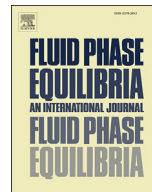




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Quadruple point determination in carbon dioxide hydrate forming system

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ABSTRACT

The quadruple point in carbon dioxide hydrate forming system, ice + water-rich liquid + hydrate + carbon dioxide-rich gas four-phase equilibrium condition, has been determined based on supercooled water-rich liquid + hydrate + carbon dioxide-rich gas and water-rich liquid + hydrate + carbon dioxide-rich gas three-phase equilibrium conditions measured in this study combined with ice + hydrate + carbon dioxide-rich gas three-phase equilibrium conditions reported in the literature (K. Yasuda, R. Ohmura, J. Chem. Eng. Data 53 (2008) 2182–2188). The intersection of the three types of the three-phase equilibrium conditions was used to determine the quadruple point. The three-phase equilibrium condition experiments were performed at temperatures between 269.45 K and 275.75 K, and at pressures between 0.825 MPa and 1.708 MPa. The determined p – T condition at quadruple point was $T = 271.6 \pm 0.2$ K and $p = 1.04 \pm 0.02$ MPa. It was also observed that the freezing of supercooled water during some experimental runs performed below the quadruple point temperature, which causes sudden increase in both pressure and temperature.

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1. Introduction

The technologies utilizing clathrate hydrates have been proposed in recent years because clathrate hydrates have several unique properties such as high gas storage capacities, guest substance selectivities, and large formation/dissociation heats. Typical examples of those technologies are transportation and storage of natural gas [1], hydrate-based carbon dioxide capture and sequestration [2], development of highly efficient heat pump/refrigeration systems [3], etc. Clathrate hydrates (abbreviated as hydrates) are crystalline water-based ice-like solid compounds, in which molecules called “guests” are trapped inside cages of hydrogen-bonded water molecules. Guest substances that can form hydrates are mainly hydrocarbons, carbon dioxide, and noble gases. Carbon dioxide is used as a guest substance for hydrate-based technologies such as desalination of seawater [4], carbon dioxide capture and sequestration [2], etc.

The reduction of high pressure required for hydrate formation is

one of the prime challenges for the hydrate-based technologies. The simplest way to reduce high pressure is lowering operational temperature. However, if the operational temperature is lower than the freezing point of water, the rate of hydrate formation and decomposition decreases by suffering from the formation of ice, another solid phase. The pressure–temperature phase diagram in a simple hydrate forming system is shown in Fig. 1. The freezing point of water in the hydrate forming system is equal to the temperature of ice phase (I) + water-rich liquid phase (L_w) + hydrate phase (H) + guest-rich gas phase (V_g) four-phase equilibrium condition. According to the Gibbs phase rule, the degree of freedom in this four-phase equilibrium is equal to zero. Therefore, the four-phase equilibrium condition is depicted as a point on the pressure–temperature diagram and sometimes called “quadruple point”. The lowest operating temperature for hydrate formation without suffering from ice formation is the temperature of the quadruple point.

The pressure–temperature condition of the quadruple point depends on the guest substance. It has been determined in the various hydrate forming systems such as methane [5,6], carbon dioxide [7,8], nitrogen [8]. The intersection of I + H + V_g and L_w + H + V_g three-phase equilibrium lines has been used to determine the quadruple point. Both lines were extrapolated to find the intersection.

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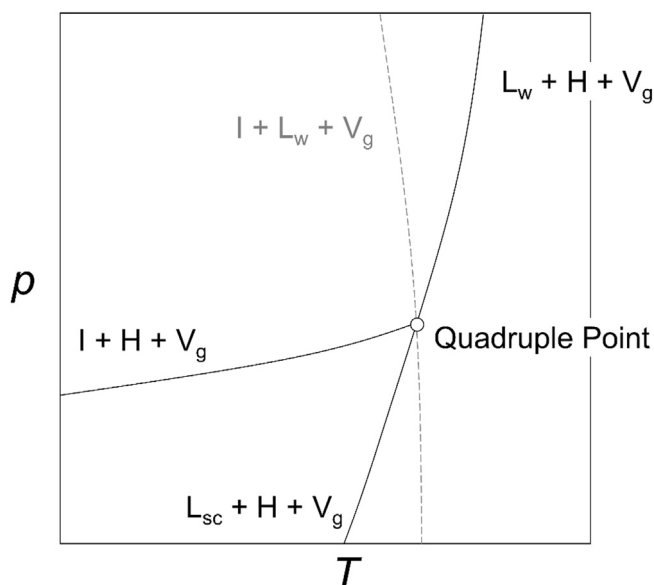


Fig. 1. Pressure–temperature phase diagram in a simple hydrate forming system.

Another line starts from the quadruple point is supercooled water-rich liquid phase (L_{sc}) + H + V_g three-phase equilibrium line. Mel'nikov et al. have reported the L_{sc} + H + V_g three-phase equilibrium conditions in propane [9], methane [10], and carbon dioxide [11] hydrate forming systems by visually observing the decomposition of hydrate crystals. The coexisting of supercooled water-rich liquid phase and hydrate phase has been evidenced by Raman spectroscopic [12] and NMR [13] measurements.

The difference in the slope between I + H + V_g and L_w + H + V_g three-phase equilibrium lines at quadruple point originates from the difference in the heat of formation/decomposition of hydrates. On the other hand, the slopes of L_{sc} + H + V_g and L_w + H + V_g three-phase equilibrium lines are the same at quadruple point, that is, the line connecting L_{sc} + H + V_g and L_w + H + V_g three-phase equilibrium conditions is a continuous function because the heat of formation/decomposition does not depend on whether the water-rich liquid phase is supercooled. Therefore, the quadruple point can be determined using the intersection of I + H + V_g and (L_{sc} or L_w) + H + V_g three-phase equilibrium lines. While I + H + V_g line is still extrapolated, (L_{sc} or L_w) + H + V_g line is interpolated to find the intersection. Thus, the accuracy of the quadruple point is expected to be improved by addition of L_{sc} + H + V_g three-phase equilibrium line.

The objective of this study was to determine the quadruple point in carbon dioxide hydrate forming system based on L_{sc} + H + V_g and L_w + H + V_g three-phase equilibrium conditions measured in this study combined with I + H + V_g three-phase equilibrium conditions reported in the literature [6].

2. Experimental section

2.1. Materials

The sample fluids used in the experiments were research-grade carbon dioxide gas supplied from Japan Fine Products Co. Ltd., and

pure water prepared in our laboratory. The former having certified purity of 0.9999 in mole fraction was used as received from the supplier. The latter was produced by treating tap water with a reverse osmosis water purifier (model RFP742HA, Toyo Roshi Kaisha, Ltd.) which was comprised an ion-exchange device and a reverse osmosis membrane element. The specifications of the materials used in the experiments are listed in Table 1.

2.2. Apparatus and procedure

A schematic diagram of the experimental setup used in this study is shown in Fig. 2. The test section for the three-phase equilibrium condition measurements was a stainless steel cylindrical vessel with the inner volume of 200 cm³. The vessel was equipped with a magnetically-driven impeller to agitate the liquid phase in the test section. The temperature inside the vessel was controlled at a prescribed value using a PID-controlled heater (model BF400, Yamato Scientific Co., Ltd.) and a cooler placed in the bath. A platinum-wire resistance thermometer (model TSA-1.6-200K-L, Class A, AS ONE Corporation) was inserted into the vessel to measure the temperature (T) in the test section. The uncertainty of the temperature measurement using this thermometer was estimated to be ± 0.1 K with 95% coverage. The inside pressure (p) of the vessel was measured by a strain-gauge pressure transducer (model PHB-A-5MP, Kyowa Electronic Instruments Co., Ltd.). The estimated uncertainty of the pressure measurements with 95% coverage was ± 0.011 MPa.

The present study follows the procedure described by Makogon et al. [14] for measuring the three-phase equilibrium temperature–pressure conditions. Each experimental run was commenced by supplying 30 g of water to the test section. The vessel was then immersed in the bath. CO₂ gas was supplied up to 3.0 MPa from a high-pressure cylinder through the pressure-regulating valve to the vessel after the air in the vessel was evacuated by a vacuum pump (model N810.3FT.18, AS ONE Corporation). Subsequently, T was decreased to 273.5 K, slightly higher than the standard freezing point of water without pressurizing by CO₂ and 7 K lower than the three-phase equilibrium temperature calculated by CSMGem [15], to initiate hydrate formation without ice formation. T was kept constant until approximately 10% of water was converted into hydrate crystals. The amount of hydrate crystals was estimated based on the observation of pressure reduction that reflected the consumption of CO₂ due to the hydrate formation combined with the composition of carbon dioxide hydrate [16]. Therefore, the coexistence of three phases, that is, liquid water, solid hydrate, and gaseous CO₂, was established. T was then set at a prescribed level in the range of 269.45 K–274.85 K while p was set at an estimated equilibrium pressure. If p was lower than the equilibrium pressure p_{eq} , the increase in p was observed due to the hydrate decomposition. On the other hand, if p was higher than p_{eq} , p decreased due to the hydrate formation. The system was left for 10 h–12 h in both cases to achieve the steady-state condition. Assuming that the pressure increased/decreased, in subsequent cycles the vessel was pressurized/depressurized slightly above/below the original stabilized value and the system was left again. It should be noted that increasing p always results in pressure reduction due to the dissolution of CO₂. However, this decrease in p is not significant compared to the decrease in p that is observed due

Table 1
Specifications of the materials used in the experiments.

Sample name	Chemical Formula	Supplier	Purity
Carbon dioxide	CO ₂	Japan Fine Products Co. Ltd.	0.9999 mol fraction was certified
Water	H ₂ O	Laboratory made	Electrical conductivity was less than 0.1 μ S/cm

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