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Structure H and Structure I Hydrate Equilibrium Data for 2,2-Dimethylbutane with Methane and Xenon

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Three-phase (ice + hydrate + vapor and liquid water + hydrate + vapor) equilibrium data are presented for xenon structure I (sI) hydrate in the temperature range 228−288 K. Four-phase (ice + hydrate + liquid hydrocarbon + vapor and liquid water + hydrate + liquid hydrocarbon + vapor) equilibrium data are reported for structure H (sH) hydrates of xenon + 2,2-dimethylbutane and methane + 2,2-dimethylbutane. The data for both of the latter systems indicated two invariant five-phase points (I + liquid water + sH + V + liquid hydrocarbon) at 273.15 K while the data for the water + xenon + 2,2-dimethylbutane system indicated an additional quintuple point (liquid water + sI + sH + vapor + liquid hydrocarbon) at 283.2 K.

Introduction

Clathrate hydrates are crystalline inclusion compounds formed by a hydrogen-bonded network of water molecules enclathrating guest molecules like methane, xenon, propane, and butane. The two common forms of clathrate hydrate known as structure I and structure II hydrates were first reported by Stackelberg and Müller (1951), and were reviewed in detail by Sloan (1990).

Structure H (sH) hydrate, discovered by Ripmeester et al. (1987), is unusual because of its ability to enclathrate molecules up to 9 Å in diameter such as methylcyclohexane in the presence of help guests such as methane or xenon. While the existence of sH hydrate was established, no equilibrium data for sH hydrates were reported until the methane + adamantane hydrate equilibria were measured in this laboratory by Lederhos et al. (1992). Subsequently sH phase equilibrium data were reported for methane + methylcyclohexane by Becke et al. (1992), a series of methane + liquid hydrocarbons by Mehta and Sloan (1993, 1994) and by Thomas and Behar (1994), and methane + methylcyclopentane and nitrogen + methylcyclopentane by Danesh et al. (1994). Structure H equilibrium data in the presence of salts have also been reported by Hütz and Englezos (1995). A statistical thermodynamics model for the prediction of sH hydrate equilibria was developed by Mehta and Sloan (1994b, 1995).

Gas hydrates may form either from ice or from liquid water. Xenon (effective diameter 0.458 nm) and methane (0.436 nm) stabilize only the small dodecahedral (5^{12}) cavity and the medium ($4^3 5^6 6^3$) cavity of sH hydrate. 2,2-Dimethylbutane (0.773 nm) can fit only into the large ($5^{12} 6^8$) cavity of sH hydrate. Because of its size, 2,2-dimethylbutane cannot fit into any cage of sI or sII hydrates. At complete cavity occupancy the unit cell of sH hydrate is composed of 34 water molecules which may enclathrate at most one 2,2-dimethylbutane molecule and five molecules of xenon or methane.

Three-component systems (such as methane + 2,2-dimethylbutane + water) have both industrial and scientific importance. Large molecules like 2,2-dimethylbutane are often present in hydrocarbon condensates. Industrial installations typically operate in the temperature range of the data reported here, providing the possibility of sH hydrate formation when water is present.

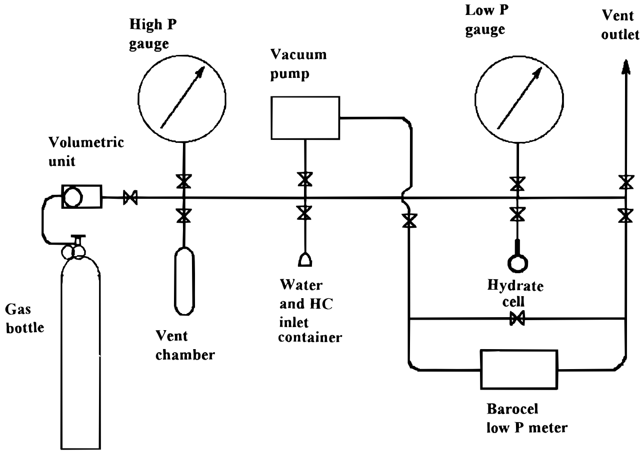

Figure 1. Schematic diagram of the apparatus.

In this work pure xenon was used to form structure I hydrate, and data were compared to the data reported by Aaldijk (1971), by Miller (1980), and by Amer (1981). Xenon + 2,2-dimethylbutane and methane + 2,2-dimethylbutane were chosen as the structure H hydrate formers. Mehta and Sloan (1993) reported four data points for methane + 2,2-dimethylbutane sH hydrate above 273 K. No previous phase equilibrium data were available for sH hydrate of the xenon + 2,2-dimethylbutane guest mixture. This work was initiated principally as an investigation of the pressure−temperature phase diagram of sH hydrate for the xenon + 2,2-dimethylbutane system.

Experimental Section

A schematic diagram of the apparatus is shown in Figure 1. A spherical stainless steel reactor rated to 1500 psia was used to form hydrates. One hundred fifty stainless steel balls of 1/8 in. diameter were placed inside the reactor, which was agitated by a Thermolyne orbital shaker at 600 rpm in order to renew the solid formation surface.

The reactor and tubing were evacuated to 8 Pa with a Trivac vacuum pump separated from the apparatus by a cold trap. The reactor was immersed in a constant temperature bath, which was maintained within ±0.3 K at temperatures below 260 K, and within ±0.2 K at higher

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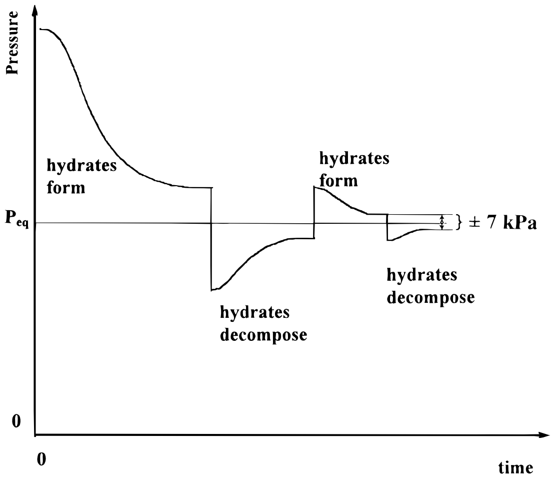

Figure 2. Schematic diagram of the experimental procedure at constant temperature.

Table 1. Pure Xenon sI Hydrate Equilibrium

T/K	*P*/MPa	*T*/K	*P*/MPa
288.15	0.01620	283.15	0.4263
273.15	0.1551	228.15	0.6984

temperatures by a Neslab temperature controller. The bath was cooled by a Neslab CC-100 II refrigerator. The pressure in the reactor was monitored by two Heise Bourdon tube gauges with ranges of 0−2068 kPa ± 1.38 kPa and 0−13790 kPa ± 13.79 kPa. A Barocel electronic differential manometer provided pressure measurements in the range 0−267 kPa ± 0.133×10^{-3} kPa.

The reactor was charged with water and liquid hydrocarbon by vacuum distillation. A weighed sample of degassed water was vacuum distilled into the cold reactor by evaporation from the inlet flask. Then the reactor was immersed in liquid nitrogen, and any noncondensed water vapor was evacuated. For sH hydrate experiments liquid hydrocarbon was also vacuum distilled into the reactor. All lines were evacuated after each vacuum distillation was complete.

Xenon of 99.999% purity and methane of 99.99% purity were obtained from Matheson Gas Products, Inc., and General Air Products, respectively. Gas was charged to the reactor at the initial experimental value, and the shaker was turned on. Pressure was recorded at intervals of 10−30 min.

A rapid drop in the pressure was observed as a result of hydrate formation as shown in Figure 2. The pressure drop occurred due to encapsulation of the gas molecules in the hydrate phase. After the initial rapid pressure drop, the rate of hydrate formation decreased gradually. In order to determine the equilibrium pressure, a trial and error procedure was adopted. The pressure in the cell was partially vented. Upon system shut-in, if the pressure increased, hydrates decomposed, and the system was below the hydrate equilibrium pressure. However, if the pressure continued to decrease after partial venting of the gas, the system was above the hydrate equilibrium pressure. Assuming that the pressure increased, in subsequent cycles the cell was recharged slightly above the original stabilized value. Again, a drop in the pressure indicated that the system was above the hydrate equilibrium pressure, and that hydrate formation had resumed.

It should be noted that increasing the cell pressure will always result in some pressure recovery due to the presence of liquid hydrocarbon. However, this pressure increase is negligible compared to the pressure increase that will be observed if hydrates dissociate.

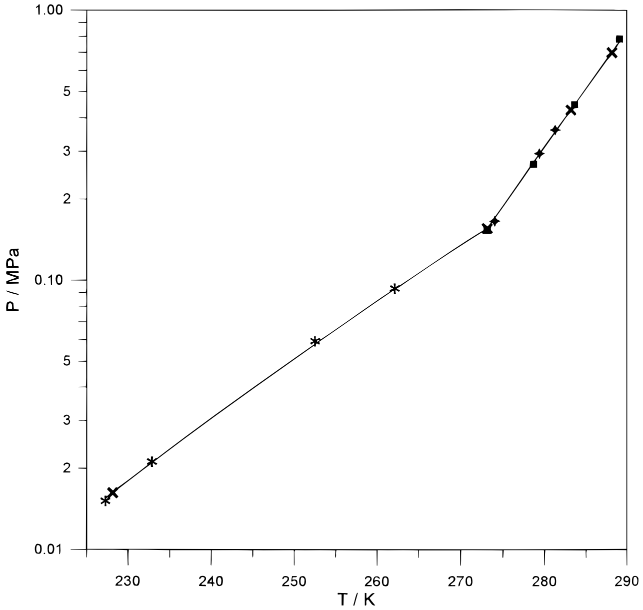

Figure 3. Equilibrium data for xenon sI Hydrate: *, I + sI + V (Miller, 1980); ×, I + sI + V (this work); ■, L_W + sI + V (Aaldijk, 1971); ◆, L_W + sI + V (Amer, 1981); ×, L_W + sI + V (this work).

Table 2. Xenon + 2,2-Dimethylbutane Hydrate Equilibrium

T/K	*P*/MPa	*T*/K	*P*/MPa
I + sH + V + L_{HC}		L_W + sH + V + L_{HC}	
233.15	0.0145	273.15	0.1315
253.15	0.0464	274.15	0.1482
263.15	0.0785	275.65	0.1812
		276.15	0.1858
L_W + sI + V + L_{HC}		277.15	0.2089
283.15	0.4525	278.15	0.2375
	0.4536		0.2412
	0.4602	279.15	0.2717
284.15	0.5005	279.65	0.2927
	0.5040	280.15	0.3103
285.15	0.5509	280.65	0.3447
	0.5568	281.15	0.3665
285.65	0.5742		0.3671
286.15	0.6057	281.95	0.3944
288.15	0.7336		
	0.7363		

The trial and error procedure was repeated until the differential between the lower formation and upper decomposition pressures was between 7 and 14 kPa. The arithmetic average of the two closest values of decomposition and formation pressures was recorded as the equilibrium pressure of hydrate formation at the given temperature. Upon completion of the experiment the reactor and tubing were evacuated.

Results and Discussion

The set of data measured for pure xenon sI hydrate formation conditions with 1 g of water in the reactor at constant temperatures is presented in Table 1. These data are consistent with the results reported by Aaldijk (1971), Miller (1980), and Amer (1981) as shown in Figure 3. The small degree of curvature in the equilibrium line for xenon sI hydrate in Figure 3 at temperatures below 273 K is attributed to the change in heat capacities of water and xenon as discussed by Makogon and Sloan (1994).

A set of data for xenon + 2,2-dimethylbutane sH hydrate equilibria is presented in Table 2. These data were obtained with 1−2 g of water and an excess amount of 2,2-dimethylbutane (0.15−1 g) in order to avoid the disappearance of the liquid hydrocarbon phase. The presence of the liquid hydrocarbon phase in the system was verified by performing a flash calculation for the xenon + 2,2-dimethylbutane mixture at the corresponding temperatures and pressures of hydrate equilibrium. Six runs for sH hydrate formation were duplicated. Figure 4 presents the xenon + 2,2-dimethylbutane sH hydrate equilibrium data in the region above and below 273.15 K and the xenon + 2,2-dimethylbutane sI hydrate equilibrium data in the region above 283.2 K.

It was concluded that xenon + 2,2-dimethylbutane sH hydrate formed below 283.2 K on the basis of the fact that the hydrate equilibrium pressure was substantially lower than that of xenon sI hydrate. Five phases coexist at the quintuple point Q_1 at 273.15 K: ice (I) + liquid water (L_W) + sH hydrate (sH) + vapor (V) + liquid hydrocarbon (L_{HC}). These phases are listed in the order of decreasing water content.

At 283.2 K there was a distinct change in the slope of the measured hydrate equilibrium locus. Above 283.2 K the hydrate equilibrium locus was found to be parallel to the pure xenon sI hydrate equilibrium locus. This indicated that above 283.2 K sI hydrate formed instead of sH. Along this sI equilibrium line, 2,2-dimethylbutane acted as a vapor phase diluent and caused the xenon + 2,2-dimethylbutane sI line to lie at the slightly higher pressure than the pure xenon sI equilibrium line.

The intersection of the sI and sH equilibrium lines in Figure 4 produces a five-phase quintuple point, Q_3 (L_W + sI + sH + V + L_{HC}), at 283.2 K where both sI and sH hydrates coexist. Such a phenomenon is thermodynamically valid, and is supported by the Gibbs phase rule and by the P−T topology determined using Schreinemakers' rules (1915−25). A comprehensive discussion of the complete phase diagram for sH hydrates using Schreinemakers' geometric approach is presented by Mehta et al. (1995). Below we present a few details of the diagram which pertain to the data obtained in this work.

The abrupt change of slope of the measured hydrate equilibrium line can be observed in Figure 4 at 283.2 K. According to the Clausius−Clapeyron equation

$$\frac{d(\ln P)}{d(1/T)} = -\frac{\Delta_d H}{zR} \qquad (1)$$

where P and T are the corresponding pressure and temperature of hydrate equilibrium. Hence, a change in the slope of a univariant line is proportional to the change in the heat of dissociation of hydrate $\Delta_d H$. The sharp change in the heat of dissociation of hydrate indicates a structural transition of hydrate.

According to the Gibbs phase rule, $\Phi = C - P + 2$, where Φ, C, and P are the number of degrees of freedom, number of components, and number of phases, respectively. In a three-component system, five different phases can coexist at an invariant quintuple point. Two quintuple points, Q_1 (I + L_W + sH + V + L_{HC}) and Q_3 (L_W + sI + sH + V + L_{HC}), exist in the data for this system. Quintuple point Q_3 is unusual because two different hydrate structures—sI and sH—coexist.

A univariant locus is formed when 1 degree of freedom is present. For example, in a three-component system, four phases coexist along a univariant locus. N univariant loci can emanate from any invariant point, where N is the number of phases which coexist in the invariant point. For example, for a two-component water + xenon system, four univariant loci, I + sI + V, I + L_W + sI, I + L_W + V, and L_W + sI + V, meet at a four-phase quadruple (I + L_W + sI + V) point. The first two of these four univariant loci have been experimentally measured (Figure 3) for the xenon + water system.

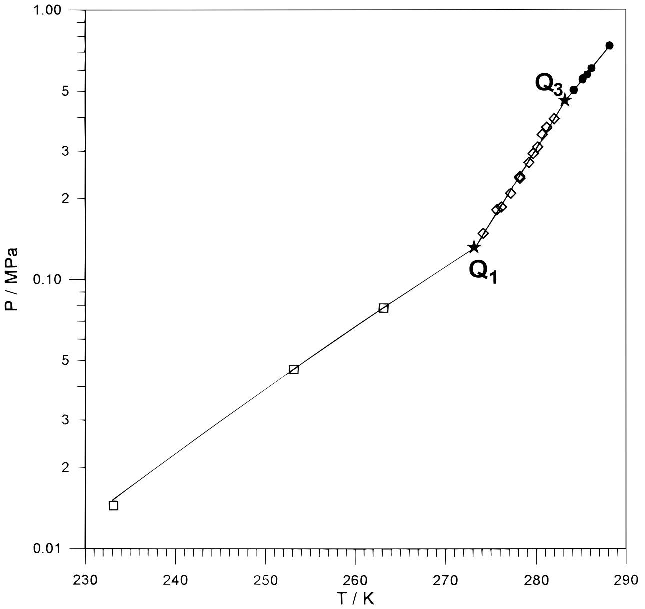

Figure 4. Equilibrium data for xenon + 2,2-dimethylbutane hydrate: □, I + sH + V + L_{HC} (this work); ◇, L_W + sH + V + L_{HC} (this work); ●, L_W + sI + V + L_{HC} (this work); ★, quintuple points Q_1 (I + L_W + sH + V + L_{HC}) and Q_3 (L_W + sI + sH + V + L_{HC}).

Table 3. Methane + 2,2-Dimethylbutane sH Hydrate Equilibrium

T/K	P/MPa	T/K	P/MPa
244.85	0.332	258.85	0.626
251.45	0.447	273.95	1.241

Experimental data for the water + xenon + 2,2-dimethylbutane system reported in Table 2 represent two univariant loci emanating from Q_1, and two univariant loci from Q_3. Quintuple points Q_1 and Q_3 bound the univariant locus where L_W + sH + V + L_{HC} phases coexist (Figure 4). The second measured locus which comes from Q_3 is the line along which L_W + sI + V + L_{HC} phases coexist. The quintuple point Q_2 (I + L_W + sI + V + L_{HC}) was found to be metastable. It was determined that below 283.2 K in the presence of a liquid hydrocarbon phase containing sH forming molecules, sI hydrate always transformed into a more stable sH hydrate.

Only some of the univariant loci and invariant points predicted by Schreinemakers' rules are stable in nature. Attempts to measure the other three univariant lines (L_W + sI + sH + V, L_W + sI + sH + L_{HC}, and sI + sH + V + L_{HC}) coming from Q_3 were unsuccessful. This suggests that sI and sH hydrates do not coexist for this system in the investigated P−T region, except at the one point measured.

Mehta and Sloan (1993) reported the spontaneous sH hydrate formation for the methane + 2,2-dimethylbutane system at initial pressures above and below sI methane hydrate equilibrium; this was unusual because in other binary systems sI hydrate was normally required as a sH hydrate initiator. In the present work we also observed the spontaneous formation of sH hydrate of xenon + 2,2-dimethylbutane without the necessity of sI hydrate as an initiating medium.

A set of data for methane + 2,2-dimethylbutane sH hydrate was also measured (Table 3). Figure 5 presents the data sets for equilibrium measurements of methane + 2,2-dimethylbutane sH hydrate above and below the ice point. A quintuple point, Q_1 (I + L_W + sH + V + L_{HC}),

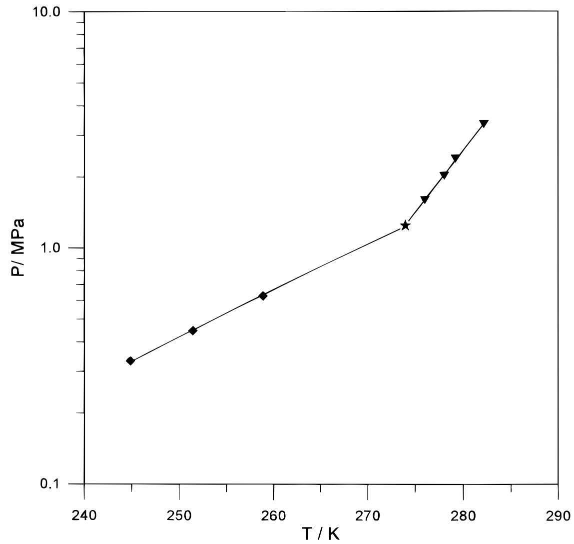

Figure 5. Equilibrium data for Methane + 2,2-dimethylbutane sH hydrate: ◆, I + sH + V + L_{HC} (this work); ▼, L_W + sH + V + L_{HC} (Mehta and Sloan, 1993); ★, quintuple point Q_1 (I + L_W + sH + V + L_{HC}).

occurs at the intersection of the two lines shown in Figure 5 at the ice point temperature.

Conclusions

Data for sI hydrate of xenon and for sH hydrates of xenon + 2,2-dimethylbutane and methane + 2,2-dimethylbutane were presented in the regions 228−288 K, 233−288 K, and 244−273 K, respectively. One quintuple point was measured for the methane + 2,2-dimethylbutane system, and two quintuple points were measured for the xenon + 2,2-dimethylbutane system. The existence of an upper quintuple point at 283.2 K and 0.452 MPa was determined where sH and sI hydrates coexist for xenon + 2,2-dimethylbutane.

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