Fluid Phase Equilibria 471 (2018) 55–60

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Thermodynamic phase equilibria and cage occupancy of NF_3 hydrate

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ARTICLE INFO

Article history:
Received 2 February 2018
Received in revised form
10 April 2018
Accepted 13 April 2018
Available online 22 April 2018

Keywords:
NF_3
Gas hydrate
Phase equilibria
Cage occupancy
Crystal structure

ABSTRACT

F-gases are man-made gases that are utilized mainly in the semiconductor industry and in refrigeration systems. Because F-gases have a high potential of contributing to global warming, various methods, including gas hydrate-based F-gas separation, for separating and recovering F-gases have been widely studied. However, gas hydrate formation with NF_3 has not been well studied in spite of its extremely high global warming potential (12,700) and its long atmospheric lifetime (740 years). In this study, the enclathration of NF_3 in gas hydrate lattices was investigated, with a focus on phase equilibria and guest distribution. The three-phase (gas hydrate (H)–liquid water (Lw)–vapor (V)) equilibria of NF_3 hydrate were measured to observe the stability conditions for NF_3 hydrate. The crystal structure of NF_3 hydrate was identified as cubic sI (*Pm3n*) with a lattice parameter of 11.87 Å through powder X-ray diffraction (PXRD). In addition, the cage-filling behavior of NF_3 hydrate was examined through both PXRD and *in situ* Raman spectroscopy. This revealed that the large ($5^{12}6^2$) cages were fully occupied by NF_3 molecules whereas the small (5^{12}) cages were less populated. The results obtained in this study would be helpful for understanding the cage-specific occupation of F-gas molecules in sI hydrate and devising possible gas hydrate-based F-gas separation methods.

1. Introduction

Gas hydrates are non-stoichiometric crystalline compounds that are formed by hydrogen-bonded water molecules and guest molecules captured inside hydrate cages [1]. They exist in three representative structures: sI (*Pm3n*), sII (*Fd3m*), and sH (*P6/mmm*). The structure of gas hydrates is generally determined by the molecular properties of guests such as the van der Waals diameter and molecular configuration or molecular interactions of guest-guest/guest-host [1]. Applications of gas hydrates include natural gas storage and transportation, CO_2 capture and storage, and desalination [2–16]. Recently, other global warming gases like F-gases have been also targeted for separation and recovery using gas hydrate formation [17–23].

F-gases are man-made gases that are usually utilized in the semiconductor industry and refrigeration systems because of their high molecular stability resulting from strong C-F bonds. However, their high chemical stability makes F-gases have significantly longer atmospheric lifetimes and higher global warming potentials [24–26]. Therefore, to minimize the emission of F-gases into the atmosphere, several methods for the separation and recovery of F-gases, such as membrane separation, adsorption, and liquefaction, have been studied [27–30]. Gas hydrate formation has been also proposed as an innovative F-gas separation method. Various F-gases, such as SF_6, CHF_3, C_2F_6, and HFC-134a, have been known to form gas hydrates alone or in the presence of suitable help gases [17–23]. In addition, the results of previous experiments have demonstrated that these F-gases from F-gas + N_2 gas mixtures are concentrated in the hydrate phase with a high separation efficiency after gas hydrate formation [19,20,22]. However, there are still several F-gases that have never been used to form gas hydrates or are lacking in the thermodynamic and structural properties of the gas hydrates they form. Nitrogen trifluoride (NF_3) is one of those F-gases.

NF_3 has been considered as a substitute for sulfur hexafluoride (SF_6) or perfluorocarbons (PFCs) for environmental reasons, and it is commonly used in the semiconductor industry. However, NF_3 is also a greenhouse gas, possessing a potent global warming potential (GWP) that is 17,200 times stronger than that of CO_2 and an atmospheric lifetime of 740 years [31]. Even though there have been a couple of studies on NF_3 hydrates, previous research was conducted on a very limited scale, including the simple structure identification and hydrate equilibrium measurement of only one or two points [32–34].

In this study, the precise nature and unique structural

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https://doi.org/10.1016/j.fluid.2018.04.013
0378-3812/

characteristics of NF_3 hydrate were investigated, with a focus on phase equilibria and cage-filling behavior for potential application to gas hydrate-based NF_3 separation. Hydrate phase equilibria of the binary NF_3 + water mixture were measured under wide pressure and temperature ranges to determine thermodynamically stable regions of NF_3 hydrate. The accurate crystal structure and cage occupancy of NF_3 hydrate were analyzed through the Rietveld refinement of powder X-ray diffraction (PXRD) patterns. *In situ* Raman spectroscopy was also used to verify the enclathration of NF_3 molecules in the hydrate cages and to confirm the cage occupancy of NF_3 molecules in the hydrate structure.

2. Experimental section

2.1. Materials and apparatus

NF_3 gas with a purity of 99.99% was supplied by RIGAS (Republic of Korea). Double-distilled deionized water was used for gas hydrate formation throughout the experiments, including phase equilibrium measurement and hydrate sample preparation for PXRD and *in situ* Raman spectroscopy. All materials were used without further purification (See Table 1).

Fig. 1 (a) shows a custom-made high-pressure equilibrium cell used for phase equilibrium measurements and gas hydrate sample preparation in this study. This high-pressure equilibrium cell was made of 316 stainless steel, with an inner volume of 250 cm^3. The cell was immersed in a water + ethylene glycol bath whose temperature was controlled by an external circulator (RW-2025G, JEIO Tech, Republic of Korea). In addition, two sapphire windows were installed at the front and the back sides of this equilibrium cell, allowing the observation of the phase transitions of the contents, while they were being vigorously agitated by an impeller-type stirrer. A thermocouple (measurable temperature range: 73.15 K–1273.15 K) was calibrated in the temperature range from 263.15 K to 303.15 K with an ASTM 63C thermometer (H-B Instrument company, USA) which has an uncertainty of 0.1 K. It was then inserted into the high-pressure cell to measure the temperature of the contents of the cell. In addition, a pressure transducer (S-10, Wika, Germany) was used after it had been calibrated in the pressure range from 0 MPa to 10.0 MPa using a Heise Bourdon tube pressure gauge (CMM-137219, Ashcroft, USA) with an uncertainty of 0.02 MPa.

Table 1
Source and purity of the materials used in this study.

Chemical Name	Source	Purity (mol%)	Analysis
NF_3	RIGAS	99.99	GC[a]
water	Laboratory made	distilled	–

[a] Gas-liquid chromatography.

2.2. Experimental procedures

Three-phase (hydrate (H)–liquid water (L_W)–vapor (V)) equilibria of NF_3 hydrate were measured to examine the thermodynamic stability regions of NF_3 hydrate. The high-pressure equilibrium cell was filled with 70 cm^3 of double-distilled water and immersed in the temperature-controlled bath. The equilibrium cell was then ventilated with the object gas at least three times to remove any residual air inside the cell. The cell was pressurized with the object gas until the pressure reached the desired experimental condition; then the temperature of the system was slowly lowered in a stepwise manner of 1.0 K/60 min. A sudden drop in pressure occurred when NF_3 hydrate started to form. The system was maintained at a constant temperature until the system pressure became constant. After sufficient time had elapsed, the temperature of the system was slowly increased in a stepwise manner of 0.1 K/90 min, and the NF_3 hydrate started to dissociate, followed by an increase in the system pressure. Even after the NF_3 hydrate had fully dissociated, the system pressure increased slightly because of thermal expansion. The intersection point between the hydrate dissociation and thermal expansion lines was designated as the three-phase (Hydrate (H)–Liquid water (L_W)–Vapor (V)) equilibrium point. The overall process to obtain the three-phase equilibrium point is shown in Fig. 1 (b).

The crystal structure of NF_3 hydrate was identified through PXRD. The hydrate samples were taken from the equilibrium cell and powdered into fine particles using a 50 μm sieve in a liquid nitrogen vessel. The PXRD measurement was performed at the PLS-II 6D C&S UNIST-PAL beamline (Pohang Accelerator Laboratory, Republic of Korea). The PXRD patterns were collected in a stepwise manner with a step size of 0.02° for $2\theta = 5–55°$ with an exposure to an energy of 12.658 keV ($\lambda = 0.9795$ Å) at 133 K. The obtained two-dimensional PXRD patterns were converted into one-dimensional

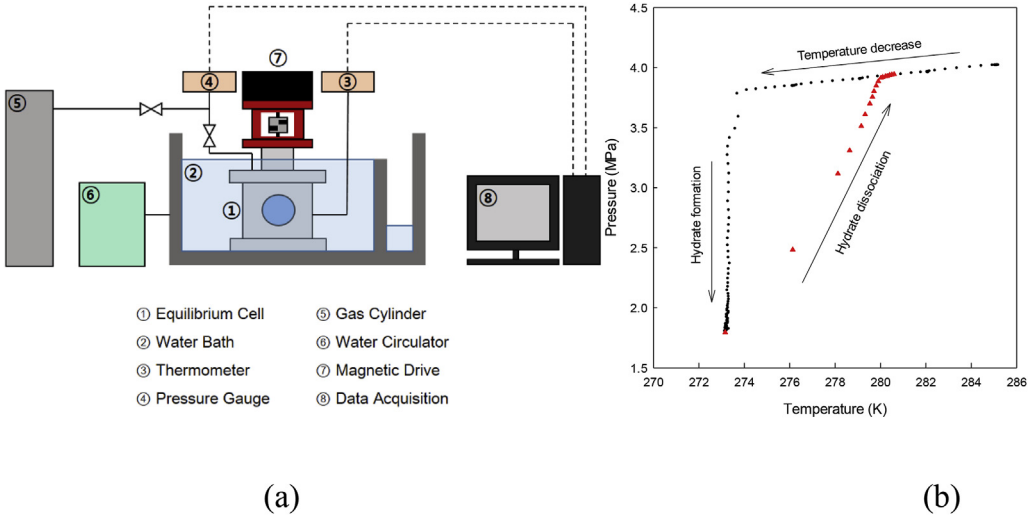

Fig. 1. (a) The high-pressure equilibrium cell used for phase equilibrium measurement.
(b) The whole process of determining a three-phase (H-L_W-V) equilibrium point of NF_3 hydrate.