the Henry's law constants derived from the binary, H_2O + CO_2, as can be seen in Table 3.

Figures 5 and 6 show that with the increase of the ratio CO_2 to CH_4 in the system, the apparent Henry's law constant of CH_4 will decrease substantially. That means that the more CO_2 is in the system, the smaller the constant is. In other words, CH_4 becomes more soluble in the presence of CO_2. The measured CH_4 solubility in the ternary mixture is (10 to 40) % more than what we calculated from the Henry's law constant derived from the binary system data, H_2O + CH_4, as can be seen in Table 3.

Acknowledgment

This research was performed in the United States Geological Survey (Menlo Park) Hydrothermal Laboratory. The authors are grateful to Dr. James Bischoff for his help in experimental work. Thanks to Dr. Ken Marsh and three anonymous reviewers for their constructive suggestions for improving the manuscript.

Literature Cited

(1) Duan, Z. H.; Mao, S. D. A Thermodynamic Model for Calculating Methane Solubility, Density and Gas Phase Composition of Methane-bearing Aqueous Fluids from 273 to 523 K and from 1 to 2000 bar. *Geochim. Cosmochim. Acta* **2006**, *70*, 3369–3386.

(2) Duan, Z. H.; Sun, R. An Improved Model Calculating CO_2 Solubility in Pure Water and Aqueous NaCl Solutions from 273 to 533 K and from 0 to 2000 bar. *Chem. Geol.* **2003**, *193*, 257–271.

(3) Ding, W. W.; Dai, J. X.; Chu, F. Y.; Han, X. Q. Geochemical Characteristics of the Fluid Inclusions in the Gangxi Fault Belt, Huanghua Depression, Bohai Bay Basin,China. *J. Zhejiang Univ. Sci. A* **2007**, *8*, 1011–1020.

(4) O'Reilly, C.; Gallagher, V.; Feely, M. Fluid Inclusion Study of the Ballinglen W-Sn-sulphide Mineralization, SE Ireland. *Mineralium Deposita* **1997**, *32*, 569–580.

(5) Yoo, B. C.; Lee, H. K. Gold-Bearing Mesothermal Veins from the Gubong Mine, Cheongyang Gold District, Republic of Korea: Fluid Inclusion and Stable Isotope Studies. *Econ. Geol.* **2006**, *101*, 883–901.

(6) Chacko, J.; Maciasz, G.; Harder, J. *Gulf Coast Geopressured-Geothermal Program Summary Report Compilation*, Executive Summary; 1998, Volume *I*.

(7) Ottlik, P. Geothermal Experience in Hungary. *Geothermics* **1988**, *17*, 531–535.

(8) Dhima, A.; de Hemptinne, J. C.; Jose, J. Solubility of Hydrocarbons and CO_2 Mixtures in Water under High Pressure. *Ind. Eng. Chem. Res.* **1999**, *38*, 3144–3161.

(9) Seyfried, W. E., Jr.; Gordon, P. C.; Dickson, F. W. A New Reaction Cell for Hydrothermal Solution Equipment. *Am. Mineral.* **1979**, *64*, 646–649.

(10) Rosenbauer, R. J.; Koksalan, T. Experimental Determination of the Solubility of CO_2 in Electrolytes: Application to CO_2 Sequestration in Deep-saline Aquifers, Geological Society of America Annual Meeting, 2002; Vol. 135, 2, October 27–30, Denver, Colorado.

(11) Price, L. C. Aqueous Solubility of Methane at Elevated Pressures and Temperatures. *A.A.P.G. Bull.* **1979**, *63*, 1527–1533.

Received for review August 22, 2007. Accepted February 16, 2008. This work is supported by Zhenhao Duan's "Key Project Funds" (No. 40537032) awarded by the National Science Foundation of China and the "Major development Funds" (code #: kzcx2-yw-124) by the Chinese Academy of Sciences.

JE700473E