Effect of temperature and pressure on hydration number of methane hydrate

*Akihiro Hachikubo[1], Ryoya Kamata[1], Hiromi Kimura[1], Yuta Komagata[1], Go Fuseya[1], Satoshi Takeya[2]

1. Kitami Institute of Technology, 2. National Institute of Advanced Industrial Science and Technology (AIST)

Gas hydrates are considered to be a potential resource of energy and a gas storage medium. Hydration number of methane hydrate decides the amount of gas in crystal lattice of gas hydrate. In the case of ideal full-occupation of hydrate cages, hydration number is 5.75. However, researchers have reported that the hydration number is around 6, because small amount of empty cages decrease the free energy and stabilize the crystal. Hydration number depends on temperature and pressure at the formation process (Cady, 1981; 1983) as van der Waals & Platteeuw model predicts. It has not been investigated how the hydration number changes over a wide temperature range. In this study, we investigated the effect of temperature and pressure on the hydration number of methane hydrate.
Small amount of fine ice powder (0.1 g) was placed in a pressure cell at 253 K, and methane was introduced and pressurized under the temperatures of 245 K, 255 K, and 273 K to form hydrate samples. The samples were retrieved under the temperature of liquid nitrogen. The Raman spectra of the C-H symmetric stretching vibrational mode of the methane molecules encapsulated in the large and small cages of the structure I were observed using a Raman spectrometer. The area ratios of the Raman peaks derived from the methane molecules in the large and small cages were determined by a peak fitting using the Voigt function, and the hydration number was estimated using a statistical thermodynamic calculation.
Generally, the hydration number of methane hydrate decreased with increasing formation pressure. This trend is consistent with the results obtained for hydrates of other guests such as xenon, hydrogen sulfide, and sulfur dioxide (Kamata *et al.*, 2020; Cady, 1981; 1983). Besides, it increased slightly with temperature. However, the change of hydration number of methane hydrate was relatively small, ranged from 5.92 to 6.11 under the pressure of 2 MPa to 21 MPa.

References

Cady GH (1981) Composition of clathrate gas hydrates of $CHClF_2$, CCl_3F, Cl_2, ClO_3F, H_2S, and SF_6. *J Phys Chem* **85**: 3225-3230
Cady GH (1983) Composition of Clathrate Gas Hydrates of H_2S, Xe, SO_2, Cl_2, CH_3Cl, CH_3Br, $CHClF_2$, CCl_2F_2, and C_3H_8. *J Phys Chem* **87**: 4437-4441
Kamata R, Kimura H, Sugimori E, Hachikubo A, Takeya S (2020) Direct measurement of hydration number of gas hydrates. *JpGU-AGU Joint Meeting 2020*, MIS32-P12

Keywords: gas hydrate, hydration number, methane

