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Structure H Hydrate Phase Equilibria of Methane + Liquid Hydrocarbon Mixtures

Ajay P. Mehta and E. Dendy Sloan, Jr.*

Center For Research On Hydrates, Chemical Engineering and Petroleum Refining Department,
Colorado School of Mines, Golden, Colorado 80401

The first phase equilibrium data are reported for mixtures of heavier liquid hydrocarbons + methane forming structure H hydrates. Four-phase equilibrium conditions (water, liquid hydrocarbon, vapor, and structure H hydrate) were measured for three systems: methane + 2,2-dimethylbutane, methane + 2-methylbutane, and methane + methylcyclohexane. These hydrocarbons constitute a small fraction of crude oil reservoirs where they coexist with various gases, including methane. Consequently this work suggests the possibility of the natural occurrence of structure H hydrates in such natural and artificial environments, and these initial phase equilibrium data have the potential to impact industrial perspectives about hydrates.

Introduction

Gas hydrates are enclosure compounds that form when water combines with small guest molecules to form a crystalline mass which can plug flow channels. Gas hydrates of interest to the natural gas industry are composed of water and molecules like methane, propane, isobutane, carbon dioxide, and hydrogen sulfide. The gas molecules occupy cavities in a network of water molecules referred to as the body-centered cubic lattice of structure I or the diamond cubic lattice of structure II. A recent monograph by Sloan (*1*) provides a review of these conventional hydrate structures. In contrast to the previously known structures, structure H hydrate (sH) has a hexagonal space group from which the denotation "H" is derived. A detailed description of its crystal structure and unit cell composition is given by Lederhos et al. (*2*).

Structure H hydrate was discovered by Ripmeester et al. (*3*) in 1987, who identified more than 24 large molecules (*4*) as structure H formers, including heavier hydrocarbons like methylalkanes and cycloalkanes, many of which are indigenous to petroleum. They concluded that small molecules (they used xenon and hydrogen sulfide below 273 K) were necessary to obtain structure H hydrate when the large molecules were used as guests.

Ripmeester's group also identified adamantane, a solid, to be a structure H former. Adamantane, 1-methyladamantane, and diamantane are three major components of diamondoids, currently being found *in situ* with methane and free water in deepwater gas fields, including Mobile Bay in the Gulf of Mexico. Thus, there is some probability that structure H hydrates might be forming from hydrocarbons and free water, coming from natural environments. Recently, Ripmeester and co-workers (*5*) have determined that structure H can be formed from components of a light naphtha fraction as well as unleaded gasoline, indicating the hydrate structure could play a role in petroleum as well as natural gas processes.

Ripmeester and co-workers used X-ray powder diffraction and NMR techniques in their studies to help them determine that the diameter of the large guest molecule may be between 7.5 and 8.6 Å (the approximate sizes of cyclohexane and methylcyclohexane, respectively). However, no phase equilibrium data were determined in these identification studies. While powder diffraction studies have identified the new structure, definitive structural determination of structure H awaits single-crystal diffraction studies.

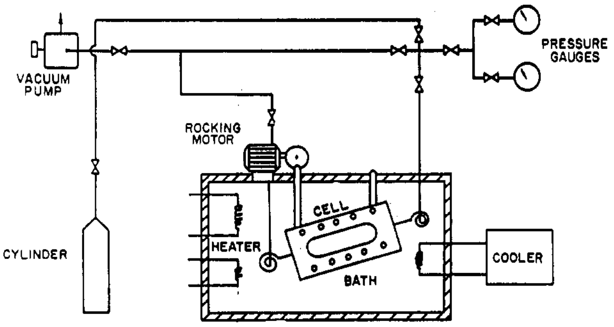

Figure 1. Experimental apparatus.

The first phase equilibrium data on structure H were reported from this laboratory by Lederhos et al. (*2*) in 1992, for the methane + adamantane system. This work reports initial phase equilibrium data on structure H for mixtures of heavier liquid hydrocarbons + methane. The systems considered were methane + 2,2-dimethylbutane, methane + 2-methylbutane, and methane + methylcyclohexane. These phase equilibrium data may impact both natural and artificial aspects of hydrocarbon reservoirs, where these molecules can be found in association with water at high pressures and low temperatures.

Experimental Procedure

The experimental procedure took advantage of the univariance of the system as confirmed by the Gibbs phase rule, $\Phi = C - P + 2$, where Φ, C, and P are the degrees of freedom, number of components, and number of phases, respectively. For example, in the three-component water + methane + 2-methylbutane system, four phases coexist at equilibrium: liquid water (L_w), liquid 2-methylbutane (L_{HC}), vapor (V), and structure H hydrate (sH). According to the Gibbs phase rule, there is exactly 1 degree of freedom. Consequently setting the temperature at which the four phases coexist at equilibrium would uniquely determine all the other intensive parameters, such as pressure, gas composition, hydrate composition, and the composition of the other two phases.

The experimental apparatus shown in Figure 1 consisted of a Jerguson sight glass cell rocked about its axis. A digital thermometer attached to a platinum resistance thermometer accurate to within ±1% was used to measure the temperature inside the cell. The cell pressure was measured by a Heise pressure gauge accurate to within ±0.1%. The cell was

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Table I. sH Hydrate Equilibrium Temperature T, Equilibrium Pressure P, and Calculated Liquid (x) and Vapor (y) Compositions for Methane (1) + 2,2-Dimethylbutane (2)

T/K	P/MPa	x_1	y_1
276.01	1.598	0.1018	0.9847
278.04	2.028	0.1333	0.9855
279.20	2.391	0.1551	0.9860
282.15	3.339	0.2068	0.9862

Table II. sH Hydrate Equilibrium Temperature T, Equilibrium Pressure P, and Calculated Compositions of Liquid (x) and Vapor (y) for Methane (1) + 2-Methylbutane (2)

T/K	P/MPa	x_1	y_1
275.25	2.654	0.1748	0.9757
276.25	2.978	0.1933	0.9760
277.85	3.640	0.2310	0.9768
278.95	4.150	0.2572	0.9761

Table III. sH Hydrate Equilibrium Temperature T, Equilibrium Pressure P, and Calculated Liquid (x) and Vapor (y) Compositions for Methane (1) + Methylcyclohexane (2)

T/K	P/MPa	x_1	y_1
275.65	1.599	0.0854	0.9980
277.65	2.137	0.1106	0.9980
279.45	2.688	0.1350	0.9980
281.15	3.357	0.1634	0.9979

immersed in a constant-temperature bath with a Plexiglass window to allow the monitoring of hydrate formation or dissociation. The bath was refrigerated by an immersion refrigeration unit, and the temperature was controlled by an immersion heater connected to a Bayley precision temperature controller, model 122, accurate to within ±0.001 K.

The experimental procedure for all three liquid hydrocarbon systems can be illustrated by that for 2-methylbutane. Initially 75 mL of distilled double-deionized water was inserted into the cell. A 200% excess of the stoichiometrically required amount of 2-methylbutane was then added. Since water and 2-methylbutane are virtually insoluble, two distinct liquid layers could be observed inside the cell.

The cell was charged with methane, and the pressure inside the cell was raised above the structure I formation pressure. In this way we first caused structure I to form inside the cell in order to create some hydrogen bonds in the aqueous phase. Now the cell pressure was dropped below the structure I formation point, whereupon a trial and error procedure was adopted to determine the structure H equilibrium point. After the system stabilized, a further pressure drop would indicate formation of hydrates as a result of the consumption of gas. Since the operating pressure was below the structure I equilibrium conditions, the formation of structure I was not feasible. All the large molecules in this study were substantially larger (>1 Å) than would fit into the largest cavity of structure II. Hence, any further intake of gas would suggest the formation of another hydrate structure, namely, structure H. On the other hand, an increase in the pressure would indicate a dissociation of structure H hydrates.

Interestingly, with the methane + 2,2-dimethylbutane and methane + methylcyclohexane systems, when the system pressure was initially raised above the structure I formation pressure, a catastrophic formation of hydrates was observed, and the pressure dropped well below the structure I condition, resulting in a hydrate plug filling the cell. This observation suggested that these systems might be able to form structure H hydrates spontaneously. In successive runs we charged the cell with methane at a pressure well below the structure I formation condition and found a rapid decrease in the pressure, with hydrates visually observed inside the cell. In this manner, we monitored the system constantly and determined the equilibrium pressures for each methane + liquid hydrocarbon system to within an error of ±30 KPa.

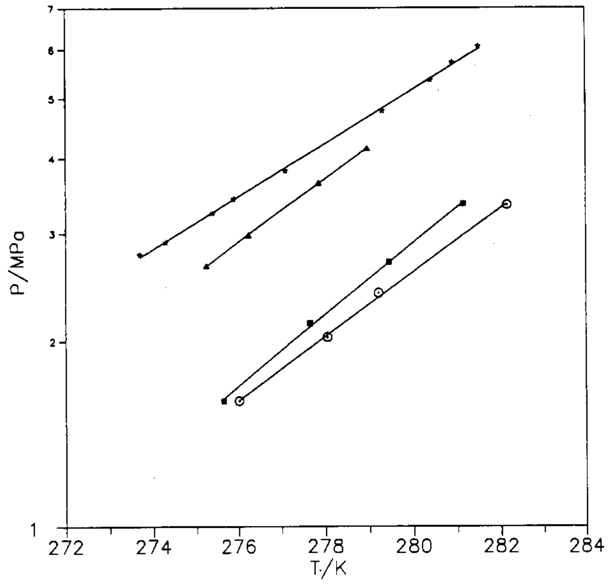

Figure 2. Comparison of phase diagrams of structure H and structure I hydrates: (★) sI methane, ref 6; (▲) sH 2-methylbutane + methane, this work; (■) sH methylcyclohexane + methane, this work; (⊙) sH 2,2-dimethylbutane + methane, this work.

Results and Discussion

The four-phase equilibrium data for structure H hydrates composed of methane and each of the three liquid hydrocarbon systems are given in Tables I–III. In each table are also the results of a water-free, flash calculation performed at the equilibrium temperature and pressure of structure H formation, using the Peng–Robinson equation of state. The interaction parameter for each methane + liquid hydrocarbon system was taken as zero, lacking a better estimate. The results of the flash calculations indicate the vapor phase composed of a mixture which is largely methane with small amounts (less than 2%) of the liquid hydrocarbon.

Figure 2 compares the structure H four-phase equilibrium line for the three liquid hydrocarbon systems with data of structure I methane hydrates, measured by Deaton and Frost (*6*) in 1946. The structure H formation pressures for the methane + 2,2-dimethylbutane system and the methane + methylcyclohexane system are in close proximity (within ±10%) of each other, but they are about 40% of the pressures for the three-phase line of methane structure I hydrates. These low formation pressures indicate that structure H hydrates of these liquid hydrocarbon systems are extremely stable.

On the other hand, the methane + 2-methylbutane system did not exhibit the same spontaneity in forming structure H as the methane + 2,2-dimethylbutane and methane + methylcyclohexane systems. The structure H equilibrium line does lie below the structure I line but at considerably higher pressures than the other systems. The formation pressures for 2-methylbutane are about 80% of those for the three-phase methane structure I line. Therefore, higher pressures would be required to obtain the same driving force for the methane + 2-methylbutane system, as those for the methane + 2,2-dimethylbutane and methane + methylcyclohexane systems.

Katz and co-workers (*7*) have suggested that structure I and II hydrates might act to denude oil of viscosifiers, in known instances of "dead" highly viscous oil found associated with hydrates in natural permafrost regions. The size of the structure H large cavity and the phase equilibrium conditions both suggest that structure H hydrates may find applications in preferential denudation of light petroleum components.

Conclusions

This work represents the first phase equilibrium data for the structure H hydrates using 2-methylbutane, 2,2-dimethylbutane, and methylcyclohexane, with methane as the small help gas molecule. The work of determining the phase equilibrium conditions of the new hydrate structure provides the foundation for a new domain of hydrate research.

Some of the hydrocarbons reported as structure H formers occur in natural as well as in industrial environments. Many of these like methylcycloalkanes and methylbutanes constitute a small fraction of crude oil reservoirs which also contain many structure II forming molecules; thus, we might expect to find structure H hydrates to be present in association with structure II hydrates. The partitioning of crude oil and certain structure H forming hydrates may have major implications in petroleum geochemistry.

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