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Equilibrium Dissociation Pressures for *p*-Cresol + Methane and *p*-Cresol + Nitrogen Clathrates at Temperatures above the Normal Melting Temperature of *p*-Cresol

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Clathrate phase equilibria for the two binary *p*-cresol + methane and *p*-cresol + nitrogen systems were measured above the normal melting temperature, 307.6 K, of *p*-cresol. Three-phase (clathrate + liquid + vapor) dissociation pressures ranged from 79.7 bar to 300.0 bar for the *p*-cresol + methane system and 99.9 bar to 338.8 bar for the *p*-cresol + nitrogen system. In additon, the three-phase (solid + liquid + vapor) equilibrium data of the *p*-cresol + nitrogen system are presented for comparison.

Introduction

Clathrates are a type of inclusion compound. Inclusion compounds generally consist of two molecular components spatially arranged so that one component physically entraps the other. The molecular component which becomes the entrapping framework is called the host, whereas the entrapped molecular component is called the guest. Inclusion compounds can be divided into three types according to their host−guest geometrical arrangements; layer, cage, and channel. The clathrate is a cage-type inclusion compound and occurs when the host molecules form hydrogen-bonded polyhedral cages. Each cage is capable of enclosing a guest molecule. A cage and its accommodated molecule are taken as a unit cell. Three-dimensional clathrate structures can be generally determined by the X-ray diffraction method. Clathrates are usually subdivided into those formed in aqueous and nonaqueous systems, depending on the host species. Clathrate structures involving an aqueous host are usually called gas hydrates or clathrate hydrates. The present study involves nonaqueous clathrates.

Studies of nonaqueous clathrates have been rarely reported in the literature, compared with the large number of hydrate studies involving water. Possible nonaqueous host molecules belonging to phenolic compounds are phenol, hydroquinone, dianin, and substituted phenols. For phenol clathrates, the types of distinct cages and limiting compositions have been reported (Atwood et al., 1984). Few structural and thermodynamic properties have been investigated for *p*-cresol clathrates. Barrer and Shanson (1976) investigated sorption isotherms of a variety of *para*-substituted phenol clathrates. They measured decomposition pressures and maximum uptakes of *p*-cresol clathrates with several guest gases such as Ar, Xe, CH_4, and C_2H_6 below 273 K. They also suggested that clathration can be an alternative separation method for mixed gases. Trofimov and Kazankin (1968) reported that *p*-cresol forms clathrate compounds with gas species of molecular size smaller than 5.1 Å. They also measured the dissociation pressures of *p*-cresol clathrates produced with suitably sized guest molecules.

In this work, the new clathrate equilibrium dissociation pressures for the binary systems *p*-cresol + methane and *p*-cresol + nitrogen were measured above the normal melting temperature of *p*-cresol. This is the most important region for studying the thermodynamic behavior of clathrates. In addition, the three-phase (solid *p*-cresol + liquid *p*-cresol + vapor) equilibrium data of the (*p*-cresol + nitrogen) system are presented for comparison.

Experimental Section

Materials. *p*-Cresol was purchased from Sigma-Aldrich Chemical Co. and had a purity of 99.1%. Methane gas with a purity of 99.99% was obtained from Scientific Gas Products Co. and nitrogen having a stated purity of 99.999% was supplied by World Gas Co. All chemicals were used as received without further purification.

Apparatus. A schematic of the experimental apparatus is shown in Figure 1. It consists of a high-pressure phase equilibrium cell immersed in a temperature-controlled bath. The bath contains about 30 L of water which is controlled by an externally circulating refrigerator/heater. The operating temperature is maintained with a temperature controller (Jeio Tech, MC-31) with ±0.1 K accuracy. The cylindrical equilibrium cell is made of 316 stainless steel and has two sapphire windows, at the front and back, that allow visual observation of clathrate formation. The cell has an internal volume of about 70 cm^3. The cell contents are agitated by a magnetic stirrer which is coupled with an immersion magnet placed under the cell in the bath. The temperature is sensed by a stainless steel K-type probe with a digital thermometer (Cole-Parmer, 8535-26) of which the resolution is ±0.1 K in the 298−328 K range. The thermometer is calibrated with an ERTCO ASTM mercury thermometer (Ever Ready Thermometer Co., Inc.). The cell pressure is measured by a Heise Bourdon tube pressure gauge (CMM 104957, 0−600 bar) accurate to within ±0.1% of the full-scale reading. A high-pressure generator (High Pressure Equipment Co., 62-6-10) is used to pressurize the system.

Procedure. An amount of approximately 45 cm^3 of *p*-cresol was initially charged in the cell. Air and vaporized *p*-cresol contained in the cell were completely eliminated by flushing the cell with methane or nitrogen up to 40 bar. *p*-Cresol has an extremely low vapor pressure of approximately 0.133 kPa at 601.8 K, and therefore flushing two times is enough to remove the air in the cell. The amount of air which might remain in the tube of the Heise Bourdon pressure gauge was assumed to have a negligible effect on altering equilibrium condition.

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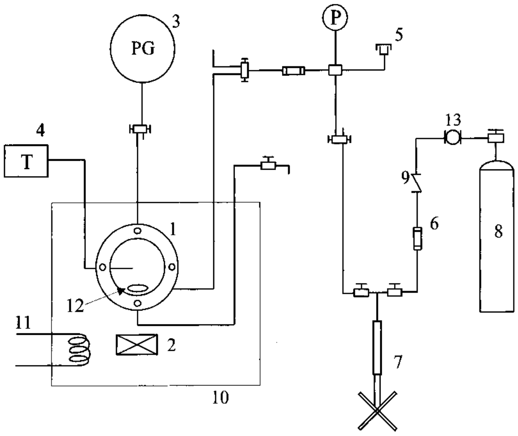

Figure 1. Schematic diagram of experimental apparatus used in this work: (1) equilibrium cell; (2) magnet; (3) Heise pressure gauge; (4) thermometer; (5) rupture; (6) check valve; (7) high-pressure generator; (8) gas cylinder; (9) line filter; (10) water bath; (11) refrigerator/heater; (12) magnetic stirrer; (13) regulator.

To diminish the hysteresis phenomena of metastability associated with clathrate formation and dissociation, once the formed clathrate crystalline was dissociated, the formation and dissociation steps were repeated more than two times in order to determine the equilibrium temperature and pressure with great accuracy.

The pressure was first adjusted to a desired pressure with either methane or nitrogen. The cell temperature was kept constant as a temperature just above that at which the *p*-cresol clathrate formed. The *p*-cresol solution was then cooled slowly to allow the *p*-cresol clathrate formation. Once the clathrate was formed, the external heater was used to change the system temperature at a rate of 1−2 K/h. As the system approached the equilibrium temperature, the clathrate dissociated with an increase in pressure due to the release of the clathrate-forming gas. When the amount of minute *p*-cresol clathrate crystal remained and the system temperature remained constant for 8 to 10 h after the system pressure was stabilized, the resulting pressure was then considered as the equilibrium dissociation pressure at the specified temperature. To obtain solid + liquid + vapor equilibrium data, a similar procedure was employed. After pressurizing the *p*-cresol-charged cell with nitrogen to a desired pressure, the *p*-cresol + nitrogen mixture was cooled down to be a stable solid. Then the mixture was heated gradually. As the melting point was approached, the bath was controlled at a constant temperature for a period of about 2−2.5 h until the disappearance of the last trace of solid was observed.

Results and Discussion

The clathrate dissociation behavior for the system containing *p*-cresol with methane and nitrogen as the guest components will be discussed. They have relatively small molecular diameters of 4.36 Å and 4.1 Å, respectively. The clathrate equilibrium dissociation pressures of the *p*-cresol + methane and *p*-cresol + nitrogen systems were experimentally determined and are presented in Table 1. For the *p*-cresol + nitrogen system, the three phase solid (*p*-cresol + *p*-cresol-rich liquid + vapor) equilibrium data were measured. The measured clathrate dissociation pressure and corresponding temperature ranges are 79.7−300.0 bar and 303.3−310.4 K for the *p*-cresol + methane system and 99.9−338.8 bar and 306.8−310.5 K for the *p*-cresol + nitrogen system. From Figures 2 and 3, the clathrate equilibrium dissociation pressures for both systems increase with temperature. This dependence for the *p*-cresol + methane system is similar to that commonly observed in gas hydrates and other clathrates. An abrupt increase of the dissociation pressures appearing near the quadruple point, as observed in the binary phenol + carbon dioxide system (Yoon and Lee, 1997), was not found in *p*-cresol containing systems.

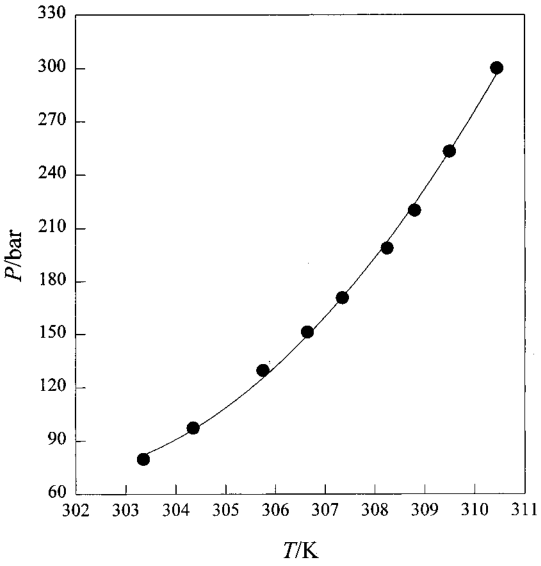

Figure 2. Three-phase, *p*-cresol clathrate + *p*-cresol-rich liquid + vapor, equilibrium data of the *p*-cresol + methane system.

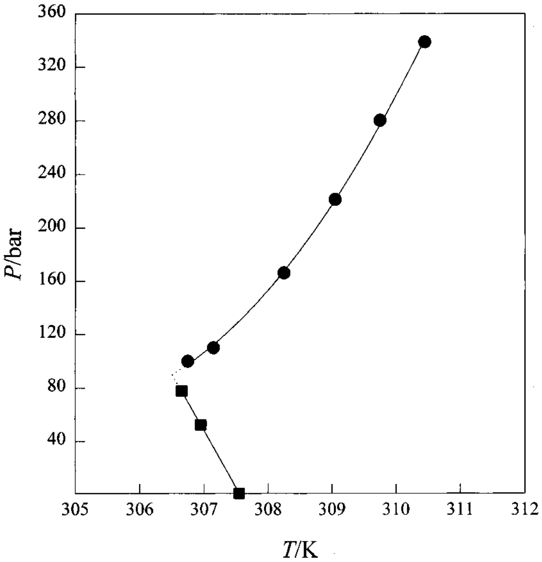

Figure 3. Three-phase equilibrium data of the *p*-cresol + nitrogen system: (●), *p*-cresol clathrate + *p*-cresol-rich liquid + vapor; (■) solid *p*-cresol + *p*-cresol-rich liquid + vapor.

Table 1. Clathrate Dissociation Pressures for the *p*-Cresol + Methane and *p*-Cresol + Nitrogen Systems

system	T/K	P/bar	system	T/K	P/bar
p-cresol +	303.3	79.7	*p*-cresol +	306.8	99.9
methane	304.3	97.4	nitrogen	307.2	110.0
	305.7	129.6		308.3	166.1
	306.6	151.2		309.1	221.1
	307.3	170.6		309.8	280.0
	308.2	198.6		310.5	338.8
	308.7	219.8		307.6	1.0[a]
	309.4	252.9		307.0	52.4[a]
	310.4	300.0		306.7	77.7[a]

[a] Three-phase (*p*-cresol solid + *p*-cresol liquid + nitrogen) equilibrium data.

As discussed by Paulaitis et al. (1983) and McHugh et al. (1988), the shape of the solid + liquid + vapor equilibrium line results from a compromise between the effect of hydrostatic pressure on the melting point of pure *p*-cresol and the solubility of gas molecules in the *p*-cresol-rich liquid phase. The negative slope of the (solid + liquid + vapor) equilibrium line reveals that the solubility effect of the gas molecule on the equilibrium line is more dominant than the hydrostatic-pressure effect. In addition, the melting point depression for the *p*-cresol + methane system was found to be larger than that of the *p*-cresol + nitrogen system. The solubility of methane in the *p*-cresol-rich liquid phase is therefore expected to be higher than that of nitrogen. A quadruple point at which four phases (solid *p*-cresol + *p*-cresol-rich liquid + clathrate + vapor) coexist was found to be 306.5 K and 89.8 bar for the *p*-cresol + nitrogen system. This quadruple point must be invariant for the two-component and four-phase systems, as can easily be shown by the Gibbs phase rule.

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