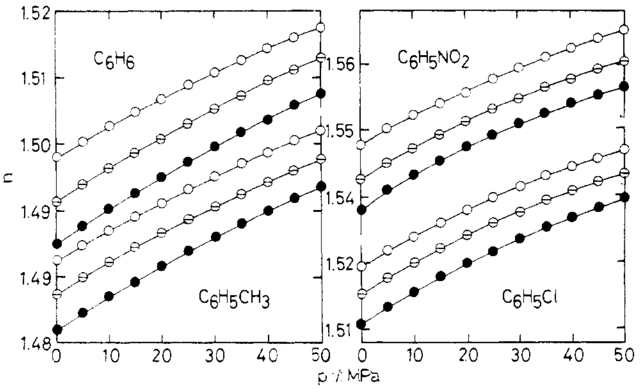

Figure 3. Refractive indexes of liquids for 632.8 nm at (○) 293.15, (⊖) 303.15, and (●) 313.15 K.

chlorobenzene, and nitrobenzene for 632.8-nm light are listed in Table III. As to the refractive indexes of various organic liquids at atmospheric pressure, it is known that they slightly decrease as the wavelength of the measuring light increases (*1*, *3*, *5*). However, the values for the wavelength of 632.8 nm, corresponding to the light source of the He-Ne laser, have been scarcely measured, except for the report of Langer and Montalvo (*2*), where the refractive index of mesitylene for 632.8 nm is reported as 1.4946 at 295.15 K and atmospheric pressure. And so, we at first estimated by the least-squares method the refractive index of mesitylene for 632.8 nm at 293.15 K from data for several wavelengths at 293.15 K reported in the literatures (*1*, *3*, *5*), and, to check the estimated values, we measured change in the refractive index with temperature over the range 293.15-295.15 K. The value at 295.15 K thus obtained is 1.4944, and this value is found to coincide with that of Langer and Montalvo (*2*). Thus, for all of the present samples, the values at 0.1 MPa in Tables III are estimated values which are determined by the same method described above.

For each compound, the observed refractive indexes increase parabolically with increasing pressure throughout the experimental range, as shown in Figure 3. From these results, it is found that the values for the temperature and pressure dependence of the refractive index, $(\partial n/\partial T)_p$ and $(\partial n/\partial p)_T$, decrease with an increase of pressure and have a tendency similar to that of the specific volume on pressure, which was estimated from the pressure dependence at ultrasonic speed, as described in our previous papers (*6*-*8*).

Literature Cited

(1) Forziati, A. F. *J. Res. Natl. Bur. Stand.* (*U.S.*) **1950**, *44*, 373.
(2) Langer, D. W.; Montalvo, R. A. *J. Chem. Phys.* **1968**, *49*, 2836.
(3) "Landolt-Bornstein Tabellen"; Springer-Verlag: West Berlin, 1962; 6 Aufl., 8 Teil, Zahlenwerte und Funktion.
(4) Richard, A. J. *J. Chem. Phys.* **1960**, *72*, 4063.
(5) Savkovic-Stevanovic, J.; Simonovic, C. *J. Chem. Eng. Data* **1976**, *21*, 456.
(6) Takagi, T. *Rev. Phys. Chem. Jpn.* **1978**, *48*, 10.
(7) Takagi, T. *Rev. Phys. Chem. Jpn.* **1978**, *48*, 17.
(8) Takagi, T. *J. Chem. Thermodyn.* **1980**, *12*, 277.
(9) Waxler, R. M.; Weir, C. E. *J. Res. Natl. Bur. Stand., Sect. A* **1963**, *67*, 163.

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Hydrates of Methane + *n*-Butane Below the Ice Point

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Three-phase vapor (V)-ice (I)-hydrate (H) and four-phase vapor-ice-hydrate-liquid hydrocarbon (L_2) equilibrium conditions were measured for mixtures of methane and *n*-butane, at temperatures below the ice point. One purpose of the experiments was to determine whether pure *n*-butane gas can form hydrates; the results led to the conclusion that *n*-butane cannot form hydrates under its own vapor pressure. The experimental results can also serve as a basis for evaluating the accuracy of models for predicting hydrate phase equilibrium (*1*). The experimental method followed to nucleate hydrates at temperatures below 273.15 K is a variation of the procedure used to form hydrates at higher temperatures.

Introduction

Gas hydrates are a form of clathrate compounds formed by water and gases of low molecular weight. Hydrates crystallize in either of two structures, commonly known as structures I and II, each of which contains two characteristic interstitial vacancies referred to as large and small cavities. The crystal lattice is made up of water molecules that are strongly hydrogen bonded. Gas molecules are enclosed in cavities formed by these lattice structures and interact with the water molecules of a cavity through dispersion forces. The formation of structure I or II is dependent on the relative stabilities of the two structures when a given gas (or gas mixture) is enclathrated at the thermodynamic conditions in effect.

Determination of gas hydrate equilibrium is important from the standpoint of assessing the potential of recovering gas from hydrate reservoirs, and in gas processing and pipeline operations. In such determinations, it is useful to establish whether the heavier components of natural gas, such as the propanes and the butanes, contribute to the hydrate formation process. The enclathration of such relatively large molecules tends to strongly stabilize the hydrate structure and thereby lower the equilibrium pressure considerably. In understanding hydrate formation, it is important to determine which large molecules can form hydrates at pressures below their vapor pressure at a given temperature. Several studies have been conducted on the formation of hydrates from pure *n*-butane or from gas mixtures containing *n*-butane; Ng and Robinson (*2*) have presented a detailed bibliography of these studies. There has been conflicting evidence, however, on the role of n-butane in hydrate formation. A systematic study of hydrate formation in

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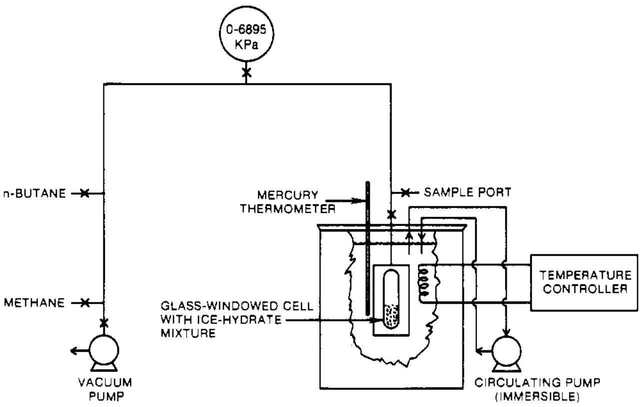

Figure 1. High-pressure experimental apparatus to study hydrate equilibrium at low temperatures.

n-butane–methane systems was conducted by Ng and Robinson (*2*), who clearly established that *n*-butane participates in hydrate formation. They showed that, over a temperature range of 273–288 K, the equilibrium pressures for hydrates of methane–*n*-butane mixtures range from 1000 to 10 000 kPa, which are lower than the equilibrium pressures of pure methane hydrate over the same temperature range. This indicates that *n*-butane is helping to stabilize the hydrate through enclathration in the large cavities of structure II. The stabilization is manifested in a reduction of the pressure needed to achieve hydrate equilibrium. No temperature-independent conclusions regarding the formation of hydrates from pure *n*-butane vapor could be drawn from this data.

The experimental work presented in this paper is an extension of the study done by Ng and Robinson (*2*). The objective of the present work was to obtain hydrate equilibrium data at temperatures below the ice point on gas mixtures of methane and *n*-butane. On the basis of the experimental results, it was possible to reach definite conclusions regarding the formation of hydrates from pure *n*-butane vapor. In addition, this work establishes a highly useful experimental procedure for measuring hydrate equilibrium at temperatures below the ice point, which can be used to study the hydrates of other gases at similar temperatures.

Apparatus and Experimental Procedure

Hydrates of methane and *n*-butane were formed in a high-pressure, glass-windowed cell of the apparatus shown in Figure 1. The cell was immersed in a well-stirred, constant-temperature, methanol–water bath. Temperature control within the bath was maintained by using a refrigeration unit in conjunction with an electronic relay control unit and a microset thermoregulator (GCA/Precision Scientific). In order to control the temperature as accurately as possible, we set the refrigeration unit at its maximum cooling capacity and controlled the temperature by means of an auxiliary heater connected to the electronic relay control unit. The temperature was measured by using a mercury-in-glass thermometer with an accuracy of ±0.05 K, which was calibrated at 273 K by using an NBS-certified thermometer. Periodic temperature measurements were made with a calibrated Beckman thermometer correct to within 0.01 K. Pressures were measured by using a Heise pressure gauge with a range of 6895 kPa and an accuracy of ±6.9 kPa.

Methane-n-Butane Quadruple Locus (VL$_2$HI). The quadruple locus is the locus of equilibrium conditions of pressure and temperature at which a hydrate phase (H) coexists with the gas phase (V), the ice (or water) phase (I or L$_1$), and a liquid hydrocarbon phase (L$_2$). From the Gibbs phase rule, such an equilibrium system is univariant. In the present study, equilibrium pressures were measured as a function of temperature.

Table I. Hydrate Equilibrium Pressures Along the VIL$_2$H and VL$_1$L$_2$H Quadruple Loci for Methane–*n*-Butane Mixtures

temp, K	press., kPa	temp, K	press., kPa
	VIL$_2$H		
255.3	417.1	264.5	661.9
256.1	430.9	255.1	682.6
257.2	458.5	265.85	710.2
258.0	479.2	269.05	813.6
259.0	499.9	269.25	827.4
259.9	524.0	270.3	875.6
260.8	544.7	271.0	903.2
261.9	575.7	271.7	937.7
263.6	620.5	272.5	979.0
263.85	634.0		
	VL$_1$L$_2$H		
273.3	1046.0	275.1	1342.0
273.85	1073.0	275.9	1504.0
274.3	1177.0	276.8	1722.0

The following experimental procedure was adopted to obtain the quadruple locus.

Before the experiment, the cell was disconnected from the rest of the system and kept partially immersed in the bath which was maintained at ~258 K. When water-saturated air was passed through the cell, fine crystals of ice were formed along the cell walls, maximizing the surface area available for hydrate formation. The cell was reconnected to the system and successively evacuated and flushed with *n*-butane in order to remove all traces of air. *n*-Butane was then very slowly introduced into the cell until a constant pressure was attained, indicating the presence of condensed butane in equilibrium with its vapor. After a sufficient amount of *n*-butane was allowed to condense, methane was introduced into the system, raising the pressure to a value that was substantially greater than the equilibrium quadruple pressure at 273.15 K (*2*).

Hydrate formation, indicated by substantial pressure decreases, was extremely slow below the ice point for either of two reasons: (a) the change of crystal structure from ice to hydrate involves a significant energy barrier; (b) the formation of a monolayer of hydrates over the surface of the ice could occlude the ice below the hydrate layer. It was found that, if the ice was very slowly allowed to melt, hydrates would be formed in preference to liquid water if the pressure was greater than the equilibrium pressure at 273.15 K. Therefore, the temperature of the bath was gradually increased to 273.15 K, at which temperature the rate of hydrate formation was found to increase considerably. By adjusting the temperature and the pressure (through the introduction of methane at regular intervals), we kept the rate of hydrate formation high in order to prevent the formation of liquid water. The bath was then slowly cooled to ~263 K, at which point the pressure was allowed to stabilize.

From equilibrium data along the quadruple locus above the ice point (*2*), a rough estimate of the quadruple point at 263 K was obtained. Gas, which was in equilibrium with the methane–*n*-butane liquid, was removed from the cell until the pressure was ~50 kPa above this estimated value. Subsequently, the bath temperature was slowly increased in steps of ~0.3–0.5 K, and, after each temperature increment, the cell pressure was allowed to reach a stable value. Pressure stability typically occurred within a time period of 6–12 h. An increase in slope of log *P* vs. *T*, as temperature is increased, is interpreted to be indicative of pressure enhancement due to hydrate dissociation. Consequently, the conditions at which the log *P* vs. *T* plot changes slope is taken as a quadruple point. Because the quadruple locus is univariant, additional points on the quadruple locus could be obtained by adjusting the temperature upward and waiting for equilibrium to be reached. The three sets of data below the ice point in Figure 2 indicate that the experiment was carried out over three ranges of temperatures.

Table II. Three-Phase (VIH) and Four-Phase (VL_2IH) Hydrate Equilibrium in the Methane-*n*-Butane System at Temperatures Below 273.15

$T = 273.05$ K		$T = 268.15$ K		$T = 262.15$ K		$T = 256.15$ K		$T = 251.15$ K	
p	y	p	y	p	y	p	y	p	y
2611	0.8	2204	0.55	1784	0.5	1480	0.5	1267	0.4
2446	0.95	1963	0.75	1529	0.9	1246	0.6	1011	0.7
2335	1.2	1728	1.15	1356	1.2	1067	1.0	805	1.1
2142	1.4	1563	1.5	1108	2.0	901	1.5	680	1.8
1894	1.95	1342	2.3	970	2.9	818	2.0	522	3.8
1618	2.75	1232	3.15	846	4.2	680	3.2	474	5.0
1384	4.1	1177	3.4	715	6.3	605	4.5	446	5.9
1136	6.6	1011	5.2	639	9.3	536	6.5	391	8.8
1011^b	10.1^b	915	6.8	570^b	12.6^b	460	10.0	336^b	13.3^b
		880	7.8			446	11.4		
		784^b	11.0^b			432^b	12.8^b		

[a] p = pressure (kPa); y = mol % *n*-butane in vapor. [b] Quadruple point.

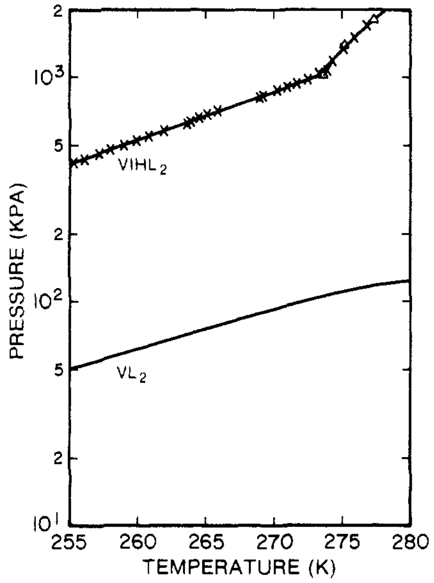

Figure 2. Experimental four-phase VIL_2H quadruple locus for methane–*n*-butane hydrates. Vapor-pressure (VL_2) data for *n*-butane are also shown (*4*); (X) experimental, (Δ) Ng and Robinson (*2*).

The data are listed in Table I.

Experiments were also carried out to obtain hydrate equilibrium data along with quadruple locus above the ice point. At temperatures greater than 273.15 K, hydrates were formed by shaking the contents of the cell and could be visually observed. An initial data point at 273.3 K was obtained by dropping the pressure below an estimated quadruple-point pressure (*2*) and noting the equilibrium value to which the pressure increases. The temperature was then increased in increments and the equilibrium pressure of hydrate dissociation at each temperature determined. The results are listed in Table I.

Methane-n-Butane Three-Phase VIH Equilibria. The three-phase vapor (V)–ice (I)–hydrate (H) equilibrium in the methane–*n*-butane system is divariant in nature. In previous studies on divariant equilibria (*3*), the temperature and gas-phase compositions were treated as the independent variables and the equilibrium pressure was experimentally determined as a function of these variables. In the present study, the temperature and the pressure of the system were chosen as the independent variables, and gas-phase compositions were determined as a function of these equilibrium conditions. The experimental procedure follows.

Hydrates of methane and *n*-butane were formed at 273.15 K by using the same procedure followed for the quadruple-locus determination. Hydrates were allowed to form, however, until all of the liquid *n*-butane was consumed. Visual observation of the contents of the cell, after freezing any liquid water present by lowering the bath temperature below 273.15 K, enabled determination of whether any liquid *n*-butane was still present. The system temperature was then raised above 273.15 K, and methane was added to form additional hydrates. As reported in the literature (*2*), the methane–*n*-butane system forms hydrates of structure II that are stable at pressures lower than the equilibrium pressure of pure methane hydrate which exists as structure I. As methane was added to the system and the concentration of *n*-butane in the gas phase was significantly reduced, hydrates of structure I, as indicated by pressures near the dissociation pressures of methane hydrate, began to form.

After a large amount of hydrates had been formed, the temperature was adjusted to 268.15 K and the pressure to a value ~50 kPa greater than the equilibrium pressure of pure methane hydrate at 268.15 K. The pressure was then reduced by ~100 kPa, and sufficient time was allowed for the system to equilibrate. A time duration of 24–36 h was usually needed to achieve equilibrium. The equilibrium pressure was noted, and a gas sample was obtained in a sampling bulb and then analyzed by standard gas chromatography. The withdrawal of the gas sample caused the system pressure to drop. A pressure reduction of ~100 kPa was effected and the system allowed to achieve equilibrium again. Thus, a sequence of equilibrium pressures and compositions at a temperature of 268.15 K was determined. In the initial stages of the experiment, the pressure tended to reach equilibrium values at the equilibrium pressure for pure methane hydrate. Apparently, this is due to the dissociation of structure I hydrates. Subsequent equilibrium pressures were below those of pure methane hydrate, indicating structure II hydrate dissociation.

The pressure–composition equilibrium curve was found to terminate at the quadruple point at 268.15 K. At the quadruple point, the system becomes univariant with the appearance of the liquid hydrocarbon phase, and the pressure and the gas composition are uniquely determined at the temperature of interest. The pressure and the gas composition at the quadruple point were measured, and the pressure was found to agree closely with the quadruple-point pressure at 268.15 K obtained from the quadruple-locus determination discussed above.

The experiment was repeated at temperature of 273.05, 262.15, 256.15, and 251.15 K, and the results are presented in Figure 3 and Table II.

Results and Discussion

Figure 2 compares the quadruple locus of the methane–*n*-butane mixture (VIL_2H) to the vapor-pressure curve of pure *n*-butane (VL_2) (*4*) over a 20 K range in temperature. It is seen that the VIL_2H and VL_2 curves do not intersect in the temperature range studied, and the respective slopes indicate that

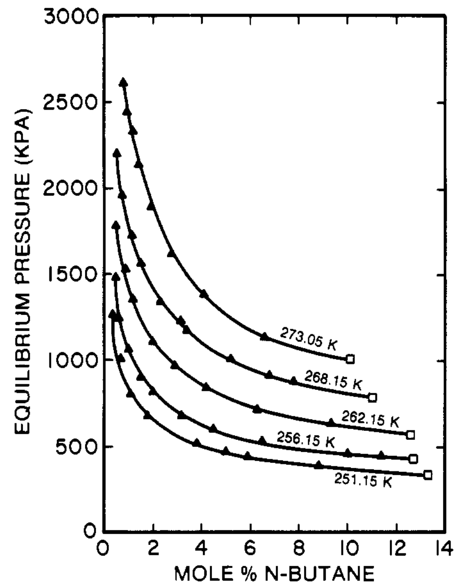

Figure 3. Experimental VIH (▲) and VL_2IH (□) equilibrium in the methane-*n*-butane system.

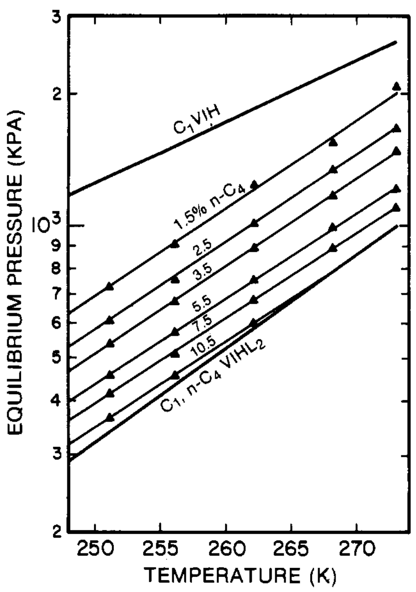

Figure 4. VIH and VL_2IH dissociation pressures of methane-*n*-butane hydrates.

the two curves are unlikely to intersect even at very low temperatures. It typical hydrate systems of mixtures of two gases of different volatility, for example, the methane-isobutane system (*5*), the VL_1L_2H quadruple locus intersects the vapor-pressure curve of the less-volatile component at the highest temperature at which hydrates of the less-volatile component can exist in the absence of liquid hydrocarbon. Since such an intersection does not occur for the methane-*n*-butane quadruple locus (Figure 2), one can reasonably conclude that pure *n*-butane vapor does not form hydrates at any temperature.

From a molecular viewpoint, the *n*-butane molecule can fit only into the large cavity of structure II hydrates and its movement within the cavity is highly restricted to torsional oscillations about the cis configuration (*6*). This would indicate that the chemical potential of pure *n*-butane in the hydrate phase is much higher than its chemical potential in the liquid phase; *n*-butane vapor would hence tend to condense to liquid rather than form hydrates. Hydrates of pure *n*-butane are expected to form only from a highly compressed liquid state if at all.

Figure 4 is a ln *P* vs. *T* plot of the pressure-composition data for methane-*n*-butane mixtures presented in Figure 3 and Table II. The graph indicates that the constant-composition curves are very nearly parallel. In theory, each constant-composition curve indicates univariant VIH equilibria and follows the Clapeyron equation

$$d \ln P/dT = \Delta H/(RT^2)$$

where ΔH is the molar heat of dissociation of the hydrate phase. It is observed that the VIH curves intersect the quadruple locus at the quadruple point; the slope of the quadruple locus also follows the Clapeyron equation, but ΔH here is indicative of a combined heat of dissociation term and heat of vaporization (of *n*-butane).

Conclusions

The experimental work described in this paper achieves three objectives. First, it conclusively shows that *n*-butane will not form hydrates under its vapor pressures at any temperature. Secondly, the experimental data obtained provide a basis for evaluating improved models for predicting hydrate equilibria of nonideal gases, such as the highly aspherical propanes and the butanes. Finally, there exist very few data for hydrate formation below the ice point; the experimental technique described here represents a straightforward and efficient method for obtaining data for the hydrates of other nonpolar gases at low temperatures.

Literature Cited

(1) van der Waals, J. H.; Platteeuw, J. C. *Adv. Chem. Phys.* **1959**, *2*, 1.
(2) Ng, H. J.; Robinson, D. B. *AIChE J.* **1976**, *22*, 656.
(3) Holder, G. D.; Grigoriou, G. C. *J. Chem. Thermodyn.* **1976**, *8*, 461.
(4) Perry, R. H.; Chilton, C. H. "Chemical Engineers Handbook", 4th ed.; McGraw-Hill: New York, 1963; Chapter 3.
(5) Wu, B. J.; Robinson, D. B.; Ng, H. J. *J. Chem. Thermodyn.* **1976**, *8*, 461.
(6) Davidson, D. W.; Ripmeester, J. A. *J. Glaciol.* **1978**, *21*, 33.

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