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Equilibrium Studies for the System Methane + Carbon Dioxide + Neohexane + Water

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Four-phase equilibrium conditions (hydrate−liquid−liquid$_{aq}$−vapor) were studied for the system methane + carbon dioxide + neohexane + water by the pressure search method. In addition, three-phase equilibrium conditions (hydrate−liquid−vapor) were determined for the same system in the absence of neohexane. Experimental conditions were varied in the temperature range of (275 to 285) K and the pressure range of (1.3 to 7.5) MPa. Equilibrium temperature and pressure values were found to agree, within the uncertainties herein reported, with existing literature values for both systems. The data were used to produce experimental contour plots that summarize the equilibrium temperature, pressure, and vapor composition on the same graph. It was observed that the equilibrium mole fraction of carbon dioxide in the vapor phase follows opposite trends in both systems, with respect to equilibrium pressure, at rather constant temperature. The data also suggest that hexagonal structure H equilibrium occurs at lower pressures and temperatures than cubic structure I (sI) when the vapor phase is methane rich; however, this phenomenon appears to be reversed as the equilibrium vapor phase becomes richer in carbon dioxide.

Introduction

Clathrate hydrates are nonstoichiometric, crystalline compounds that form when small molecules come in contact with water at appropriate temperatures and pressures. The terms "gas hydrates" and "clathrate hydrates" are now used interchangeably to designate this kind of compound.[1] Clathrates of natural gas were first observed in pipelines in 1934[2] and have since then been considered a nuisance to the gas and oil industry. Natural-gas hydrates are abundantly found in the ocean bottom and to a lesser extent in permafrost regions.[3] Conservative estimates suggest that the amount of energy stored in natural hydrates is at least twice that of all other fossil fuels combined.[4] In addition, trapping carbon dioxide as a hydrate in the bottom of the ocean has been proposed as an alternative to reduce increasing atmospheric CO_2 concentration.[5] Mixtures of carbon dioxide and methane form cubic structure I (sI) hydrates,[6] but in the presence of a larger molecule, like neohexane, the hexagonal structure H (sH) is also stable.[7,8] Structure H differs from other hydrate structures for it requires at least two guests to form a stable lattice; in addition, sH will form at lower pressures than its corresponding sI hydrate, at the same temperature.

Structure H hydrates were discovered in 1987 by Ripmeester and co-workers.[9] Since then, the study of structure H hydrates has gone beyond a laboratory curiosity: naturally occurring sH hydrates were found by Sassen in 1994,[10] and schemes to transport gas and sequester gas as a solid, in sH form, have been proposed in the past.[11,12] In particular, it has been shown that sH hydrates from methane and neohexane exhibit fast overall formation kinetics and almost 100 % enclathration of methane.[12] Servio et al.[7] have studied equilibria of methane−carbon dioxide mixtures in the presence and absence of neohexane and suggested that above a certain temperature structure H equilibrium moved into a structure I equilibrium regime. This suggestion was later confirmed by Uchida and co-workers,[8] who in addition to equilibrium measurements used Raman spectroscopy and X-ray diffraction to confirm the presence of sH hydrates. Both Servio et al.[7] and Uchida et al.[8] showed partial phase diagrams where equilibrium pressure and temperature of methane + carbon dioxide gas mixtures in the presence of neohexane were compared to mixtures in the absence of neohexane. Comparisons were based on initial gas compositions and not equilibrium, vapor-phase compositions. Servio et al.[7] used only two gas mixtures obtaining limited amounts of data, and Uchida et al.[8] did not report equilibrium vapor-phase compositions. In contrast, methane + carbon dioxide mixtures in contact with water have been studied extensively.[13–18]

In this paper, we report equilibrium pressure, temperature, and vapor-phase composition for the system methane + carbon dioxide + neohexane + water and the same in the absence of neohexane. In addition to completing the equilibrium data set for the system with neohexane, we present experimental contour plots that allow direct comparison of the equilibria of methane + carbon dioxide hydrates with methane + carbon dioxide + neohexane hydrates.

Experimental Apparatus

Experiments were carried out in a Jefri-DBR phase behavior system (Oilphase-DBR-Schlumberger) (Figure 1). The heart of the system was a high-pressure *PVT* cell consisting of a glass cylinder (20 cm in height and total void volume of 150 cm^3), secured between two full-length sight glass windows, inside a stainless steel frame. This design allowed for unimpaired visibility of the entire contents of the cell. Pressure was regulated through an automated, high-pressure, positive displacement pump (Oilphase-DBR-Schlumberger). Fluid inside the pump was connected to a floating isolation piston which exerted pressure on the mixture of interest and prevented contact with the hydraulic fluid inside the glass cylinder. The *PVT* cell was mounted inside a temperature-controlled air bath by means of

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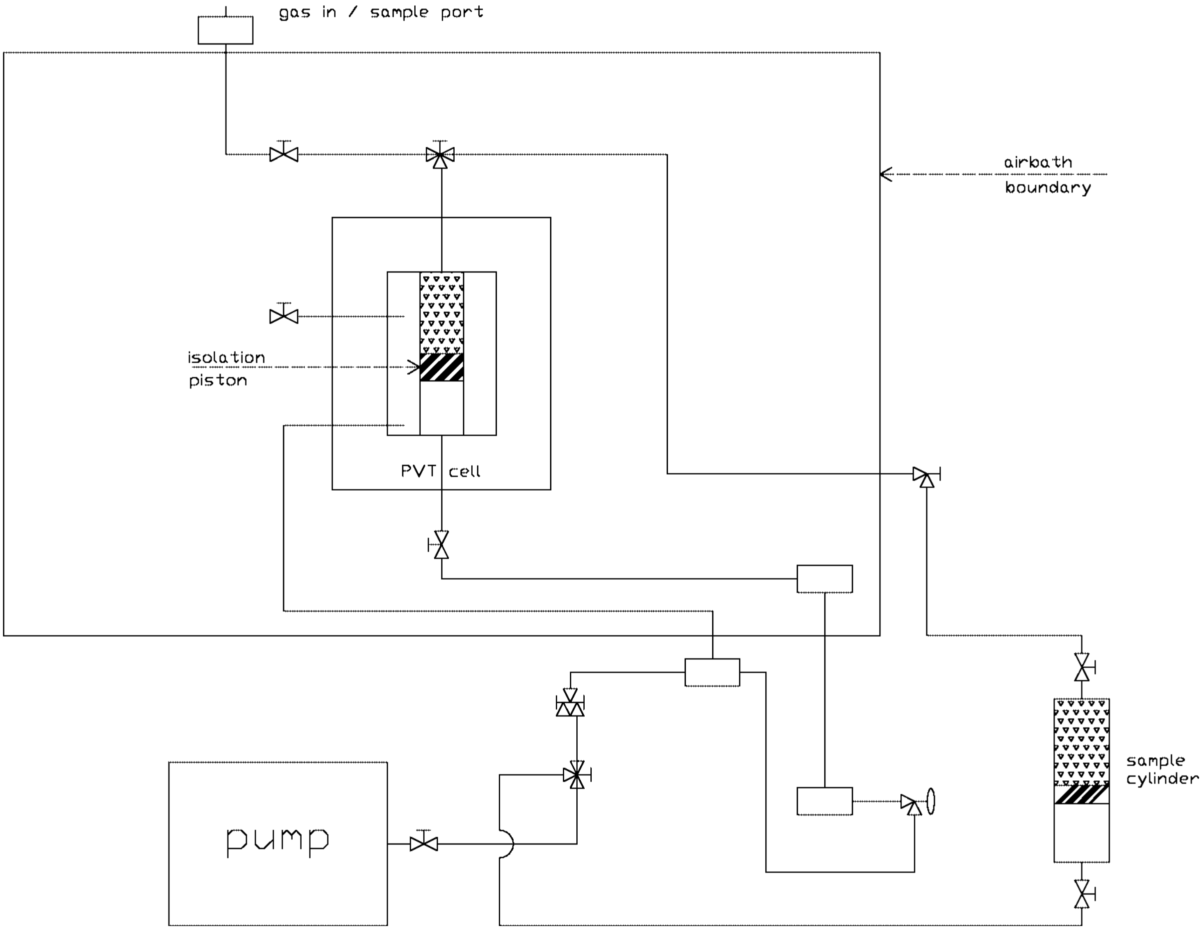

Figure 1. Experimental apparatus.

Table 1. Hydrate−Liquid−Vapor Equilibrium Temperature *T*, Pressure *p*, and Vapor-Phase Mole Fraction of Carbon Dioxide y_1, for the System Methane + Carbon Dioxide + Water

T/K	*p*/MPa	$10^2 y_1$
275.14	2.36	15.6
275.24	1.92	38.5
275.29	2.05	28.4
275.38	2.19	21.5
277.01	2.28	38.0
277.13	2.54	27.4
277.32	2.91	19.5
277.43	3.20	13.3
278.96	2.79	37.3
279.19	3.24	26.5
279.35	3.64	18.7
279.48	3.93	13.1
281.12	4.41	14.6
281.20	3.75	35.1
281.22	4.08	25.0
282.74	4.74	34.7
282.97	5.17	22.1
282.97	4.52	45.5
283.38	6.16	13.6
284.73	5.63	44.4
284.74	5.88	33.6
285.33	6.56	21.3
285.34	7.47	15.1

Table 2. Hydrate−Liquid−Liquid$_{aq}$−Vapor Equilibrium Temperature *T*, Pressure *p*, and Vapor-Phase Mole Fraction of Carbon Dioxide y_1, for the System Methane + Carbon Dioxide + Neohexane + Water

T/K	*p*/MPa	$10^2 y_1$
275.28	1.37	32.0
275.29	1.61	62.3
275.32	1.63	69.9
275.49	1.37	12.9
277.14	1.63	16.3
277.20	1.93	52.0
277.25	1.79	41.6
277.34	2.15	63.2
279.42	2.85	51.5
279.44	2.65	44.6
279.45	2.92	66.2
279.51	2.39	20.7
281.02	3.17	44.9
281.03	3.50	54.0
281.05	2.92	21.4
281.23	3.64	65.9
282.72	3.75	21.8
282.83	4.18	40.5
282.85	4.43	51.7
284.77	5.78	46.6
284.90	5.93	56.1
285.30	5.69	23.1
285.35	6.10	35.4

a bracket, attached to a horizontal shaft. An electric motor powered the shaft, which oscillated through sixty degrees about its center of gravity at forty cycles per minute. Temperature and pressure inside the *PVT* cell were monitored with a platinum RTD probe and a pressure transducer (both supplied with the phase behavior system). Using a coverage factor of $k = 2$ and assuming the corresponding standard uncertainty had a normal distribution, each expanded uncertainty was estimated to be $U_T = 0.2$ K and $U_P = 14$ kPa, for temperature and pressure, respectively.

Vapor-phase samples were taken using a previously evacuated sample bomb and analyzed with a gas chromatograph (Varian CP3800) equipped with a gas sampling, injection valve. After

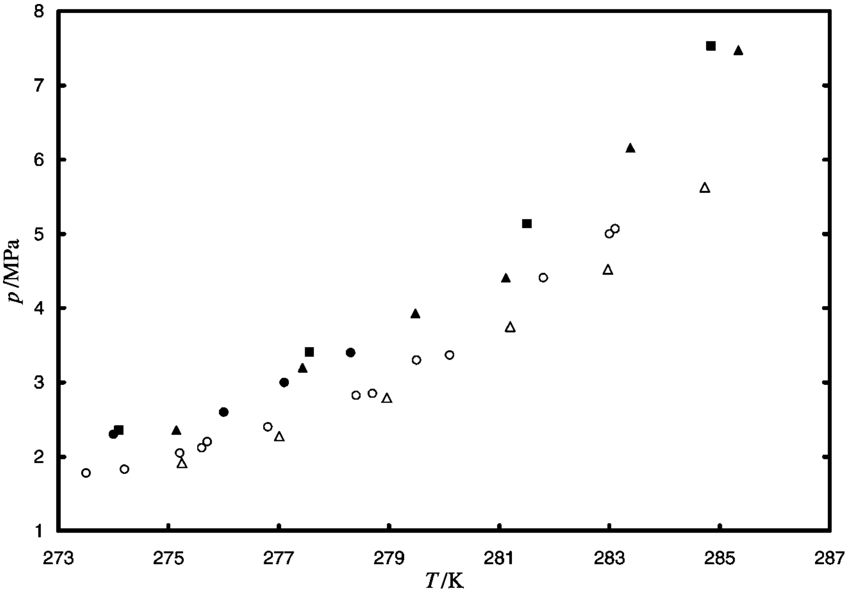

Figure 2. Hydrate−liquid−vapor equilibrium conditions for the system methane + carbon dioxide + water. Black, solid markers represent gas mixtures initially containing a mole fraction of 80 % CH_4 and 20 % CO_2. Empty markers represent gas mixtures initially containing a mole fraction of 50 % CH_4 and 50 % CO_2. ▲ and △, this work; ■, ref 17; ● and ○, ref 7.

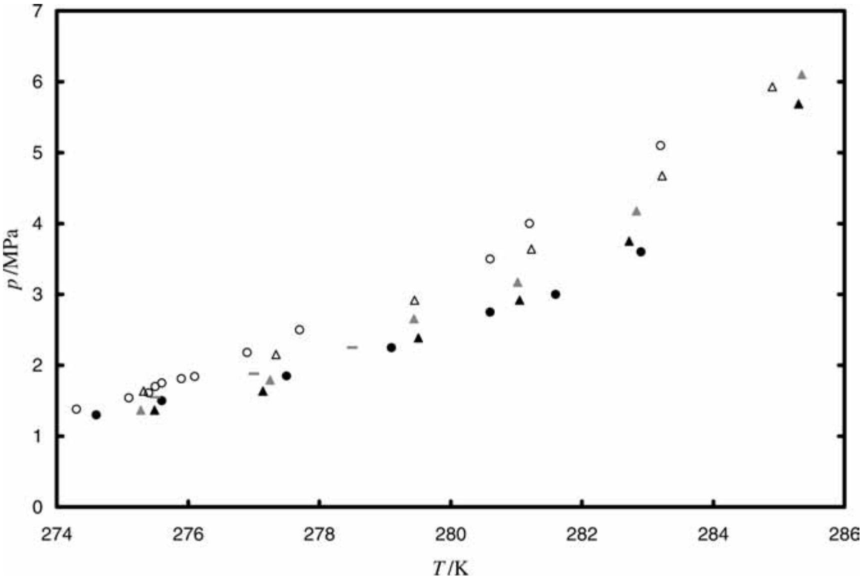

Figure 3. Hydrate−liquid−liquid$_{aq}$−vapor equilibrium conditions for the system methane + carbon dioxide + neohexane + water. Black, solid markers represent gas mixtures initially containing a mole fraction of 80 % CH_4 and 20 % CO_2. Gray, solid markers represent gas mixtures initially containing a mole fraction of 70 % CH_4 and 30 % CO_2. Empty markers represent gas mixtures initially containing a mole fraction of 50 % CH_4 and 50 % CO_2. ▲, gray triangle, and △, this work; ● and ○, ref 7; -, ref 8.

injection, separation of the gas mixture was achieved by passing the sample through an arrangement consisting of a 0.5 m × 1/8″ precolumn, packed with 80 to 100 mesh Hayesep T (Varian Inc.), and a 2.6 m × 1/8″ column, packed with 80 to 100 mesh Hayesep R (Varian Inc.). The effluent was monitored with a thermal conductivity detector.

Experimental Procedure

Gas mixtures containing a mole fraction of 80 %, 70 %, 60 %, and 50 % methane, respectively, the balance being carbon dioxide, were supplied by MEGS Specialty Gases. The *PVT* cell was filled with 30 cm^3 of distilled water and 15 cm^3 of neohexane (2,2-dimethylbutane). These liquids were then brought into contact with the gaseous mixture under study. For the three-phase equilibrium experiments, neohexane was not added. Agitation was commenced once all the necessary chemicals were loaded into the *PVT* cell. Temperature control of the bath was then started, and the temperature inside the *PVT* cell was allowed to equilibrate overnight, while pressure was kept constant to a value just below the expected equilibrium pressure. Hydrates were formed by increasing the pressure above the equilibrium point for pure methane hydrate. When a considerable amount of hydrate crystals were observed in the *PVT* cell, pressure was reduced in steps of 30 kPa, allowing for temperature in the cell to equilibrate between each decrement. Pressure reduction was achieved by retracting the floating isolation piston inside the *PVT* cell with the help of the positive displacement pump, and care was taken to ensure the temperature in the cell was constant within ± 0.5 K for at least 30 min before proceeding with the next pressure decrease. The procedure was repeated until visual confirmation of hydrate-phase disappearance. The equilibrium temperature and pressure

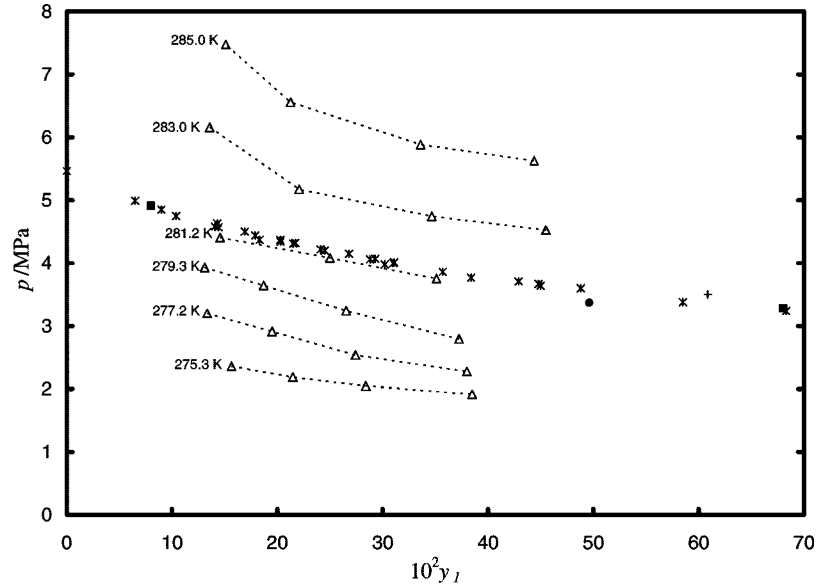

Figure 4. Hydrate−liquid−vapor equilibrium isotherms for the system methane + carbon dioxide + water. Equilibrium, vapor-phase mole fraction of CO_2, y_1. △, this work; ∗, ref 16 at 280.3 K; ■, ref 15 at 280.2 K; ● ref 7 at 280.1 K; +, ref 18 at 280.2 K. The curves connecting the experimental data were drawn to increase the readability of the graph; curve fitting should not be inferred.

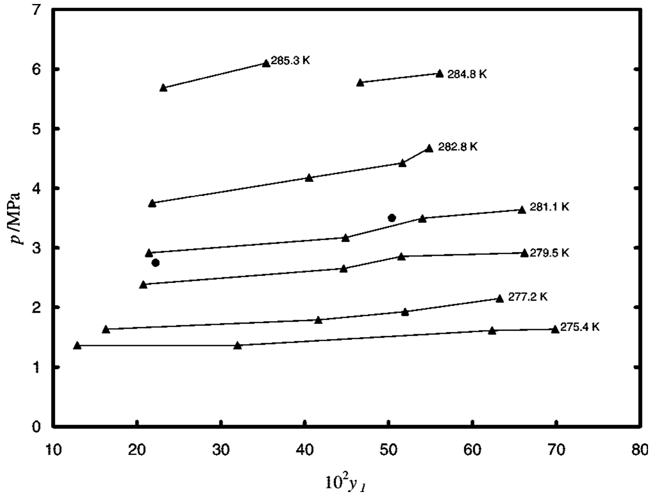

Figure 5. Hydrate−liquid−liquid$_{aq}$−vapor equilibrium isotherms for the system methane + carbon dioxide + neohexane + water. Equilibrium, vapor-phase mole fraction of CO_2, y_1. ▲, this work; ●, ref 7 at 280.6 K. The curves connecting the experimental data were drawn to increase the readability of the graph; curve fitting should not be inferred.

values were taken as the average between the conditions at which the last hydrate crystal was observed and the conditions at which the last hydrate crystal disappeared. A vapor-phase sample was taken immediately after complete hydrate decomposition and analyzed by gas chromatography.

Using the method described above to determine the equilibrium point for both the system with neohexane and that without, it was estimated that the standard uncertainties were as follows: for temperature $u_T = 0.5$ K, for pressure $u_p = 0.03$ MPa, and for vapor-phase mole fraction $u_{y1} = 0.02$. With a coverage factor of $k = 2$ and assuming the corresponding standard uncertainty had a normal distribution, each expanded uncertainty was estimated to be $U_T = 1.0$ K, $U_P = 0.06$ MPa, and $U_{y1} = 0.04$.

Results and Discussion

Table 1 and Table 2 present the complete three-phase and four-phase equilibrium data for the systems methane + carbon dioxide + water and methane + carbon dioxide + neohexane + water, respectively. Figure 2 and Figure 3 show three-phase (hydrate−liquid−vapor) and four-phase (hydrate−liquid−liquid$_{aq}$−vapor) equilibrium temperature and pressure, respectively, for gas mixtures initially containing a mole fraction of 80 %, 70 %, and 50 % methane, the balance being carbon dioxide. These figures are shown to offer a comparison against the data available in the literature where analysis of the results was made based on the feed vapor-phase composition and not on the equilibrium vapor-phase composition. To increase readability, data from mixtures used in this work but not available in the literature are not presented in Figure 2 and Figure 3, but rather incorporated into Figure 4 to Figure 6. Equilibrium pressure and temperature values for gas mixtures in contact with water only (Figure 2) and with water and neohexane (Figure 3) agree with previously reported values within our estimated expanded uncertainties.[7,8,17] As can be seen from Figure 2, equilibrium pressure at constant temperature decreases with increasing initial carbon dioxide concentration. This trend is expected since pure carbon dioxide hydrate forms at lower pressures than pure methane hydrate.[19] Figure 3 shows how the presence of neohexane inverts the trend: mixtures with higher initial carbon dioxide concentration form hydrates at higher pressures at constant temperature. Uchida et al.[8] explained this effect by postulating that sH stability is controlled by methane occupancy of the 5^{12} cage, and thus increasing carbon dioxide concentrations tend to destabilize structure H.[8]

Figure 4 shows equilibrium isotherms for the system methane + carbon dioxide + water. Since experimental isotherms are presented in this work, comparison with the literature was made with the only available experimental isotherm[16] and with data points at the same temperature as ref 16 from other researchers.[7,15,18] The four data sets are in agreement within the estimated expanded uncertainties from this work. At constant temperature, increasing equilibrium concentrations of carbon dioxide in the vapor phase occur at lower equilibrium pressures. Figure 5 displays equilibrium isotherms for methane + carbon dioxide mixtures in the presence of water and neohexane. Comparison with Servio et al.'s work[7] is done at the same temperature as in Figure 4. Agreement between both studies is observed within the estimated expanded uncertainties from this

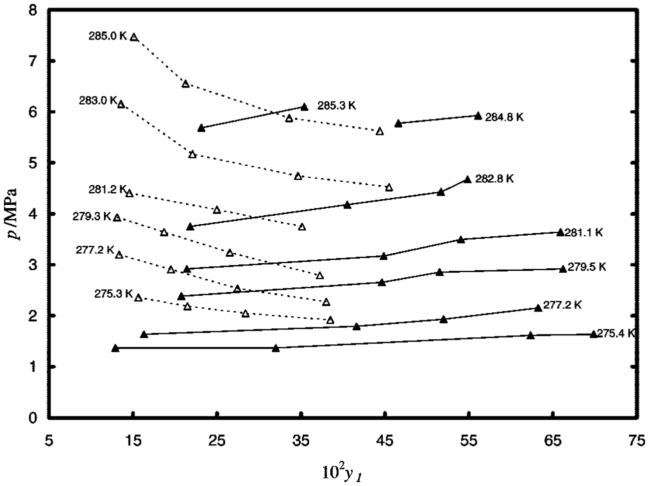

Figure 6. ▲, Hydrate−liquid−liquid$_{aq}$−vapor equilibrium isotherms for the system methane + carbon dioxide + neohexane + water. △, Hydrate−liquid−vapor equilibrium isotherms for the system methane + carbon dioxide + water. Equilibrium, vapor-phase mole fraction of CO_2, y_1. The curves connecting the experimental data were drawn to increase the readability of the graph; curve fitting should not be inferred.

work. The isotherms in Figure 5 show a trend opposite to those in Figure 4: at constant temperature, increasing equilibrium concentrations of carbon dioxide in the vapor phase occur at higher equilibrium pressures. This is more clearly seen by superimposing both sets of data (Figure 6). From Figure 6, it can be inferred that structure H equilibrium occurs at lower pressures and temperatures than sI when the vapor phase is methane rich; however, this phenomenon appears to be reversed as the equilibrium vapor phase becomes richer in carbon dioxide. The latter might explain why Uchida et al.[8] observed structure I formation for a gas mixture initially containing a mole fraction of 70 % methane, the balance being carbon dioxide, in the presence of water and neohexane, at conditions below the expected equilibrium pressure and temperature for the same gas mixture in the presence of water only.

Conclusion

Four-phase equilibrium conditions (hydrate−liquid−liquid$_{aq}$−vapor) and three-phase equilibrium conditions (hydrate−liquid−vapor) were determined for the systems methane + carbon dioxide + neohexane + water and methane + carbon dioxide + water, respectively. The data presented here were found to agree with the available literature data within the uncertainties herein reported. Experimental isotherms were presented. It was observed that the equilibrium mole fraction of carbon dioxide in the vapor phase follows opposite trends in both systems, with respect to equilibrium pressure, at constant temperature. The data also suggest that structure H equilibrium occurs at lower pressures and temperatures than sI when the vapor phase is methane rich; however, this phenomenon appears to be reversed as the equilibrium vapor phase becomes richer in carbon dioxide.

Supporting Information Available:

Representative raw data plot, showing temperature and pressure readings leading to the determination of a three-phase or a four-phase equilibrium point. This material is available free of charge via the Internet at http://pubs.acs.org.

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