

## 수소불화탄소를 포함하는 혼합기체의 가스 하이드레이트 상평형

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### Hydrate Phase Equilibria for the Gas Mixtures Containing HFC

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**Key words** : HFC(수소불화탄소), gas hydrate(가스 하이드레이트), phase equilibria(상평형), global warming(지구온난화)

**Abstract** : (HFC(hydrofluorocarbon, 수소불화탄소)는 오존층 파괴 지수가 낮기 때문에 CFC(chlorofluorocarbon)의 대체 물질로 냉매와 발포제로 널리 사용되고 있는 물질이다. 하지만 HFC는 지구온난화 지수가 높은 기체이므로 대기중으로 방출되는 것을 막기 위해 분리/회수하여 재활용하는 것이 중요하다. 본 연구에서는 공기와 HFC의 혼합기체로부터 HFC만을 분리해 내는 방법으로 가스 하이드레이트 형성법을 제안하였다. 이 방법의 열역학적 타당성을 검증하기 위하여 질소+HFC-134a 혼합기체에 대하여 275-285 K의 온도 범위와 1-27 bar의 압력범위에 걸쳐서 가스 하이드레이트 상평형을 측정하였다. 질소는 가스 하이드레이트를 형성하기 위하여 0 °C에서 150 bar이상의 높은 압력이 필요한 반면 HFC-134a는 대기압에 가까운 낮은 압력이 필요하다. 두 기체의 평형 압력의 차가 크다는 것은 가스 하이드레이트 형성법을 이용할 경우 기체의 분리 효율이 매우 높다는 것을 나타낸다. 그리고, 본 실험을 통해서 얻어진 혼합기체의 하이드레이트상(H)-액상(L<sub>w</sub>)-기상(V)의 3상 평형선이 순수한 HFC-134a의 3상 평형선에 가깝게 위치하였다. 이는 가스 하이드레이트를 이용한 분리법이 낮은 압력에서 운전될 수 있음을 나타낸다. 이 분리법은 낮은 압력에서 운전되어 경제적일 뿐만 아니라 물 이외의 다른 매개체를 사용하지 않기 때문에 환경 친화적인 공정이라 할 수 있다.

## 1. Introduction

Clathrate hydrates are non-stoichiometric crystalline compounds formed when guest molecules of suitable size and shape are incorporated in the well-defined cages of the host lattice made up of hydrogen-bonded water molecules. These compounds exist in three distinct structures termed structure I, II, and H<sup>(1)</sup>. Gas hydrates are of particular interest in environmental and energy fields.

Several hydrate-based separation concepts have been proposed for recovering global warming gases or organic contaminants from gaseous or aqueous mixtures<sup>(2-4)</sup>. It should be noted, however, that the hydrate formation pressure is greatly enhanced when small-sized guest molecules such as N<sub>2</sub> or CH<sub>4</sub> are involved in the hydrate formation. The high-pressure requirement for hydrate formation can be one of the decisive obstacles to commercializing the hydrate-based separation process. To overcome this inherent problem and to compete with

conventional methods, a hydrate promoter which remarkably reduces the required hydrate formation pressure has been used as an additive<sup>(2)</sup>. However, addition of the promoter makes the system more complex and reduces gas storage capacity in hydrate cages because most of the large cages are occupied by the promoter molecules. Therefore, a system that has a low hydrate formation pressure without needing a promoter

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should be selected to make the hydrate-based separation process more competitive.

In the present study, we focused on a new method for separating HFCs (hydrofluorocarbons) from gas mixtures using gas hydrate formation. HFCs were developed as an alternative to conventional CFCs (chlorofluorocarbons) and have been widely used as refrigerants for refrigeration and air-conditioning and as foaming agents for plastics because of their low atmospheric ozone-depletion potential<sup>(5)</sup>. Since HFCs usually exist as gas mixtures with N<sub>2</sub> after use as refrigerants or foaming agents, it is necessary to separate and recover HFCs from these gas mixtures to prevent the release of global warming gases into the atmosphere. In this study, HFC-134a (CH<sub>2</sub>FCF<sub>3</sub>) was chosen as the HFC target material. Guest molecules containing fluorine have higher boiling points and larger molecular sizes than their hydrocarbon counterparts and the resulting clathrate hydrates are stable at relatively low pressures in comparison to N<sub>2</sub> which requires extremely high hydrate formation pressure at a specified temperature<sup>(5)</sup>. A sharp difference in hydrate equilibrium pressure between HFC-134a and N<sub>2</sub> renders a new hydrate-based HFC-134a separation process for gas mixtures that is attractive from a separation efficiency point of view, because high selectivity for HFC-134a can be expected in the hydrate phase.

The present work attempted to provide fundamental key information required to check the thermodynamic feasibility of the hydrate-based HFC-134a separation process. First, three-phase equilibria (*p-T*) of hydrate (H), liquid water (L<sub>w</sub>), and vapor (V) for HFC-134a + N<sub>2</sub> + water mixtures with various HFC-134a vapor compositions (10, 20, 40, 60 and 80 mole %) were carefully measured to determine the stability region of the mixed hydrates. Second, the compositions of the hydrate and vapor phases (*p-x*) at a three-phase equilibrium state were analyzed for identical mixtures to ascertain actual separation efficiency.

## 2. Experimental

### 2.1 Materials and Apparatus

The HFC-134a + N<sub>2</sub> gas mixtures (10, 20, 40, 60 and 80 mole % of HFC-134a) were supplied by Takachiho Gas Company (Japan). Ultra high purity water was used for this experiment. A schematic diagram of the experimental apparatus used in this study is shown in Figure 1. The apparatus was constructed to measure the hydrate dissociation pressure and temperature and to analyze the compositions of the hydrate and vapor phases both at an equilibrium state and throughout hydrate formation via an on-line gas chromatograph. An

equilibrium cell with an internal volume of about 200 cm<sup>3</sup> was made of stainless steel. Two sapphire sight glasses were installed at the front and back sides of the cell to allow visual observation of the inside. The cell content was vigorously agitated by an impeller-type stirrer. A cooling tube was also installed to initiate hydrate nucleation by cooling an interface between the water and vapor phases. The equilibrium cell was immersed in a water bath that contained a water and ethanol mixture as a coolant to control the temperature. The actual temperature of the cell was measured by a platinum resistance thermometer (Hart Scientific, 1502A, USA) with an accuracy of 0.02 K. A pressure transducer (Druck, PDCR902, 0-50 bar, UK) and a pressure indicator (Druck, DPI145, UK) were used to measure the system pressure with a claimed accuracy of 0.025 % for the readings. For measuring the compositions of the vapor and hydrate phases, a sampling valve (Rheodyne, Model 7010, USA) with a loop volume of 20 μl was installed and connected to a gas chromatograph (Shimadzu, GC-14B, Japan) through a high-pressure metering pump (Eldex, USA). A thermal conductivity detector (TCD) and an SM-6 column (Shinwa, Japan) were used as the detector and the column, respectively. For the kinetic experiments, the system was maintained at a constant pressure by using a micro-flow syringe pump (ISCO, 500D, USA) operated in constant pressure mode. As the system pressure decreased due to the hydrate formation, the syringe pump instantaneously supplemented the gas to the equilibrium cell to keep the system pressure constant.

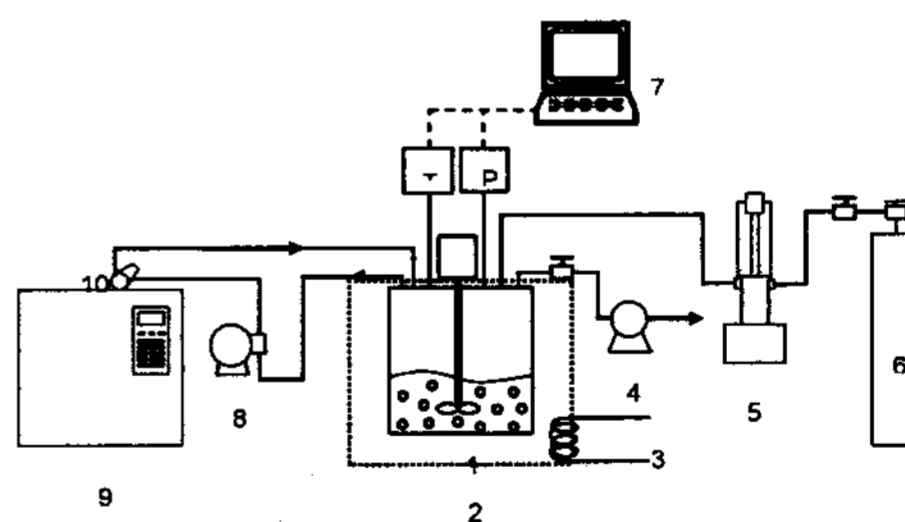


Fig. 1. Schematic diagram of experimental apparatus used in this study.

### 2.2 Materials and Apparatus

For the equilibrium measurement experiment, approximately 50 cm<sup>3</sup> of water was loaded into the equilibrium cell. The cell was evacuated with a vacuum pump two or three times. After the cell was pressurized to the desired pressure with the gas mixtures, the cell was slowly cooled to about 5 K below the expected hydrate forming temperature. The temperature of the water bath was programmed to increase or decrease at a rate of 0.5

K/hr. This continuous cooling or heating rate was confirmed as being slow enough to obtain the equilibrium dissociation point. The temperature and pressure profiles during hydrate formation and dissociation were recorded on a computer. The H-L<sub>w</sub>-V equilibrium points at each vapor composition were determined as the intersection between the hydrate dissociation and thermal expansion lines.

When measuring the equilibrium compositions, the experiments were carried out more carefully. To maintain the three-phase (H-L<sub>w</sub>-V) equilibrium at the final state, an excess of water was added so that it was not completely converted into hydrate. The final state was also confirmed to be the three-phase (H-L<sub>w</sub>-V) equilibrium by visual observation. In excess water condition, once nucleation occurs and hydrate formation proceeds, the pressure of the system spontaneously approaches that of H-L<sub>w</sub>-V coexistence at a specified temperature. The equilibrium cell was left as it was for 24 hours to reach an equilibrium state at a specified temperature, and then the vapor phase composition was analyzed by gas chromatography. On the other hand, the corresponding composition of the hydrate phase in coexistence with the vapor and liquid water phases was also measured by gas chromatography after the vapor phase had been evacuated with a vacuum pump to 0.05 bar within 10 seconds and all of the hydrate phase was dissociated.

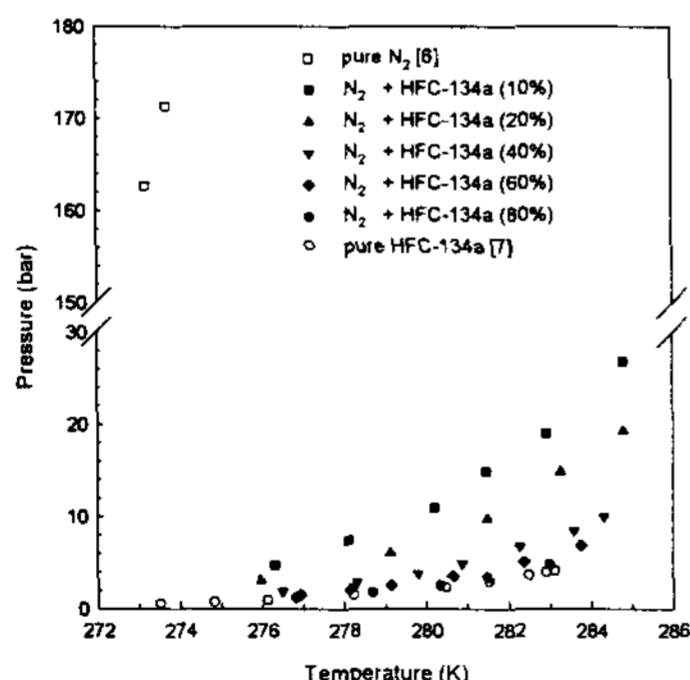


Fig. 2 Hydrate phase equilibria for the HFC-134a + N<sub>2</sub> + water mixtures.

### 3. Results and Discussion

In this work, we attempted to develop a new method for separating HFC-134a from a gas mixture using gas hydrate formation, and we attempted to confirm its feasibility through thermodynamic verification and other related techniques. The three-phase (H-L<sub>w</sub>-V) equilibria

of the ternary HFC-134a + N<sub>2</sub> + water mixtures with various HFC-134a vapor compositions (10, 20, 40, 60 and 80 mole %) were measured and are presented in Figure 2. The equilibrium measurements for the mixed gas hydrates were conducted over the wide temperature and pressure ranges of 275-285 K and 1-27 bar, depending on the vapor phase compositions. As can be seen in Figure 2, the H-L<sub>w</sub>-V lines of the ternary HFC-134a + N<sub>2</sub> + water mixtures are generally located nearer to that of the binary HFC-134a + water mixture than that of the binary N<sub>2</sub> + water mixture. N<sub>2</sub> is known to form structure II (sII) hydrate and, from its molecular size, HFC-134a is also expected to form sII hydrate<sup>(1)</sup>. However, HFC-134a can occupy only large cages, due to its large molecular size, while N<sub>2</sub> can occupy both small and large sII cages. Accordingly, despite the extremely high equilibrium pressure of pure N<sub>2</sub> hydrate at a specified temperature, HFC-134a occupation of the large cages results in a remarkable stabilization of the mixed HFC-134a + N<sub>2</sub> hydrates, which could be interpreted as having some advantages from an operational point of view, i.e., a low-pressure requirement for hydrate formation and enrichment of HFC-134a in the hydrate phase.

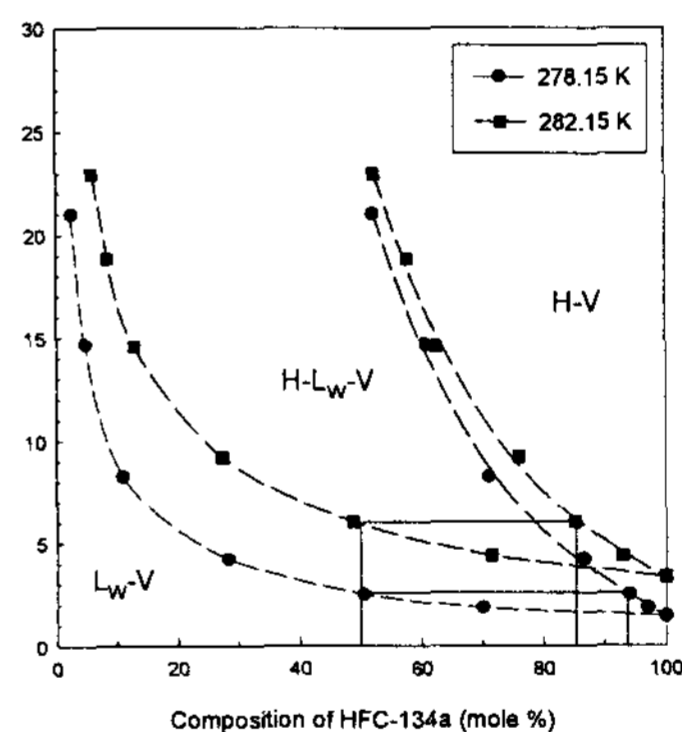


Fig. 3 Pressure-composition diagram for the HFC-134a + N<sub>2</sub> + water mixtures.

HFC-134a at 278.15 and 282.15 K, respectively, as determined from Figure 3. The equilibrium pressures for the equimolar gas mixture were 2.5 bar at 278.15 K and 6 bar at 282.15K, respectively. Selectivity of HFC-134a in the hydrate phase appeared to be better at a lower temperature than a higher one. The above result means that only one step of hydrate formation and subsequent dissociation is required to obtain more than 90 mole % HFC-134a from the equimolar gas mixture. One additional step, which can be carried out at a much lower pressure, can yield almost pure HFC-134a. The gas component captured in the hydrate phase can be easily

recovered by dissociation of the hydrate phase after raising the temperature or reducing the pressure.

#### 4. Conclusion

In the present study, a new separation method was proposed for separating HFC-134a from gas mixtures of N<sub>2</sub> and HFC-134a using gas hydrate formation. To check the thermodynamic validity of this separation method, three-phase equilibria of hydrate (H), liquid water (L<sub>w</sub>), and vapor (V) for the HFC-134a + N<sub>2</sub> + water mixtures with various HFC-134a vapor compositions (10, 20, 40, 60 and 80 mol%) were carefully measured in the temperature and pressure ranges of 275-285 K and 1-27 bar, respectively. The composition of the hydrate and vapor phases at a three-phase equilibrium state were also analyzed for the HFC-134a + N<sub>2</sub> + water mixtures to confirm the actual separation efficiency. In addition, the kinetic experiments were performed to obtain the required time for reaching an equilibrium state. Through close examination of overall experimental results, it was verified that more than 99 mol% HFC-134a could be obtained from gas mixtures after hydrate formation and subsequent dissociation processes.

The HFC-134a separation process using gas hydrate formation has several advantages from an operational point of view. The operation can be conducted over mild temperature (275-285 K) and low pressure (1-27 bar) ranges, depending on the vapor phase compositions. In most cases the operation can be carried out at pressures lower than 10 bar. The separation medium consists only of water and no additive is needed to lower the hydrate formation pressure. Therefore, this separation process is very environmentally friendly. In spite of the above advantages, additional work on continuous operation should be carried out in the near future, to treat larger amounts of gas stream, and finally to commercialize this method.

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