MEASUREMENTS OF HCFC-142b HYDRATE PROPERTIES RELATING TO THE SEPARATION FROM ITS MIXTURE

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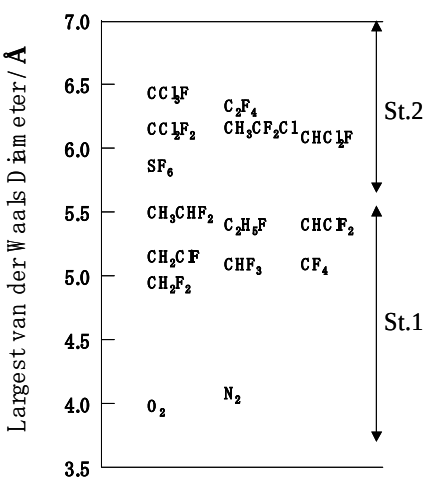
Introduction

So far many kinds of fluorocarbone have been used as foaming agents in industry. Until mid of 1990, CFC-11 had been utilized and from mid of 1990, owing to the Global warming problem, HCFC-141b or HCFC-142b has replaced CFC-11. Now, industry begins to use HFC-245fa or HFC-134a, whose ODP is Zero, instead of HCFC. These foaming materials have been provided as heat insulating materials. Thus, wastes of insulating materials include many kinds of fluorocarbon, and in addition, replacement by air progresses in it. To recover a specified kind of fluorocarbon from the wastes, separation of the fluorocarbon from their mixture or that from the air mixture is necessary.

Fluorocarbons are classified according to its van deer Waals diameter in Table 1. Almost all kinds of fluorocarbon can make hydrates if they contact with water under specific temperature and pressure conditions. There are two types of crystal in hydrates. Molecules whose van deer Waals diameter is less than 55 nm make Type I crystals, while that whose van deer Waals diameter is more than 55 nm make Type II crystals.

Table 1. van der Waals Diameter of each Fluorocarbon



If mixed gases composed of two components whose condition of forming hydrates is different, the molecules which are likely to make hydrates tend to exist in the hydrate phase at high ratio. By repeating formation and dissociation of hydrates we can increase the ratio of the specific component in the hydrates and finally obtained pure substance. In this report HCFC142b is adopted as the representative of fluorocarbones.

Experimental Apparatus and Method

The apparatus used in this experiment is illustrated in Fig.1. The heart of this apparatus was a cylindrical cell made by TAFMAX-V glass whose volume was approximately 300 cm3 and maximum pressure was 1.0 MPa. To reduce the necessary time for reaching an equilibrium state, the cell was equipped with a stirrer (Nitto, S200) driven magnetically from the outside of the cell. It was also equipped with a cooling tube to help the nucleation of hydrates. By cooling the interface between liquid and vapor phases, the hydrates nucleation can be initiated. A gas supply, a vent and a vacuum line were connected to the cell. For evacuation a vacuum pump (Edwards, E2M1.5) was used. The whole cell was immersed in a water-ethanol bath whose temperature was controlled by a constant temperature circulator (EYELA, PCC-7000). The circulator enabled the bath temperature to vary with a maximum rate of 1.0K/min.

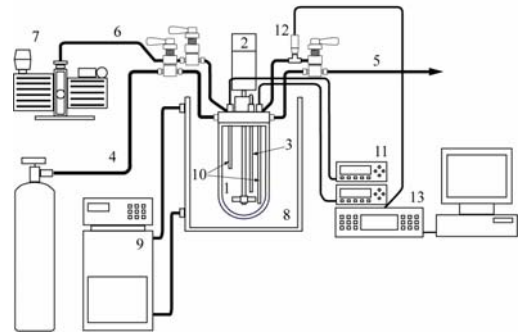


Figure 1. Experimental apparatus for Measurements of HCFC-142b Hydrate Properties

The actual temperature in the cell was measured by platinum resistance probes with thermometers (Hart Sci., 1502A). The probes were calibrated such that deviation from the secondary national standard was within 0.02K. A pressure transducer (Drug, PDCR902, 0.5MPa) and a pressure indicator (Drug, DPI145) were used for equilibrium pressure measurement with claimed accuracy of 0.025% of reading. To minimize the temperature drift of the pressure transducer, room temperature was always kept at 293K.

Tap water was deionized, distilled, purified by an ultrapure water system (Millipore, Milli-Q) and finally provided to experiments. HCFC-142b with stated purity of 99.98 wt% was supplied by Takachiho chemical (Japan).

For the measurement of H-L_w-V equilibrium line, the cell containing about 100cm3 of water was evacuated until the system pressure was almost equal to vapor pressure of water, and then charged with HCFC-142b up to about 0.2MPa. This procedure was repeated three times. After the cell was pressurized by HCFC-142b up to proper pressure with carefully avoiding liquefaction, the cell and inner contents were cooled down to specified temperature. Then hydrate nucleation was induced by injecting liquid nitrogen to the cooling tube. Once phase transformation from false V-L_w two-phase coexistence to H-L_w-V coexistence started, pressure spontaneously approached to the equilibrium pressure. During the phase transformation mixing was continued for six hours. After the mixing was stopped, the cell was placed stationarily for at least eight hours. Then the pressure was adopted as the equilibrium pressure at the specified temperature.

Model

Liquid Phase Model and Vapor Phase Model. To predict the H-Lw-V equilibrium condition a liquid phase and a vapor phase model are necessary in addition to a hydrate phase model. In this research, Soave-Redlich-Kwang equation of state and MHV2 mixing rule were adopted for this purpose. In the MHV2 mixing rule, the van der waals parameter *a* and *b* are obtained by solving the equation

$$q_1\alpha + q_2\alpha^2 = \sum_{i=1}^{c} x_i\left(q_1\alpha_i^0 + q_2\alpha_i^{0^2}\right) + \sum_{i=1}^{c} x_i \log\gamma_i + \sum_{i=1}^{c} x_i \log\frac{b}{b_i^0} \qquad (1)$$

where α is defined by

$$\alpha = \frac{a}{bRT} \qquad (2)$$

x_i represents mole fraction of component i, γ_i is the activity coefficient, q_1 and q_2 denote constants whose values are $q_1 = -0.478$ and $q_2 = -0.0047$ respectively, and the superscript 0 refers to the pure substance.

The activity coefficient γ_i can be calculated by using UNIQUAC model. To apply UNIQUAC model to the activity coefficient calculation we must determine so called UNIQUAC parameters of each molecule. These are the van der Waals volume parameter r_i, the van der Waals area parameter q_i, and the interaction parameter τ_{ij}. The values of r_i and q_i are determined from the geometrical data of each molecule.

Hydrate Phase Model. As for a hydrate phase model, we adopted von dear Waals & Plattuuew model.

$$\mu_w^H = \mu_w^\beta - RT\sum_{i=1}^{2} \nu_i \log\left(1 + C_i f_1^H\right) \qquad (3)$$

In equation (3) the constant C represents the langmuir constant and is given by equation (4).

$$C_{j_k} = \frac{4\pi R_c^3}{k_b T}\int_0^1 \exp\left(-\frac{\tilde{\omega}\left(r^*\right)}{k_b T}\right) r^{*2} dr^* \qquad (4)$$

Here, ϖ is the cell potential and is given by equation (5).

$$\tilde{\omega}\left(r^*\right) = 2z\varepsilon\left\{\frac{\sigma^{*12}}{r^*}\left(\delta^{10} + a_c^*\delta^{11}\right) - \frac{\sigma^{*6}}{r^*}\left(\delta^4 + a_c^*\delta^5\right)\right\} \qquad (5)$$

Here, σ and ε are Kihara potential parameters which express the interaction between molecules. To determine these values regression procedure is necessary. σ indicates the position where the interaction became zero, and ε expresses the depth of the potential well.

Experimental Results and Determination of Molecular Parameters of HCFC-142b

UNIQUAC Parameters of HCFC-142b. Table 2 summarized the values of the UNIQUAC parameters of HCFC-142b and water. These values were obtained by the regression of Carey's V-L data[1]. Figure 2 shows the comparison between calculated and experimental values.

Table 2. UNIFAC Parameters of HCFC142b and Water

r_{142b}	2.678
q_{142b}	2.488
r_{H2O}	0.920
q_{H2O}	1.400
$\tau_{142b-H20}$	1649.606
$\tau_{H20-142b}$	474.884

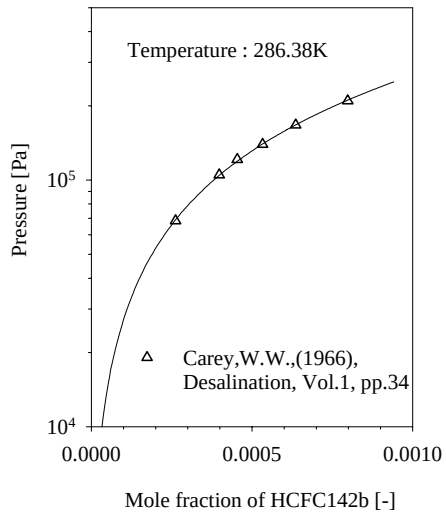


Figure 2. Solubility of HCFC142b in water

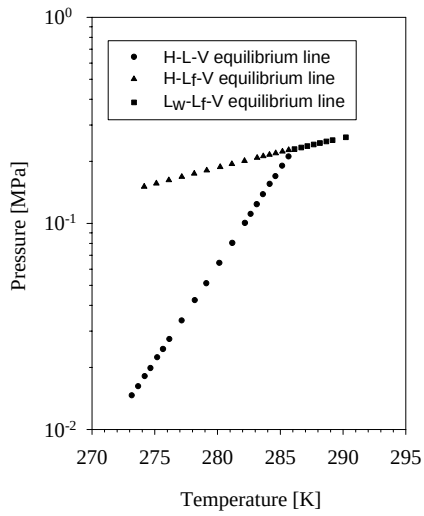


Figure 3. Three phase equilibrium lines of HCFC142b hydrates

Table 3. Kihara Potential Parameters of HCFC-142b

Core radius a	4.6020E-11
Distance parameter σ	4.1969E-10
Depth of potential well ε/k	699.99

Kihara Potential Parameters of HCFC-142b. The whole results of equilibrium measurement are plotted in Figure 3. The values of Kihara potential parameters determined by the regression method were summarized in Table 3.

References

(1) Carey, W.W., Desalination, **1966**, 1,34.