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# Hydrate Equilibrium Conditions for Cyclopentane and a Quaternary Cyclopentane-Rich Mixture

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Experimental data on hydrate formation of cyclopentane and a 98.40 mass % purity cyclopentane mixture containing three impurities (0.48 mass % pentane, 0.48 mass % 2-methyl butane, and 0.72 mass % 2-methyl propane) in water were measured. The measurements were carried out in a transparent sapphire cell (100-cm$^3$ effective volume) by applying a pressure-search method in the temperature range (273.3−280.8) K and the pressure range (6.9−19.8) kPa.

## Introduction

In the oil and gas industry, it is important to determine the hydrate phase boundary to avoid hydrate formation. In general, hydrates normally form in one of three repeating crystal structures (structure-I, structure-II, and structure-H). (Sloan, 1998). Structure-I, a body-centered cubic structure, forms with natural gases containing molecules smaller than propane. Structure-II, a diamond lattice within a cubic framework, forms when natural gases or oils contain molecules larger than ethane but smaller than pentane. And the structure-H hydrate (Ripmeester et al., 1991) requires the presence of a help gas (like methane, nitrogen, and carbon dioxide) for the $5^{12}$ and $4^3 5^6 6^3$ cages, but the molecules in the $5^{12}6^8$ cage can be as large as the size of common components of naphtha and gasoline. Benzene (Danesh et al., 1993), cyclohexane (Tohidi et al., 1996), and experimental hydrate dissociation data for cyclopentane and neopentane in their binaries and ternaries with methane or/and nitrogen hydrate formation characteristics have been reported (Tohidi et al., 1997). Cyclopentane hydrate has been known since 1950. It can form gas hydrates without any need for a help gas (Ripmeester et al., 1990, 1991). The original work on cyclopentane hydrate appeared in an unpublished thesis; some of the important parameters were summarized in the article by Davidson (1973). However, there are no further experimental data.

In the present work, hydrate formation data have been measured for cyclopentane as well as a quaternary cyclopentane-rich mixture (pentane, 2-methylbutane and 2-methylpropane) in the presence of water in the temperature range (273.3−280.2) K and the pressure range (6.9−19.8) kPa.

## Experimental Section

***Apparatus.*** The experiments were carried out using a high-pressure *PVT* cell for hydrate studies manufactured by Sanchez Technology Company (France). The schematic diagram of the experimental apparatus is given in Figure 1. The apparatus consisted of a "full view" cylindrical sapphire cell with variable-volume controlled by a motorized movable piston. The maximum effective volume of the cell was approximately 100 cm$^3$, and the minimum effective volume was 13.6 cm$^3$. The maximum working pressure was 40 MPa. The sapphire cell was installed in an air bath, which had a working temperature range of 253 K to 393 K.

The formation/dissociation of hydrate crystals in solution was observed directly through the transparent sapphire cell. The cell contents were mixed with a stirrer and a circulating pump. The stirrer was driven by a DC motor located at the end of the piston and a magnetic coupling mounted outside the cell. The cell pressure was measured using a COLE-PARMER (G-68000) absolute pressure transducer (0−0.9 MPa), and the cell temperature was measured using platinum resistance thermometers. The accuracy of temperature and pressure measurements was ±0.01 K and ±0.1 kPa, respectively. The signals of pressure, temperature, and volume were acquired by a data acquisition system driven by a personal computer. The cell pressure, cell temperature, cell volume, air bath temperature, flow, and stirring velocity data from the acquisition system were saved at sampling intervals on a computer hard disk.

***Materials and Preparation of Samples.*** Research grade (better than 99.5% purity) cyclopentane purchased from Shanghai First Reagent Factory (Shanghai, China) was used in this work. The composition of a quaternary mixture (98.40 mass % cyclopentane, 0.48 mass % pentane, 0.40 mass % 2-methylbutane, and 0.72 mass % 2-methylpropane) purchased from Meilong Cyclopentane Chemicals Co. Ltd. (Guangdong, China) was analyzed using gas chromatography (Hewlett-Packard Corp., Model 6890). The deionized water was redistilled prior to use.

***Experimental Procedure.*** The experimental procedure used in this work is the same as that reported in our previous work (Fan et al., 1999). Prior to charging the cell with a solution, it was rinsed with deionized water to wash out the residual solution that remained from the previous experiment. After the cell was evacuated, about 15 cm$^3$ of water was charged into the thoroughly cleaned sapphire cell. Then, the desired amount of cyclopentane was injected into the cell using a sample syringe, and the system was allowed to remain at the selected temperature to form hydrates. The presence of hydrates in the cell was deter-

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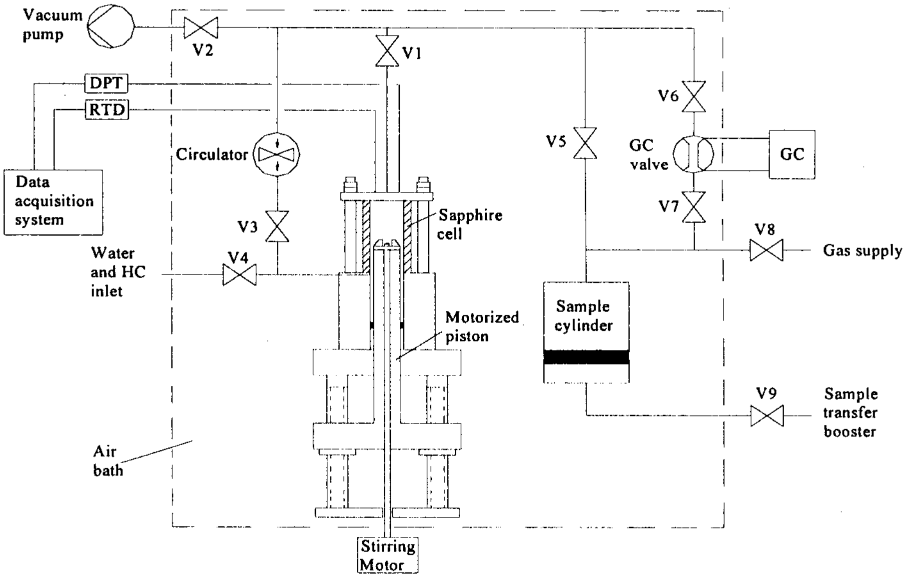

**Figure 1.** Schematic diagram of the experimental system: DP, differential transducer; RTD, resistance thermocouple detector; V1–V9, valves.

**Table 1. Measured Hydrate Dissociation Conditions for a 99.5 mass % Purity Cyclopentane in Water**

| phase | *T*/K | *P*/kPa |
|---|---|---|
| $L_W$–H–V | 273.36 | 6.9 |
| | 274.34 | 8.1 |
| | 275.23 | 9.2 |
| | 276.49 | 11.2 |
| | 277.51 | 13.2 |
| | 278.87 | 16.3 |
| | 279.87 | 18.9 |
| | 280.22 | 19.8[a] |

[a] $Q_2$ quadruple point.

mined both by visual observation and by graphic solution. The equilibrium experimental data are obtained using the "pressure search" procedure (Bishnoi et al., 1993; Fan et al. 1999). Once hydrates were observed, temperature was raised stepwise, and at least 4 h was required for equilibrium to be reached at each temperature. The temperature and pressure were logged continuously, and the equilibrium data were plotted on a scatter-gram. The point at which the slope of the *P*–*T* curve sharply changed was considered to be the hydrate dissociation point. A different temperature was subsequently selected, and the procedure was repeated to obtain the other hydrate equilibrium data.

## Experimental Results and Discussion

***Hydrate Formation of Cyclopentane in Water.*** It was found that it was difficult to form the hydrate of cyclopentane initially. After the temperature in the cell was lowered below 273 K for 24 h, the hydrates started to form. For checking the experimental apparatus and procedure adopted in this work, the $Q_2$ quadruple point (liquid water–liquid cyclopentane–vapor cyclopentane hydrate, that is, Lw–Lcp–H–Vcp) of the 99.5 mass % cyclopentane in water was measured and compared with the data reported in the literature (Davidson, 1973). The cyclopentane $Q_2$ quadruple point occurred at a temperature of 280.22 K and a pressure of 19.8 kPa, very close to the temperature of 280.8 K reported by Davidson (1973). The measured data were listed in Table 1, and the comparison with the literature data was plotted in Figure 2. Those experimental hydrate data for cyclopentane range from 273.36 K to 280.22 K and from 6.9 kPa to 19.4 kPa. As can be seen from Figure 2, the data measured in this work match very well with the quadruple point. It should be emphasized that the reproducibility of the hydrate formation pressures reported in this work is good. These are the first complete experimental data to show that cyclopentane can form a gas hydrate without any need for a help gas.

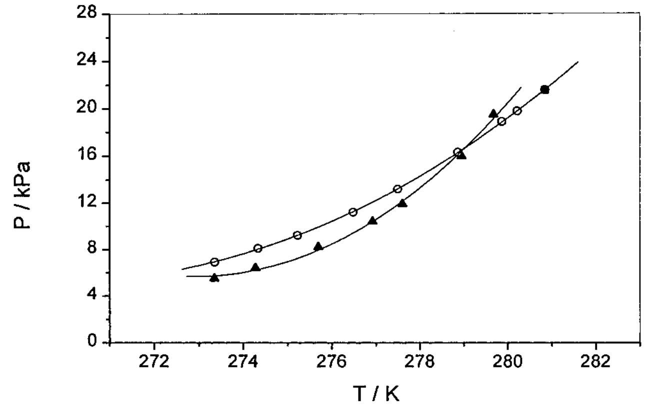

**Figure 2.** Experimental hydrate dissociation data for cyclopentane (○) and a cyclopentane-rich quaternary mixture containing 98.40 mass % cyclopentane, 0.48 mass % *n*-pentane, 0.40 mass % 2-methylbutane, and 0.72 mass % 2-methylpropane in water (▲): (■) $Q_2$ from Davidson,1973; (—) smoothing curve.

**Table 2. Hydrate Dissociation Conditions of a Cyclopentane-Rich Quaternary Mixture Containing (mass %): 98.40 % Cyclopentane, 0.48 % Pentane, 0.40% 2-Methylbutane, and 0.72% 2-Methylpropane in Water**

| phase | *T*/K | *P*/kPa |
|---|---|---|
| $L_W$–H–V | 273.35 | 5.5 |
| | 274.28 | 6.4 |
| | 275.70 | 8.2 |
| | 276.93 | 10.4 |
| | 277.61 | 11.9 |
| | 278.95 | 16.0 |
| | 279.68 | 19.5[a] |

[a] $Q_2$ quadruple point.

***Hydrate Formation of a Quaternary Cyclopentane-Rich Mixture.*** Table 2 presents the hydrate formation data for a quaternary cyclopentane-rich mixture in water. The composition (mass %) of the quaternary mixture was

98.40% cyclopentane, 0.48% pentane, 0.48% 2-methylbutane, and 0.72% 2-methylpropane. A comparison between the data from cyclopentane and from the quaternary mixture measured in this work was shown Figure 2. The effect of impurities in the cyclopentane is distinctive. At high temperature (above 279.5 K) the dissociation pressure of cyclopentane/*n*-pentane/2-methylbutane/2-methylpropane hydrate is higher than that of pure cyclopentane, that is, the presence of impurities is inhibiting, rather than promoting the formation of the hydrate. The crossover of the curves for pure and impure samples may occur because 2-methylpropane formed a structure-II hydrate while the others could not form hydrate without a help gas. It may contribute to extra stability at lower temperature, whereas it destabilizes hydrate at higher temperatures.

## Conclusions

In this work, experimental data on hydrate formation of cyclopentane in water were determined. The effect of the presence of impurities (*n*-pentane/2-methylbutane/2-methylpropane) in cyclopentane-rich mixtures on the hydrate formation conditions in water was also studied. The measured data are useful for testing the applicability of the existing hydrate models for cyclopentane-rich mixtures.

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