Structure H Clathrate Hydrate Equilibria of Methane and Adamantane

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The first phase equilibrium data are presented for Structure H hydrates. The data represent the initial formation of these hydrates from methane, with adamantane—a previously determined Structure H former. Temperature and pressure conditions are consistent with hydrocarbon production/transportation/processing facilities. Structure H hydrates are shown to contain molecules indigenous to petroleum, which may not be present in natural gas.

Introduction

Clathrate hydrates are inclusion compounds, in which host water molecules encage guest molecules, with one guest per cage at most. Structure H hydrate was discovered first by Ripmeester et al. (1987), almost 40 years after the determination of the two well-known clathrate hydrate structures commonly called I (*s*I) and II (*s*II). The new clathrate was designated "H" due to its hexagonal spacegroup in order to distinguish structure H (*s*H) from seven other hydrate structures proposed by Jeffrey (1984), many of which are hypothetical; *s*I and *s*II each have cubic spacegroups.

Stability of *s*H hydrate requires the presence of a small help gas (both Xe and H_2S were previously used) together with a large guest of a diameter between 7.5 Å and 8.6 Å (the approximate sizes of cyclohexane and methyl cyclohexane, respectively). Ripmeester and Ratcliffe (1990) determined 24 large guests for *s*H, each of which is too large to occupy either *s*I or *s*II. Recently Ripmeester et al. (1991) demonstrated that *s*H can be formed from components of a light naphtha fraction or components of gasoline, thus indicating a hydrate structure that can participate in petroleum as well as natural gas processes.

In identifying *s*H occupants, Ripmeester and coworkers used Xe and H_2S as the small guests to provide low pressures needed for glass ampules in NMR and powder diffraction studies. Since NMR evidence was presented that Xe participated in both small cavities of *s*H, we thought it likely that methane (slightly smaller than Xe) would also occupy both small cavities. One large guest molecule was adamantane ($C_{10}H_{16}$), which was shown to occupy *s*H by Ripmeester and Ratcliffe. Adamantane, a spherical polycyclic hydrocarbon with a diameter of about 7.8 Å, is one of the major components of diamondoids that have been found in pipelines in deepwater gas fields including Mobile Bay in the Gulf of Mexico.

There were two objectives of this work: (1) to provide the first phase equilibrium data for *s*H hydrates and (2) to form a *s*H hydrate with methane (and a larger guest). Phase equilibrium data for *s*H hydrates of methane and adamantane may impact both artificial and natural aspects of hydrocarbon reservoirs, production, and transportation, where both chemicals are found in association with water at high pressures and low temperatures.

Crystal Structure of *s*H

The unit crystal for *s*H hydrate has several unusual features. ^{129}Xe NMR spectra, together with powder X-ray and neutron diffraction, provide evidence that the new unit crystal is isostructural with the clathrasil dodecasil-1H of Gerke and Gies (1984) which has host molecules of SiO_2 rather than H_2O. While such previous studies provide strong evidence that the proposed structure is that of *s*H, absolutely definitive structural determination awaits single crystal X-ray or neutron diffraction studies.

There are three cavity types in *s*H, as shown in Figures 1a, 1b, and 1c. Figure 1a is the pentagonal dodecahedron, given the abbreviation 5^{12} indicating 12 pentagonal faces. The 5^{12} cavity is pervasive in *s*I and *s*II, as reviewed by Sloan (1990). Figure 1b shows the smallest cavity ($4^35^66^3$) to have three square faces, six pentagonal faces, and three hexagonal faces; the square faces are uncommon to any previously determined clathrate hydrate. The largest cavity ($5^{12}6^8$), in Figure 1c, has 12 pentagonal and eight hexagonal faces, with six hexagons

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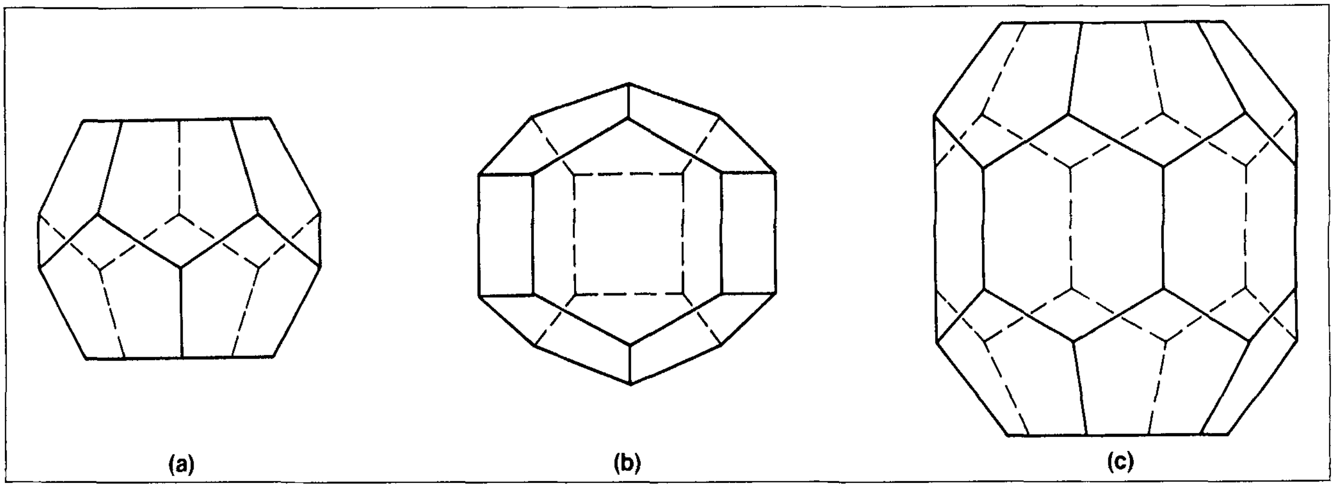

Figure 1. Three cavity types in Structure H hydrate: (a) 5^{12} (b) $4^3 5^6 6^3$ (c) $5^{12} 6^8$.

girdling the cavity, and a hexagon each at the cavity top and bottom.

The unit crystal has 34 water molecules and is composed of three-5^{12} cavities, two-$4^3 5^6 6^3$ cavities, and one-$5^{12} 6^8$ cavity for a composition of $3(5^{12})\cdot 2(4^3 5^6 6^3)\cdot 1(5^{12} 6^8)\cdot 34H_2O$. Figure 2 is an orthogonal view of the structure. Figures 3, 4 and 5 are approximate top, front and side views for *s*H, shown for convenience along cavity alignment channels. In each of the three drawings the unit crystal is shown in slashed lines.

In Figure 3 within the unit crystal rhombus, two $4^3 5^6 6^3$ cavity outlines (each shown with three pentagonal faces) are drawn with dark lines; four other $4^3 5^6 6^3$ cavities are shown along the sides of the rhombus. Four $5^{12} 6^8$ cavities are shown at the vertices of the rhombus; the portions of these cavities combine to make one complete $5^{12} 6^8$ cavity within the unit crystal. The pentagonal faces of the 5^{12} cavities are aligned with those of the two other cavity types and therefore are hidden.

In Figure 4, outlines of three of the $5^{12} 6^8$ cavities are darkened. The fourth $5^{12} 6^8$ cavity of Figure 3 is aligned behind the middle $5^{12} 6^8$ in Figure 4. As the side views of these large cavities illustrate, the hexagonal faces are not planar as are the hexagons in *s*I and *s*II. The two square faces connecting the three large cavities each belong to a $4^3 5^6 6^3$ small cavity that is completely within the unit crystal. Six 5^{12} cavities are shown protruding from the top and bottom edges of the unit crystal to illustrate their "connecting" role to layers composed of one-$5^{12} 6^8$ and two-$4^3 5^6 6^3$ cavities within the unit crystal.

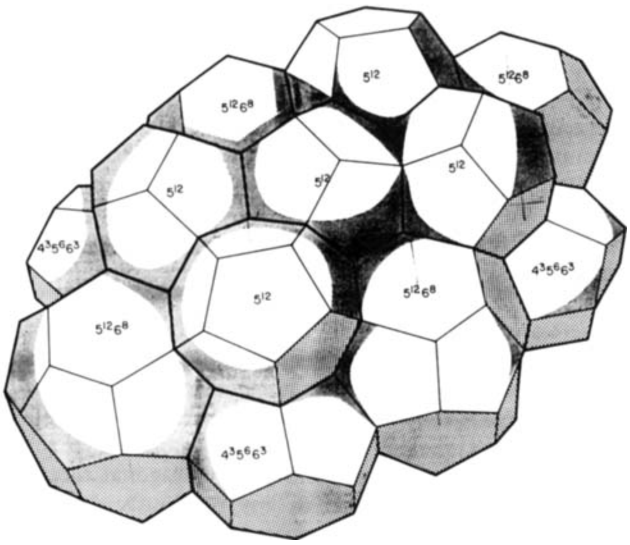

Figure 2. Orthogonal view of Structure H.

In Figure 5, the darkened 5^{12} cavities are shown protruding from the upper and lower edges and vertices of the unit crystal. The two large $5^{12} 6^8$ cavities, protruding from the left and right sides of the unit crystal, are aligned and thus hide the other two $5^{12} 6^8$ cavities in Figure 3. The square face at the center connects the two $4^3 5^6 6^3$ cavities that are completely contained within the unit crystal.

Experimental Apparatus and Procedure

The three chemicals used in this study had the following purities: water was de-ionized; 99.99% pure methane was obtained from General Air Products; and adamantane with a purity of 99+% (sublimation point 482-485 K) was purchased from Aldrich Chemical Company. Methane and adamantane were used as received without further purification.

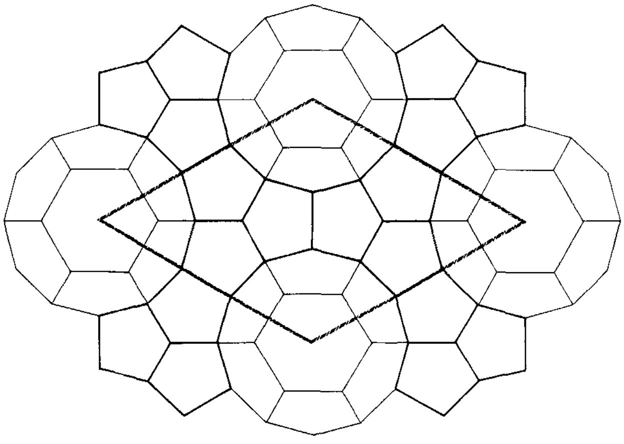

Figure 3. Top view of Structure H showing four $5^{12} 6^8$ cavities and six $4^3 5^6 6^3$ cavities (darkened lines).

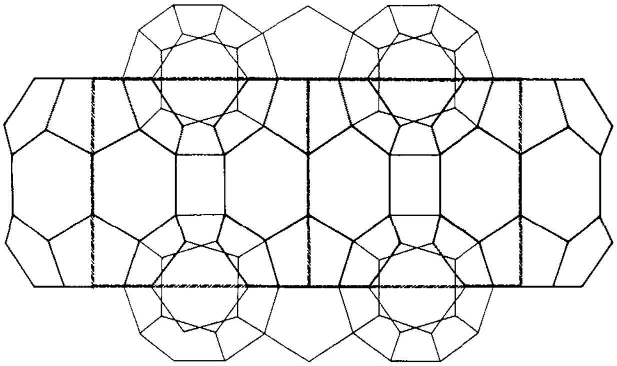

Figure 4. Front view of Structure H showing three $5^{12}6^8$ cavities (darkened lines) and six 5^{12} cavities.

The apparatus in Figure 6 consisted of a Jerguson sight glass cell, rocked about its axis. The cell was immersed in a refrigerated, constant temperature bath, regulated by a Bayley Precision Controller, Model 122. The temperature was sensed by a 100 Ω platinum resistance thermometer, accurate to within 1%, and the pressure was determined by a Heise gage, accurate to within 6.9 kPa.

Initially an excess amount of solid adamantane was loaded into the cell. Adamantane has a very low vapor pressure and is immiscible in water; the solid adamantane persisted throughout the course of the experiment. Secondly, an excess (50 mL) of water was inserted, and air was evacuated by pumping on the system. The temperature of the system was stabilized, and excess methane was admitted to the system at a pressure sufficient to form *s*I hydrate. After *s*I hydrates were formed, creating some additional hydrogen bonding in the aqueous phase, the pressure was reduced to a point well below the *s*I hydrate equilibrium to dissociate the *s*I hydrates.

After the system stabilized, if the pressure decreased, indicating consumption of gas via *s*H hydrate, the system pressure was assumed to be above the equilibrium point. On the other hand, if the pressure increased, indicating gas release due to *s*H hydrate dissociation, the equilibrium condition was taken to be at a higher pressure. Through such a trial and error system of *s*H hydrate formation and dissociation, equilibrium pressures were determined for each of four temperatures. Determination of each equilibrium data point required several weeks. The accuracy of each point is estimated to be within ±17 kPa.

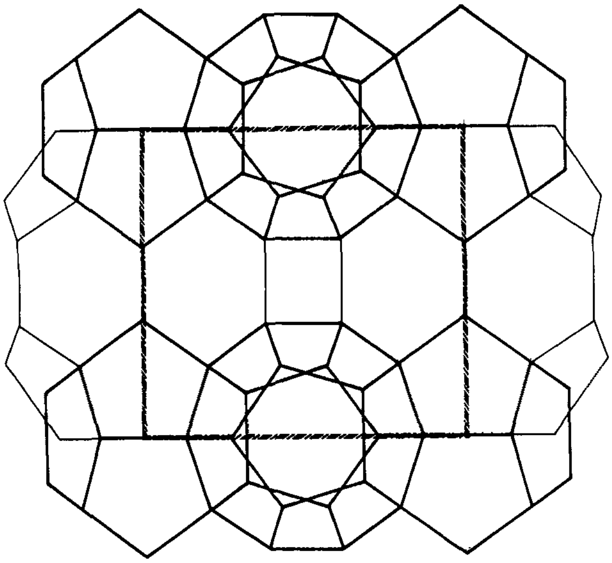

Figure 5. Side view of Structure H showing six 5^{12} cavities (darkened lines) and two $5^{12}6^8$ cavities.

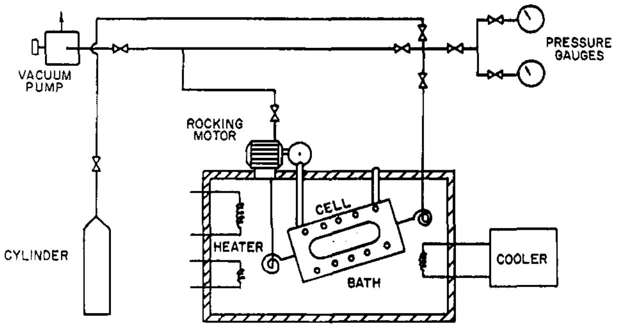

Figure 6. Experimental apparatus.

The experimental procedure took advantage of system univariance as determined by the Gibbs Phase Rule. That is, with three nonreactive components, and four phases [aqueous liquid (L_W)-hydrate (*s*H)-vapor (V)-solid adamantane (A), listed in the order of decreasing phase water concentration], only one degree of freedom was available. Setting the temperature at which the four phases co-exist thus uniquely determined all other intensive variables, such as pressure, gas composition, and hydrate composition. Such a procedure obviated the need for difficult measurements of adamantane concentration in the vapor phase, which was extremely low due to adamantane's low vapor pressure.

Experimental Results and Discussion

Table 1 gives four-phase data points for *s*H hydrates of methane and adamantane at four temperatures. Also presented in the table are calculated adamantane and water compositions in the predominantly methane vapor. The compositions were computed using vapor pressure measurements, the Poynting correction, and the Peng-Robinson equation for vapor-phase nonideality. Measurements of adamantane solubility in methane are not currently available.

Figure 7 compares the *s*H data together with three-phase (V-L_W-H) equilibrium data, obtained by Deaton and Frost (1946), for methane hydrate (*s*I) and Gas C (*s*II) hydrate. Gas C was composed of 78.4 mol % CH_4, 6.0% C_2H_6, 3.6% C_3H_8, 2.4% C_4H_{10}, 9.4% N_2, and 0.2% CO_2. Interestingly, Figure 7 shows

Table 1. *s*H Hydrate Formation from Methane and Adamantane

Measured Temp. (K)	Measured Pres. (MPa)	Cal. Gas-Phase Adamantane Mole Frac.	Cal. Gas-Phase Water Mole Frac.
275.09	1.779	3.3×10^{-6}	4.2×10^{-4}
276.90	2.165	3.6×10^{-6}	3.9×10^{-4}
278.42	2.510	4.2×10^{-6}	3.8×10^{-4}
280.17	3.001	5.3×10^{-6}	3.8×10^{-4}

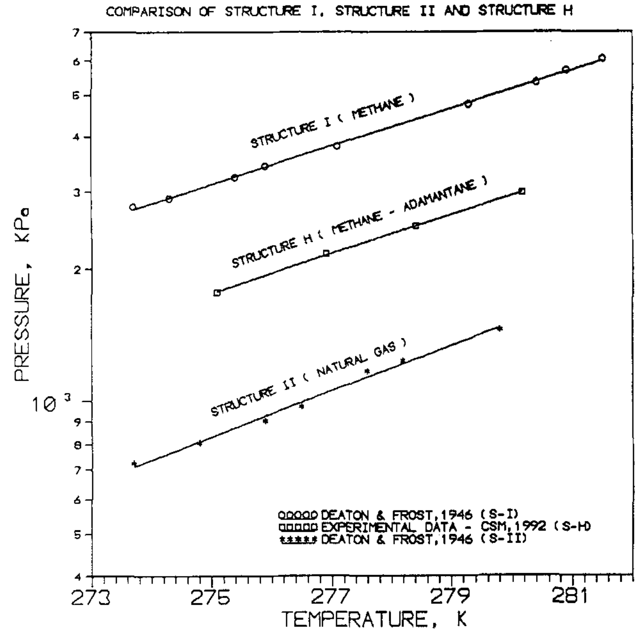

Figure 7. *s*H-phase equilibrium data compared to *s*I (methane) and *s*II (Deaton and Frost, Gas C) data.

the four-phase equilibrium line of *s*H hydrate to be parallel (to within 2%) but at pressures approximately 55% of that for the three-phase line for methane *s*I hydrate. A small part of the slope similarity may be due to the fact that the vapor phase is almost entirely methane, as shown in Table 1. The vapor phase has the principal effect on compressibility of the isochoric system, since neither the aqueous liquid, the solid adamantane, nor the *s*H phase is appreciably compressible.

The validity of the Clapeyron equation for univariant systems was indicated by van der Waals and Platteeuw (1959). The extension to the nonideal gas Clausius-Clapeyron equation enables an estimation that the heat of dissociation for *s*H is similar to that of *s*I hydrates, about 57 kJ/mol, as measured by Handa (1986).

Many simple *s*I and *s*II hydrate equilibrium lines exhibit a sharp slope deviation at the quadruple point obtained by the three-phase (L_W-H-V) pressure-temperature intersection with essentially the vapor pressure curve—more accurately the three-phase (L_W-V-L_{HC}) line—of the pure hydrate former. For *s*H equilibria, there is an analogue to the fact that methane has no upper quadruple temperature, because the critical point of methane vapor pressure occurs at 191 K. In *s*H equilibria, the fact that the vapor phase has so little adamantane and water suggests that there will be no upper quintuple (L_W-*s*H-V-L_{HC}-A) point for the four phase (L_W-*s*H-V-A) *s*H line in the temperature range of interest. Both the sealed tube melting point of adamantane (541 K) and the lower quintuple (I-L_W-*s*H-V-A) condition at 273 K are outside common interests of the industry. If a solid phase (either ice or *s*H) occurs, fluid flow will be hindered.

Katz and coworkers (Verma et al., 1975) suggested that *s*I or *s*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. Both *s*H hydrate phase equilibria conditions and the *s*H large cavity size suggest that *s*H hydrates are also likely candidates for the removal of light components from petroleum. Other instances of *in situ* *s*H hydrates may be determined in the future.

Conclusion

The first structure H hydrates are reported that form with methane as the small component. Four-phase *s*H equilibrium data are reported for methane and adamantane hydrates. These initial equilibrium data, together with the findings of Ripmeester et al., suggest that *s*H hydrates may occur in hydrocarbon processes, both in the natural gas industry and in the petroleum industry. The characteristics of *s*H hydrate formation reinforce the concept that such hydrates may occur *in situ*. There is a need for single-crystal X-ray diffraction data to determine the definitive crystal structure.

Acknowledgment

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