

Effect of pressure on hydration number of clathrate hydrates revealed by weight measurement

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The hydration number of gas hydrate is an indicator of how much gas is being stored in hydrate crystals. The hydration number is not stoichiometric and the value varies depending on the sample. For example, the hydration number of methane hydrate is reported to be 6.2 ± 0.2 (Uchida *et al.*, 1999) and it is larger than the theoretical value of 5.75 due to the presence of empty small cages. Raman spectroscopy is one of the methods to estimate the hydration number of gas hydrates. In order to estimate the hydration number, it is necessary to obtain the peak area ratio of the guest molecules in each of the large and small cages and use the statistical thermodynamic model. Depending on the type of gas molecules, it is difficult to separate the Raman peaks (e.g., N_2 and O_2). Since Raman peaks cannot be observed in the case of noble gases, we attempted to derive the hydration number of gas hydrate by separating the hydrate-bound gas and water and measuring their weights in this study. This paper reports the effect of formation pressure on hydration number of gas hydrates.

Carbon monoxide hydrate (crystallographic structure I) and mixed gas hydrate enclathrated carbon monoxide and argon (crystallographic structure II) were formed. Fine powder ice of 5 g was sealed in a pressure cell. The cell was evacuated at 77 K, and then a certain amount of guest gas was introduced. Then the temperature of the cell was slowly raised to 0 °C to promote hydrate formation. In the case of low pressure (close to the equilibrium pressure), the formation time was set to 1-2 weeks to raise the purity of gas hydrate. After the formation of hydrate samples, the cell was evacuated at 77 K to remove the excess gas, and then the sample was dissociated in the cell at a room temperature. The cell was weighed, and then the valve of the cell was opened to reduce the internal pressure to atmospheric pressure, and the weight was measured again. The weight of the remaining gas in the cell (atmospheric pressure) gas was estimated from the equation of state of the ideal gas. Thus, the weights of the hydrate-bound gas and water were obtained independently, and the hydration number was determined from these weights. In the case of mixed gas hydrates of carbon monoxide and argon, the gas composition of the hydrate-bound gas was measured using a gas chromatograph.

In this study, the hydration number of carbon monoxide hydrate and mixed gas hydrate of carbon monoxide and argon decreased slightly with formation pressure. Here, their rates of decrease with formation pressure were smaller than that of pure argon hydrate (crystallographic structure II). In previous study, the hydration number of argon hydrate increases at lower pressures was considered to be due to the difficulty of Ar entering into the small cages (Kamata, *et al.*, 2020) since the crystallographic structure II has higher ratio of small dodecahedral cages than the crystallographic structure I. However, the mixed gas hydrate of carbon monoxide and argon belongs to the structure II being same as pure carbon monoxide hydrate. This indicates that the pressure dependence of the hydration number of gas hydrates is determined by the type and composition of the gas rather than the crystallographic structure.

References

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