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$H-L_W-V$ Equilibrium Measurements for the $CH_4 + C_2H_6 + H_2O$ Hydrate Forming System

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Three-phase equilibrium conditions for the CH_4 (1) + C_2H_6 (2) + H_2O (3) system in $H-L_W-V$ equilibrium were determined to ascertain the effects of pressure, temperature, and gas-phase composition in the temperature region above the freezing point of water as well as to construct a 3D phase diagram. The obtained equilibrium temperature, pressure, and gas-phase compositions were in the range of (275 to 281) K, (0.7 to 2.7) MPa, and $y_1 = (0.30 \text{ to } 0.85)$, respectively. Along any given isotherm and isobar, the equilibrium pressure increased and the equilibrium temperature decreased, respectively, with increasing mole fraction of methane in the gas phase for both structure I and structure II hydrates. At constant gas-phase compositions, the system followed the exponential trend seen for pure gases, with equilibrium pressures close to that of simple ethane hydrates even at high concentrations of methane in the system. A 3D representation of the phase diagram was constructed of the system. The diagram consists of two planes due to the presence of both structure I and structure II. The structure change is seen by the intersection of the two planes, and there is no significant discontinuity in the phase plane diagram.

Introduction

Clathrate hydrates are nonstoichiometric crystalline solids. Hydrates form when water molecules link together through hydrogen bonding and form cages that entrap gases and volatile liquids suitable for hydrate formation.[1] Sir Humphry Davy was the first to describe these crystalline structures in 1810.[2] Over 100 years later, hydrates were recognized to plug gas pipelines.[3] The implication of this discovery was an exponential allocation of resources toward the hydrate field, in particular to map the phase equilibrium curves, and toward finding suitable hydrate inhibitors.[1]

More recently, other reasons to research hydrates have surfaced. Hydrates formed from natural gas have been discovered in situ.[4] Large deposits of natural gas hydrates have been located in the ocean and permafrost regions.[5] Conservative estimates suggest the corresponding amount of energy to exceed that found in all other hydrocarbon sources combined.[6] These natural hydrates could pose a global threat as the vast amounts of methane stored in the form of hydrate could lead to an acceleration of the global warming process if decomposed due to the high greenhouse gas potential of methane.[1,7] On the contrary, carbon dioxide sequestration using hydrate technology has been suggested as a way to mitigate global warming.[8] Another field of growing interest is that of hydrate formation from multiple gas hydrate formers. The combination and ratios of mixed hydrate formers can alter the resulting structure and hence also the equilibrium conditions of a system significantly.[9] Understanding mixed systems is essential when applying hydrate technology to gas sequestration and separation.

CH_4 and C_2H_6 are known to form structure I (S I) as simple hydrates.[9] $H-L_W-V$ equilibrium for these systems ($CH_4 + H_2O$ and $C_2H_6 + H_2O$) were investigated by Deaton and Frost in the 1940′s. Deaton and Frost also performed $H-L_W-V$ equilibrium experiments for the CH_4 (1) + C_2H_6 (2) + H_2O (3) system, but only over a limited gas-phase composition range.[10] In 1980, Holder and Grigoriou performed additional experiments to investigat this binary gas system.[11] Holder and Hand also modeled the system as a S I but found disagreements between the proposed model and the data at certain gas-phase compositions.[12] Hendriks et al. later investigated binary gas mixture systems, including the CH_4 (1) + C_2H_6 (2) + H_2O (3) system, from a thermodynamic point of view. They conjectured that over a given gas-phase composition range the structure II (S II) hydrate is formed despite the simple hydrates in the mixture being S I.

The structural dependency of hydrates on gas-phase composition for the CH_4 (1) + C_2H_6 (2) + H_2O (3) system was experimentally proven by Subramanian et al. Using Raman and NMR spectroscopic techniques, they determined a change in hydrate structure from S I to S II between (0.722 and 0.750) mol fraction of methane in the vapor phase at 274 K.[13] Subramanian et al. also demonstrated that the system will return to S I with methane vapor phase mole fraction $y_1 > 0.992$.[14] X-ray experiments were performed on the system of interest at 263 K by Takeya et al. and demonstrated that for methane gas-phase compositions between $y_1 = 0.79$ and 0.98 S II is present.[15] Spectroscopy analysis of the system has also been performed under very high pressures by Hirai et al.[16] Hashimoto et al. presented isothermal phase equilibria for the CH_4 (1) + C_2H_6 (2) + H_2O (3) system at three separate isotherms and combined the results with Raman spectroscopic analysis.[17] The effect of inhibitors on S I and S II have been studied by Ohno et al. by altering the gas-phase composition of the system.[18]

Up to this point, no reliable data (only loading composition reported, not equilibrium) have been presented in the literature for the CH_4 (1) + C_2H_6 (2) + H_2O (3) system below 279 K. In the present work, equilibrium data have been obtained for the CH_4 (1) + C_2H_6 (2) + H_2O (3) system at temperatures near and above the freezing point of water. These results are

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Table 1. Hydrate−Liquid−Vapor Equilibrium[a]

T/K	p/MPa	y_1	y_{1L}
275.1	0.69	0.309	0.300
275.2	1.03	0.612	0.600
275.3	1.41	0.838	0.850
277.1	0.92	0.307	0.300
277.1	1.25	0.603	0.600
277.2	1.23	0.601	0.600
277.2	1.76	0.839	0.850
278.2	1.90	0.837	0.850
279.1	2.14	0.837	0.850
279.1	1.17	0.307	0.300
279.2	1.52	0.608	0.600
279.3	1.52	0.609	0.600
281.1	1.92	0.605	0.600
281.1	2.65	0.838	0.850
281.2	1.90	0.611	0.600
281.2	1.45	0.303	0.300

[a] Temperature T, pressure p, vapor-phase mole fraction of methane y_1, and loading composition of methane y_{1L} for the system CH_4 (1) + C_2H_6 (2) + H_2O (3) under H−L_W−V equilibrium.

combined with existing data to elicit the effect of composition on equilibrium pressure at given isotherms along with the effect of temperature on equilibrium pressure at set compositions. A 3D representation of the data for the CH_4 (1) + C_2H_6 (2) + H_2O (3) system is also presented. Due to the presence of a structure change, a large number of equilibrium data are required to properly describe the resulting equilibrium planes for the given mixture. The equilibrium data determined in this work have been obtained using a technique that satisfies the phase rule and that previously have been used to describe a binary a gas mixture system.[19]

Experimental Apparatus

Experiments were carried out in a Jefri-DBR phase Behavior System (Oilphase-DBR- Schlumberger) described in detail in a previous work.[19] The system consists of a refrigerated PVT cell with pressure regulated by an automated, high-pressure, positive displacement pump (Oilphase-DBR-Schlumberger). The hydraulic fluid inside the pump is connected to a floating isolation piston located inside the PVT cell. The piston isolates the hydraulic fluid from the process side of the PVT cell.

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 with a volume of 2 cm^3 and analyzed with a gas chromatograph (Varian CP3800) equipped with a gas sampling injection valve. After injection, separation of the gas mixture was achieved by passing the sample through an arrangement consisting of a 0.5 m × 1/8 in. precolumn, packed with 80 to 100 mesh HayesepT (porous polymer from Varian Inc.), and a 2.6 m × 1/8 in. column, packed with 80 to 100 mesh HayesepR (porous polymer from Varian Inc.). The effluent was monitored with a thermal conductivity detector.

Experimental Procedure

UHP (99.95 %) CH_4 + C_2H_6 gas mixtures provided by MEGS were added to the system which then was pressurized to a value within the hydrate formation region and left overnight to equilibrate and saturate. Once hydrates were observed formed, the system was allowed to equilibrate, and pressure, temperature, and system volume as well as the presence of hydrates in the bulk were monitored. When all parameters reached steady state values, a gas sample was taken out of the gas phase and analyzed in the GC. A more detailed procedure can be found in a previous work.[19] The estimated standard uncertainties were as follows: for temperature $u_T = 0.2$ K, for pressure $u_p = 0.03$ MPa, and for vapor phase mole fraction $u_{y1} = 0.015$. With a coverage factor of $k = 2$ and assuming the corresponding standard uncertainty had a normal distribution, each expanded uncertainty was estimated to be $U_T = 0.4$ K, $U_p = 0.06$ MPa, and $U_{y1} = 0.03$.

Results and Discussion

The accuracy of the system was confirmed through a comparison of the data presented in Table 1 with equilibrium data obtained by Hashimoto at the 279 K isotherm both for S

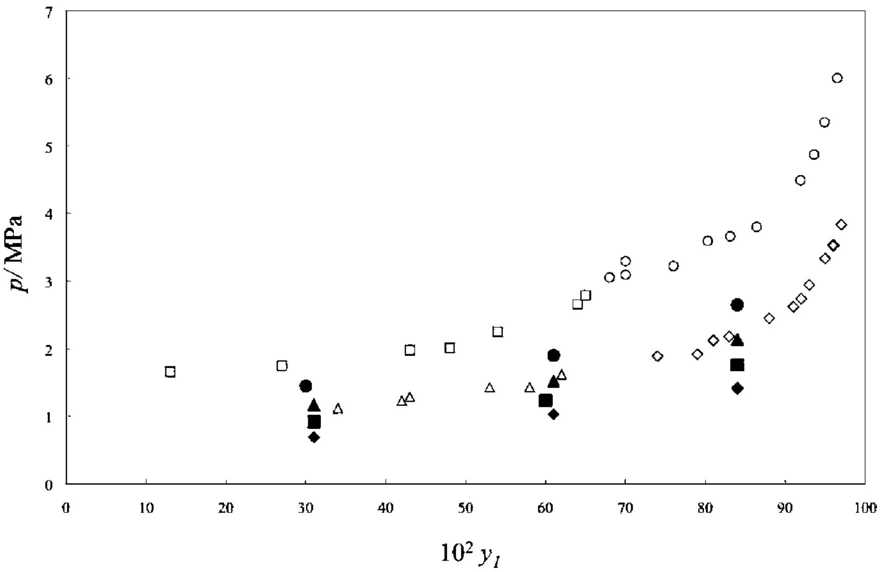

Figure 1. Hydrate−liquid$_{aq}$−vapor equilibrium isotherms for the methane (1) + ethane (2) + water system (3). y_1, equilibrium vapor-phase mole fraction of CH_4; ◆, this work at 275 K; ■, this work at 277 K; ▲, this work at 279 K; ●, this work at 281 K; △, equilibrium data at 279 K, S I;[17] ◇, equilibrium data at 279 K, S II;[17] □, equilibrium data at 283 K, S I;[17] ○, equilibrium data at 283 K, S II.[17]

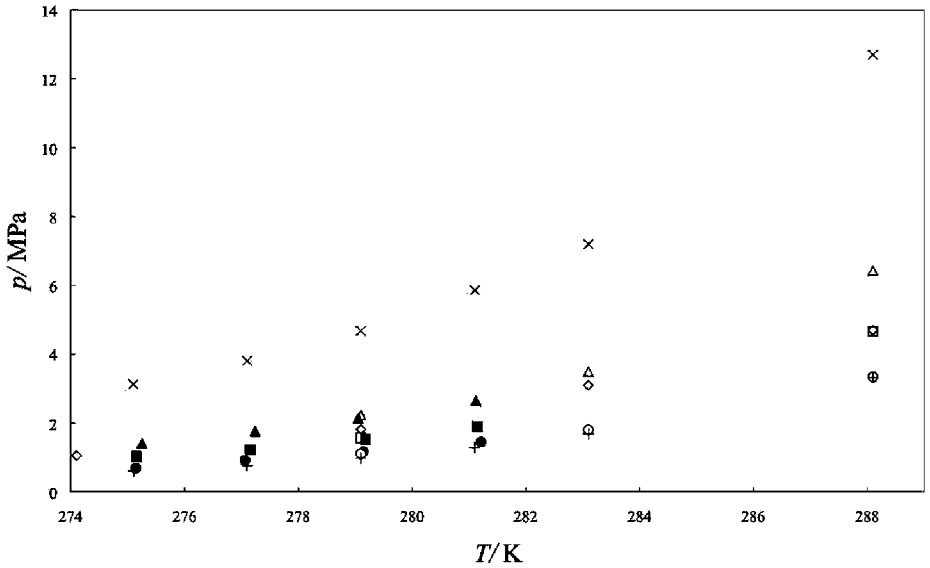

Figure 2. Hydrate−liquid$_{aq}$−vapor equilibrium for constant gas-phase compositions for the methane (1) + ethane (2) + water system (3). ●, this work, $y_1 = 0.31$; ■, this work, $y_1 = 0.61$; ▲, this work, $y_1 = 0.84$; ○, $y_1 = 0.31$;[17] □, $y_1 = 0.61$;[17] △, $y_1 = 0.84$;[17] ◇, S I−S II transition composition;[13,17] +, $y_2 = 1.00$;[10] ×, $y_1 = 1.00$.[10]

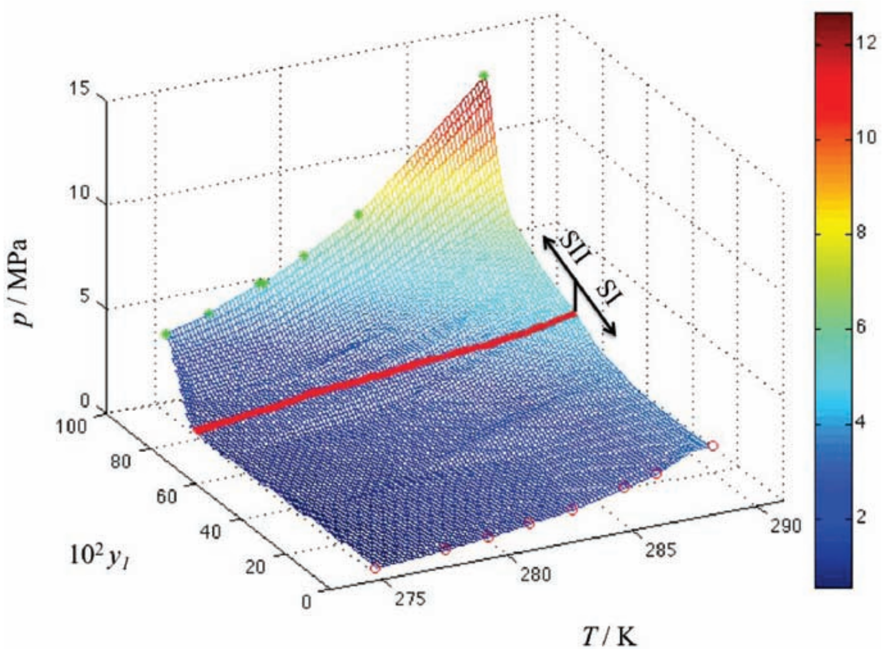

Figure 3. Structure I and structure II 3D plane representations of the hydrate−liquid$_{aq}$−vapor equilibrium for the methane (1) + ethane (2) + water system (3). y_1, equilibrium vapor-phase mole fraction of methane; red —, quadruple line, $H_{S\,I}$−$H_{S\,II}$−L_{aq}−V equilibrium;[13,17] *, pure methane[10] (SI); ○, pure ethane[9] (SI).

I and S II hydrates.[17] Hashimoto's data were within the experimental uncertainty of the presented work at the common isotherm as demonstrated in Figure 1. No uncertainties were reported by Hashimoto, but one replicate exists in the reported data showing a relative difference in vapor fraction of 5.4 % for identical operating conditions. Aside from the data presented by Hishimoto, no other equilibrium data have been found for the system with equilibrium (not loading) composition reported. An equilibrium composition is required to justify an equilibrium point at a given temperature and pressure in a system containing a binary gas mixture due to the resulting 2 degrees of freedom.[19]

The effect of pressure changes on the CH_4 (1) + C_2H_6 (2) + H_2O (3) system in H−L_W−V equilibrium with a constant gas-phase composition was studied, and the results are graphed in Figure 2. Interpolated values extracted from the data of Hashimoto were also included to allow for trend observation over a larger temperature range.[17] Equilibrium values for pure ethane and methane from Deaton and Frost were also included to illustrate the boundaries of the system.[10] Along any given isotherm maintaining a constant gas-phase composition, the three phase equilibrium pressures exhibit much the same type of trend behavior as that of pure methane and ethane. The equilibrium pressure increases exponentially with increasing temperature. This is the case for both structure I ($y_1 = 0.31$ and 0.61) and structure II ($y_1 = 0.84$) hydrates. All equilibrium data are found to be within the boundaries formed by the pure systems being structure I hydrates. The equilibrium values are much closer to those of pure ethane than those of pure methane even at gas-phase compositions close to $y_1 = 0.85$.

Figure 3 present a 3D representation of the S I and S II equilibrium planes. The mole fraction of methane in the gas phase, temperature, and pressure are represented by the x and y and z axes, respectively. The planes represent all available data for the CH_4 (1) + C_2H_6 (2) + H_2O (3) system in $H-L_W-V$ equilibrium. Spectroscopy data obtained from the literature[13−15,17] were used to define the structural transition region from S I to S II, indicated by the red transition line, and the plane borders (both S I) are represented by the equilibrium conditions for pure methane and pure ethane acquired by Deaton and Frost, Reamer et al., and Holder and Hand.[9,10] The gas-phase composition at which the structure changes between S I and S II is dependent on temperature and pressure. The structure change region appears in (0.60 to 0.75) mol fraction of methane in the gas phase for the examined temperature and pressure range. The region defining the line bordering the two structures is likely to contain both structures simultaneously. The structure change is illustrated by the red line intersection of two planes as demonstrated in Figure 3 where the entire mixture composition range is shown. There is no discontinuity appearing in the 3D model of the equilibrium planes due to the structure change for the CH_4 (1) + C_2H_6 (2) + H_2O (3) system. In the structure I section of Figure 3, the equilibrium plane is very flat and, as a result, has an equilibrium pressure very insensitive to gas-phase composition changes. In the structure II section of Figure 3, the equilibrium plane is very curved and shows that equilibrium pressure is very sensitive to both temperature and gas-phase composition changes. For both structure I and structure II, it was observed that along any given isotherm and isobar on the plane, the hydrate equilibrium pressure increases, and the equilibrium temperature decreased, respectively, with increasing mole fraction of methane in the gas phase.

Conclusion

Three phase equilibrium conditions for the CH_4 (1) + C_2H_6 (2) + H_2O (3) system in the $H-L_W-V$ equilibrium were determined to ascertain the effects of pressure, temperature, and gas-phase composition. A 3D phase diagram of the system is presented. The data of this work agree well with data in the literature at 279 K. Along any given isotherm and isobar, the equilibrium pressure increased and the equilibrium temperature decreased, respectively, with increasing mole fraction of methane in the gas phase both for structure I and structure II hydrates. At constant gas-phase composition, the system followed the exponential trend seen for pure gases, with equilibrium pressures close to that of simple ethane hydrates even at high concentrations of methane in the system. The equilibrium pressure of structure I is found to be less sensitive to temperature and composition changes than structure II.

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