



Isothermal phase equilibria for the (HFC-32 + HFC-134a) mixed-gas hydrate system [☆]

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ABSTRACT

Isothermal phase equilibria (pressure-composition relations in hydrate, gas, and aqueous phases) in the {difluoromethane (HFC-32) + 1,1,1,2-tetrafluoroethane (HFC-134a)} mixed-gas hydrate system were measured at the temperatures 274.15 K, 279.15 K, and 283.15 K. The heterogeneous azeotropic-like behaviour derived from the structural phase transition of (HFC-32 + HFC-134a) mixed-gas hydrates appears over the whole temperature range of the present study. In addition to the heterogeneous azeotropic-like behaviour, the isothermal phase equilibrium curves of the (HFC-32 + HFC-134a) mixed-gas hydrate system exhibit the negative homogeneous azeotropic-like behaviour at temperatures 279.15 K and 283.15 K. The negative azeotropic-like behaviour, which becomes more remarkable at higher temperatures, results in the lower equilibrium pressure of (HFC-32 + HFC-134a) mixed-gas hydrates than those of both simple HFC-32 and HFC-134a hydrates. Although the HFC-134a molecule forms the simple structure-II hydrate at the temperatures, the present findings reveal that HFC-134a molecules occupy a part of the large cages of the structure-I mixed-gas hydrate.

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1. Introduction

Gas hydrate, which is one of clathrate inclusion compounds, is a crystalline solid. Clathrate hydrates consist of the host framework of hydrogen-bonded water molecules. The enclathration of guest species stabilizes the hydrate structure. There are some hydrate unit-cells formed by the combination of several different-shaped cages, for example, structure-I (s-I) consists of two small cages (dodecahedron (5^{12}), hereafter S-cage) and six middle cages (tetra-kaidecahedron ($5^{12}6^2$), M-cage), and structure-II (s-II) consists of sixteen S-cages and eight large cages (hexakaidecahedron ($5^{12}6^4$), L-cage) [1]. The size of guest species as well as pressures and temperatures determine which structure is formed.

Gas hydrates get much attention as newly refrigerant materials, because gas hydrates have appropriate properties for cold energy storage [2,3]. Hydrofluorocarbons (HFCs) are well-known refrigerant materials due to the thermodynamic characteristics and chemical stabilities. The hydrates prepared from HFCs have larger enthalpy than liquefied HFCs [4,5]. The phase equilibrium relations and the dissociation enthalpies for some simple HFC hydrates have

been reported [6–9]. The studies on HFCs mixed-gas hydrate systems, however, are rarely reported.

In the present study, isothermal phase equilibria (pressure-composition) in an HFCs mixed-gas hydrate system including typical refrigerant gases, difluoromethane (HFC-32) and 1,1,1,2-tetrafluoroethane (HFC-134a), were investigated. The main purpose of the present study is to reveal the three-phase equilibrium relations of (hydrate, gas, and aqueous phases) in the (HFC-32 + HFC-134a) mixed-gas hydrate system for the improvement of refrigerant cycles. In addition, the hydrate structures and the cage occupancies of guest species are discussed, based on the Raman spectra.

2. Experimental

2.1. Isothermal phase equilibrium measurements

The high-pressure cell with sapphire windows was used for isothermal phase equilibrium measurements. The inner volume and maximum working pressure were 150 cm³ and 10 MPa, respectively. The gas mixture of HFCs prepared at a desired composition was introduced into the evacuated high-pressure cell. The contents were pressurized with water up to a desired pressure by a high-pressure pump. A pressure gauge (Valcom VPRT) was used for measuring the pressure of system. The high-pressure cell was im-

[☆] Paper for gas hydrate initiative.

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mersed in the thermostatted bath, which was cooled down by circulating the thermostatted water. The system temperature was measured by use of a thermistor probe (Takara D-632). The maximum uncertainties of the temperature and the pressure were 0.02 K and 0.004 MPa, respectively. The magnetically-driven mixing-bar was moved in a vertical direction for the efficient agitation at the interface between gas and aqueous phases. The phase behaviour was observed through the sapphire windows. After establishing the three-phase equilibrium state, the small amounts of samples in the gas and aqueous phases were taken from the cell in order to analyze the equilibrium compositions by TCD gas chromatograph (TCD-GC, Shimadzu GC-14B). The maximum uncertainties of the mole fractions in the gas and aqueous phases were 0.005. These experimental procedures were repeated with various compositions to obtain the three-phase equilibrium (pressure-composition) relation.

It is very difficult to simultaneously take out the sample of hydrate phase from the same three-phase equilibrium state. In the case of measuring equilibrium composition in hydrate phase, therefore, the mixed-gas hydrate was prepared with different experimental setup by the same means mentioned above. The high-pressure cell was cooled down at the temperature 243 K after draining the free water remaining in the cell. Then, the hydrate crystal was taken from the cell and allowed to be dissociated at room temperature and atmospheric pressure. The equilibrium composition of hydrate phase was analyzed by the same TCD-GC. The maximum uncertainty of the mole fraction in hydrate phase was 0.01. The effective uncertainties of the temperature and the pressure were 0.02 K and 0.02 MPa, respectively.

2.2. Raman spectroscopic analysis

The high-pressure optical cell with sapphire windows was used for Raman spectroscopic analysis, and the mixed-gas hydrates were generated by the same procedure as the isothermal phase equilibrium measurements. The inner volume and maximum working pressure of the optical cell were 0.1 cm³ and 400 MPa, respectively. The thermostatted water was circulated in the jacket of the high-pressure optical cell by a temperature control unit (Taitec CL-80R), and the system temperature was measured by a thermistor probe (Takara D-641). The contents were agitated by vibration of an enclosed ruby ball from outside. After the generation of the mixed-gas hydrates, the gradual increasing and decreasing of system temperature was repeated several times to prepare hydrate single crystals under three-phase coexisting states of (hydrate, gas, and aqueous phases). The maximum uncertainties of the temperature and the pressure were 0.02 K and 0.02 MPa, respectively.

Hydrate single crystals were analyzed by *in situ* Raman spectroscopy using the laser Raman microprobe spectrometer with the multichannel charge-coupled device (CCD) detector (Jobin-Yvon T64000). The CCD detector was maintained at $T = 140$ K by liquid nitrogen to reduce heat noises. An argon ion laser beam (wave length: 514.5 nm, generate power: 100 mW) condensed to 2 μm in spot diameter was irradiated from the objects lens through the sapphire windows. And the backscatter was taken in with the same lens. The spectral resolution was approximately 0.7 cm⁻¹. Raman shifts were calibrated by the bright lines of neon in the air.

2.3. Materials

The HFC-32 (CH₂F₂, mole fraction purity: >0.999) and HFC-134a (CH₂FCF₃, mole fraction purity, >0.996) were obtained from the Daikin Industries, Ltd. The distilled water was purchased from Wako Pure Chemical Industries, Ltd. All of the materials were used without further purification.

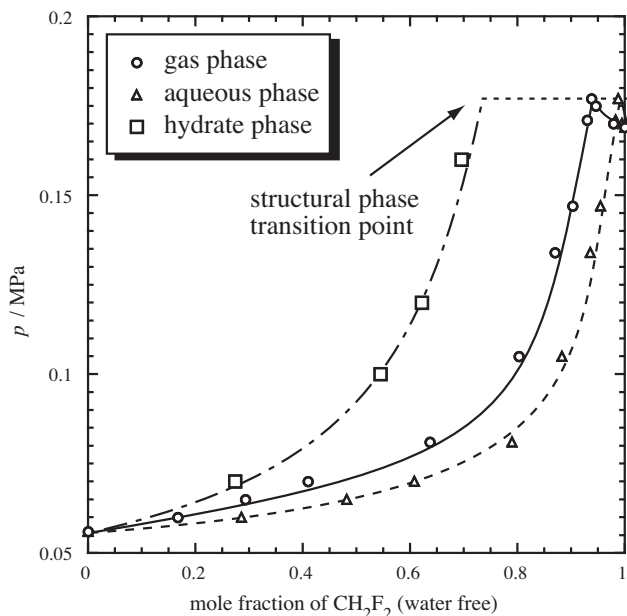


FIGURE 1. Isothermal phase equilibria of hydrate, gas, and aqueous phases in the (HFC-32 + HFC-134a) mixed-gas hydrate system at $T = 274.15$ K.

3. Results and discussion

Isothermal pressure (p)-composition (x, y, z) diagrams for the {HFC-32(1) + HFC-134a(2)} mixed-gas hydrate system at $T = 274.15$ K, 279.15 K, and 283.15 K under three-phase equilibrium conditions of hydrate, gas, and aqueous phases are shown in figures 1 to 3, respectively. The horizontal axis in figures 1 to 3 indicates the equilibrium composition of HFC-32 on a water-free basis. Table 1 summarizes the p - x, y relations for each isotherm obtained without the dissociation of hydrate samples. The obviously unreasonable data in the aqueous phase were removed, due to the incidental involvement of hydrate crystal in the sample of aqueous phase. Table 2 summarizes the p - z relation for each isotherm. The symbols of x_1 , y_1 , and z_1 stand for the composition of HFC-32 in

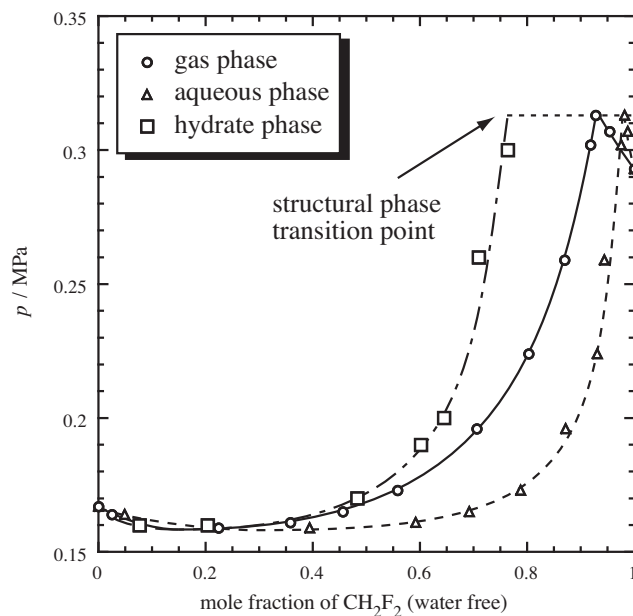


FIGURE 2. Isothermal phase equilibria of hydrate, gas, and aqueous phases in the (HFC-32 + HFC-134a) mixed-gas hydrate system at $T = 279.15$ K.

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