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Phase equilibria and azeotropic behavior of $C_2F_6 + N_2$ gas hydrates

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ABSTRACT

C_2F_6 (hexafluoroethane, R116) is a fluorinated gas (F-gas) widely used in semiconductor industries, which also has a high global warming potential and a long atmospheric lifetime. In this study, the thermodynamic and structural characteristics of the $C_2F_6 + N_2$ gas hydrates were investigated for gas hydrate-based C_2F_6 separation from emission sources. This experiment measured the three-phase (hydrate, liquid water, and vapor [H-L_W-V]) equilibria of ternary C_2F_6 (10, 20, 40, 60, and 80%) + $N_2 + H_2O$ systems and indicated the possible existence of hydrate azeotropes at certain temperature ranges. Powder X-ray diffraction (PXRD) revealed that the ternary $C_2F_6 + N_2 + H_2O$ systems form structure II (sII) hydrates (*Fd3m*) for all C_2F_6 concentrations considered in this study. The pressure-composition diagram obtained at two different temperatures (275.15 K and 279.15 K) demonstrated that C_2F_6 is highly enriched in the hydrate phase at 275.15 K, whereas at 279.15 K, the $C_2F_6 + N_2 + H_2O$ systems have a hydrate azeotrope where the composition of the hydrate phase is the same as the composition of the vapor phase. The overall experimental results clearly indicate that hydrate-based C_2F_6 separation is thermodynamically feasible and the higher separation efficiency is achievable at lower temperature ranges.

1. Introduction

Gas hydrates are non-stoichiometric compounds which are generally formed with host water molecules and guest gas molecules. There are three main structures of gas hydrates: structure I (sI), structure II (sII) and structure H (sH) [1]. Primarily, the species and molecular sizes of guest molecules determine the structure of gas hydrates. Since their discovery, gas hydrates have been studied and applied in various fields. For example, natural gas hydrates, which are deposited in the permafrost regions or deep ocean sediments of the continental margins, are considered as a future energy source [2]. Gas hydrates have been also utilized for natural gas storage and transportation, desalination, and carbon dioxide capture and sequestration [3–14]. In particular, using gas hydrates to separate greenhouse gases has been studied for various target gases, including carbon dioxide and several fluorinated gases (F-gases) [9–18].

C_2F_6 is an artificial F-gas that is widely used in semiconductor industries and refrigeration systems. However, due to its high global warming potential (~9200 times higher than that of CO_2) and long atmospheric lifetime (~1000 years), separating and recovering C_2F_6 from emission sources has been a long-term problem [19–23]. In this study, gas hydrate formation was suggested as one of the means to separate C_2F_6 from emission sources. However, there is no reliable information about gas hydrates formed with gas mixtures of C_2F_6 and N_2. This information is indispensable for developing the overall C_2F_6 separation process.

Therefore, this study aims at investigating the thermodynamic and structural characteristics of $C_2F_6 + N_2$ gas hydrates with a primary focus on hydrate phase equilibria and structure identification. In order to examine the thermodynamic stability of $C_2F_6 + N_2$ hydrates, the three-phase (hydrate, liquid water, and vapor [H-L_W-V]) equilibria of ternary $C_2F_6 + N_2 + H_2O$ systems were experimentally measured using five different C_2F_6 concentrations (10, 20, 40, 60, and 80%). The structure of the $C_2F_6 + N_2$ hydrates was identified through powder X-ray diffraction (PXRD). Lastly, a pressure-composition diagram which represents equilibrium C_2F_6 concentrations in both vapor and hydrate phases at two different temperatures (276.15 K and 279.15 K) was obtained to observe the selective partition of C_2F_6 between the vapor and hydrate phases.

2. Experimental

2.1. Materials and apparatus

PSG Gas Co. (Republic of Korea) provided a C_2F_6 gas with a purity of 99.999% and RIGAS (Republic of Korea) provided $C_2F_6 + N_2$ gas mixtures with five different C_2F_6 concentrations (10, 20, 40,

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60, and 80 mol%). The gas mixtures were prepared on a molar basis, and the accurate compositions of each gas mixture are presented in Table 1. Double-distilled and deionized water was used for gas hydrate formation. All materials were used without further purification.

For hydrate phase equilibrium measurements and sample preparation, this study used a high-pressure cell made of type 316 stainless steel with an internal volume of 250 cm^3. The high-pressure cell was immersed in a water bath whose temperature was controlled by an external circulator (RW-2025G, JEIO Tech, Republic of Korea). The cell was equipped with two sapphire windows at its front and back sides, which enabled visual observation of phase transition occurring during gas hydrate formation and dissociation. An impeller-type stirrer vigorously agitated the inner content of the cell. A thermocouple with a temperature range of 73.15 K to 1273.15 K was calibrated using an ASTM 63C thermometer (H-B Instrument company, USA) with an uncertainty of 0.1 K. This thermocouple was inserted in the high-pressure cell to measure the temperature of the inner content. A pressure transducer (S-10, Wika, Germany) was calibrated using a Heise Bourdon tube pressure gauge (CMM-137219, Ashcroft, USA) with a maximum error of ±0.02 MPa was used to measure the system pressure.

2.2. Hydrate phase equilibrium measurements

For the three-phase (H-L_W-V) equilibrium measurement, the high-pressure equilibrium cell was filled with 80 cm^3 of water and ventilated at least three times with the object gas mixture to remove any residual air in the cell. Then, the object gas mixture was injected up to the desired pressure, and the temperature of the system was slowly lowered below the ice point. When it was confirmed that most of water had converted into ice, the temperature was increased to and maintained at 273.15 K. Then, a drastic pressure drop was observed as ice particles served as nucleation sites and gas hydrates began to form and grow. After a sufficient time had passed and the system pressure became constant, the temperature was slowly increased in a stepwise manner (0.1 K/90 min). The temperature increase caused gas hydrate dissociation, resulting in the increase of the system pressure. After the gas hydrates had completely dissociated, the system pressure was increased slightly due to thermal expansion. The intersection point between the hydrate dissociation and thermal expansion lines was designated as the H-L_W-V equilibrium. The whole process to obtain the H-L_W-V equilibria is presented in Fig. 1.

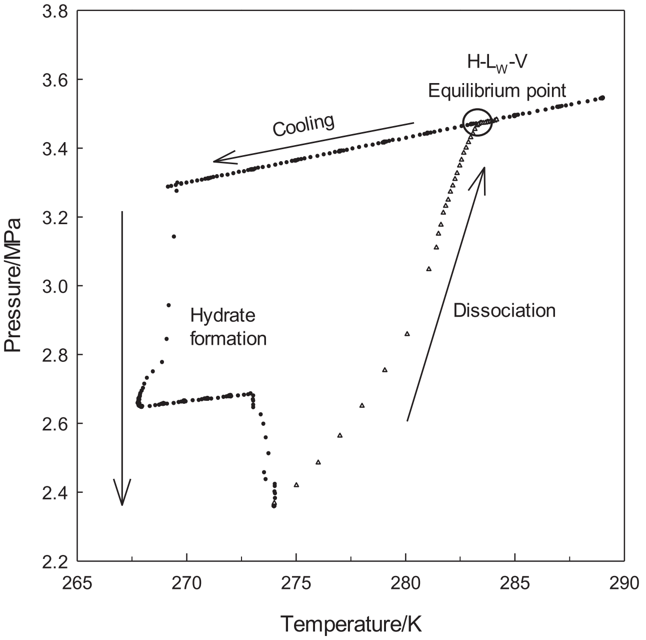

Fig. 1. The whole process of determining the three-phase (H-L_W-V) equilibrium point of the C_2F_6 (20%) + N_2 (80%) + H_2O system.

2.3. Structure identification

The crystal structure of $C_2F_6 + N_2$ hydrates with different C_2F_6 concentrations (10, 20, 40, 60, and 80%) were identified through PXRD. The X-ray diffraction patterns were measured by PLS-II 6D C&S UNIST-PAL beamline of the Pohang Accelerator Laboratory in the Republic of Korea, which is equipped with Cu Kα1 radiation ($\lambda = 1.5406$ Å). The PXRD patterns were collected in a stepwise manner with a step size of 0.02° for 2θ region of 5–55° at 123.15 K. The collected patterns were analyzed through the Chekcell program.

2.4. Pressure-composition analyses

The compositions of C_2F_6 at the equilibrium point were analyzed with a gas chromatograph (7890A, Agilent Technologies, USA) equipped with a thermal conductivity detector (TCD) and a Porapak Q column (Supelco, USA). The analysis was conducted on equilibrium compositions of C_2F_6 in both the vapor and hydrate phases at two different temperatures (275.15 K and 279.15 K). A sampling valve (Model 7010, Rheodyne, USA) with a 5 μl loop and a high-pressure metering pump (Eldex, USA) were connected to the gas chromatograph. To establish the H-L_W-V equilibrium state, the high-pressure cell was filled with an excess amount of water (100 cm^3), preventing the complete conversion of liquid water phase into the hydrate phase. After hydrate nucleation, the system was left for 24 h to reach the H-L_W-V equilibrium state at a specified constant pressure and temperature condition. A micro-flow syringe pump (ISCO Model 500D, Teledyne, USA) was used to keep the system pressure constant. After confirming that

Table 1
Materials used in this study (based on mol%).[a]

Chemical Name	Source	N_2 (mol%)	C_2F_6 (mol%)	Analysis[b]
Pure C_2F_6	PSG Gas	-	99.999	GC[c]
Pure N_2	PSG Gas	99.999	-	GC[c]
C_2F_6 (80%) + N_2 (20%)	RIGAS	19.9	80.1	GC[c]
C_2F_6 (60%) + N_2 (40%)	RIGAS	39.9	60.1	GC[c]
C_2F_6 (40%) + N_2 (60%)	RIGAS	59.7	40.3	GC[c]
C_2F_6 (20%) + N_2 (80%)	RIGAS	79.8	20.2	GC[c]
C_2F_6 (10%) + N_2 (90%)	RIGAS	89.9	10.1	GC[c]
De-ionized water	Direct-Q® 3UV			–

[a] Standard uncertainty u is *u(composition)* = 0.1 mol% (for $C_2F_6 + N_2$ gas mixtures).
[b] Analysis done by supplier.
[c] Gas-liquid chromatography.

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