

Gas Separation of Semiclathrate Hydrates for CH₄ + CO₂ Mixed Gas

Kosuke Ikeda^{*1}, Takutya Yasoyama², Hiroyuki Miyamoto², Sanehiro Muromachi³.

¹Graduate School of Mechanical Systems Engineering, Toyama Prefectural University,
5180 Kurokawa, Imizu-shi, Toyama 939-0398, Japan

²Department of Mechanical Systems Engineering, Toyama Prefectural University,
5180 Kurokawa, Imizu-shi, Toyama 939-0398, Japan

³Energy Process Research Institute, National Institute of Advanced Industrial Science and
Technology (AIST),
16-1 Onogawa, Tsukuba-shi, Ibaraki, 305-8569

* To whom correspondence should be addressed.

E-mail : u153003@st.pu-toyama.ac.jp Tel : +81-766-56-7500 FAX : +81-766-56-6182

Abstract

In recent years, semiclathrate hydrates which form from water, ionic substance with/without gas are expected for gas storage, separation, and cool energy storage applications. It has been reported that gas separation properties of semiclathrate hydrates depend on pressure, temperature, aqueous composition of ionic substance and choice of ionic substance. In this study, semiclathrate hydrates were formed with four ionic substances (tetra-*n*-butylammonium (TBA) bromide (TBAB), TBA chloride (TBAC), tetra-*n*-butylphosphonium (TBP) bromide (TBPB), and TBP chloride (TBPC)), and gas separation properties of CH₄ + CO₂ mixed gas were investigated. Measurements were performed with a high pressure cell at three different aqueous compositions of ionic substance (0.1, 0.2, 0.3 in mass fraction) and two different pressure levels (3 MPa, 5 MPa). The gas in the cell before and after hydrate formation were collected, and the composition was analyzed by a gas chromatograph. The results showed that at 5 MPa, the gas incorporated into the TBA-based hydrates had a higher CO₂ composition than the TBP-based hydrates with all the aqueous compositions. It was also shown that the lower the aqueous composition, the higher the CO₂ composition in hydrate phase.

Keywords

Semiclathrate hydrate, Gas separation properties, Mixed gas, methane, CO₂, biogas

1. Introduction

In recent years, with concerns about global warming, developing renewable energy process has become urgently important. Biogas, which is one of the renewable energies, based on methane (CH_4) and carbon dioxide (CO_2) needs to be refined at its use. Semiclathrate hydrates can be used for refining methane and carbon dioxide from biogas.

Semiclathrate hydrates form from water and ionic substance such as quaternary ammonium salts and are similar to clathrate hydrate such as methane hydrate [1,2]. In their structures, water molecules ionic substances build cage-like hydrogen bond network. Industrial applications based on semiclathrate hydrates are proposed based on that they can incorporate gas under relatively higher temperature and lower pressure conditions than clathrate hydrates which usually require low temperature and high pressure for formation.

In this study, we perform gas separation by semiclathrate hydrates and analyze gas separation properties due to changes in ionic substances and thermodynamic conditions. We used semiclathrate hydrates of four types of ionic substances: tetra-*n*-butylammonium bromide (TBAB), tetra-*n*-butylammonium chloride (TBAC), tetra-*n*-butylphosphonium bromide (TBPB) and tetra-*n*-butylphosphonium chloride (TBPC). The experiments were conducted at pressures of 5 MPa and 3 MPa.

2. Experimental

2.1. Materials

The gases and ionic substances used in this study are summarized in Table 1 and Table 2.

Table 1

Gases used in this work.

Component	Source	Purity
CO_2	Hokusan Co., Ltd.	>99.999 vol%
CH_4	Air Water East Japan Co., Ltd.	>99.999 vol%

Table 2

Ionic substances in this work.

Component	Source	Composition
TBAB	Wako Pure Chemical Industry Co, Ltd.	>98%
TBAC	Sigma-Aldrich Co., Ltd.	>98%
TBPB	Sigma-Aldrich Co., Ltd.	>98%
TBPC	Tokyo Chemical Industry Co., Ltd.	80% (in water)

Pure water was used to prepare the ionic aqueous solution. The composition of the TBPC

aqueous solution was adjusted using a refractometer.

2.2. Apparatus and Procedure

In this study, we used a hydrate generator by AKICO Co., Ltd. and a gas chromatograph manufactured by GL Science Co., Ltd. An aqueous solution of ionic substance with adjusted composition was injected into a high pressure cell. The cell was evacuated with a vacuum pump and charged with CO₂ and CH₄ gas. Hydrate was generated at a temperature 2–3 K lower than equilibrium temperature. The gas in the cell were collected before and after hydrate formation and the composition was analyzed by the gas chromatograph.

The amount of gas in the gas phase was calculated by the following formula:

$$n^G = \rho^G \times V^G \quad (1)$$

where, ρ^G is the density of the gas phase calculated by REFPROP ver.10 (Lemmon et al [4]), and V^G is the volume of the gas phase. The amount of gaseous component i in the hydrate phase was calculated by

$$n_i^H = n_i^G - n_i'^G \quad (2)$$

where, n_i^G and $n_i'^G$ are the amounts of gaseous component i in the gas phase before and after hydrate formation, respectively. The CO₂ composition in the hydrate phase was calculated by

$$\phi_{CO_2} = \frac{n_{CO_2}^H}{n_{CO_2}^H + n_{CH_4}^H} \quad (3).$$

3. Results and discussion

The experiments were performed at 3 and 5 MPa. Fig. 3 shows results of CO₂ mole fraction of gas captured in hydrate phase. Experiments were performed three times with each aqueous solution. This figure shows the weighted average of the three measurements based on uncertainty. At the initial pressure of 5 MPa, the lower the aqueous composition, the higher the CO₂ composition in the hydrate phase. At 5 MPa, the TBA series showed a higher CO₂ composition than the TBP series at any aqueous solution composition.

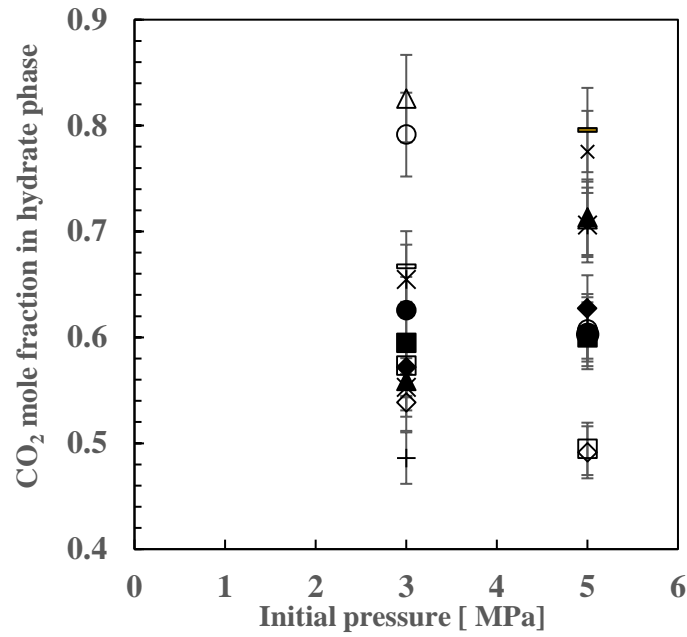


Fig. 5 The CO₂ mole fraction in hydrate phase. Symbol: ●, TBAB with $w = 0.3$; ○, TBAC with $w = 0.3$; ■, TBPB with $w = 0.3$; □, TBPC with $w = 0.3$; ▲, TBAB with $w = 0.2$; △, TBAC with $w = 0.2$; ◆, TBPB with $w = 0.2$; ◇, TBPC with $w = 0.2$; ×, TBAB with $w = 0.1$; —, TBAC with $w = 0.1$; *, TBPB with $w = 0.1$; +, TBPC with $w = 0.1$. (w denotes aqueous composition of ionic substance on mass basis.)

The amount of CO₂ and CO₂ mole fraction in hydrate phase shown in this study revealed that TBAC hydrate shows high CO₂ selectivity. According to Muromachi et al. [3,5,6], CO₂ selectivity of semiclathrate hydrates differs due to experimental conditions and hydrate structure. The differences in CO₂ selectivity between subjected ionic substances may be caused by this manner. The present experiments were conducted in a cell with a sufficient volume, which can provide reliable data for gas separation.

5. Conclusion

In this study, we conducted gas separation experiments of CO₂ +CH₄ mixed gas by semiclathrate hydrates with different ionic substances and formation conditions. TBAC showed the highest CO₂ composition in hydrate phase with certain aqueous composition compared to other ionic substances. At presentation, we will show additional discussion about physical properties and gas separation performance of these materials.

References

- [1] G. A. Jeffrey; In “Inclusion Compounds”, eds J. L. Atwood, J. E. D. Davies, D. D. MacNicol; vol, 1 (1984) chapter 5, Academic Press; London.
- [2] D. W. Davidson, In “Water. A Comprehensive treatise”, ed. F. Franks; Vol. 2 (1973) Chapter 3, Plenum Press; New York, NY.
- [3] S. Muromachi, A. K. Udachin, K. Shin, S. Alavi, L. I. Moudrakovski, R. Ohmura, Ripmeester, J. A. Chem Commun, Vol. 50 (2014) 11476-11479.
- [4] E. W. Lemmon, I. H. Bell, M. L. Huber, M. O. McLinden, REFPROP Reference Fluid Thermodynamic and Transport Properties, Ver. 10.0, National Institute of Standards and Technology, 2018.
- [5] S. Muromachi, K.A. Udachin, S. Alavi, R. Ohmura, J. A. Chem. Commun. Vol. 52 (2016) 5621-5624.
- [6] S. Muromachi, Y. Yamamoto, S. Takeya, Korean J. Chem. Eng, Vol. 33 (2016) 1917-1921.