Equilibrium pressure of clathrate hydrates encaged $^{13}CH_4$

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Methane molecule is composed of carbon and hydrogen, and three kinds of isotopologues, $^{12}CH_4$ (98.9%), $^{13}CH_4$ (1.1%), and CH_3D (0.013%) exist in nature. We often measure stable carbon isotope ($^{13}C/^{12}C$) of methane to understand its gas origin. Since their weight of isotopologues differ with each other, physicochemical properties of them are also different. Pure methane hydrate must be "mixed-gas hydrate" of their isotopologues. Ozeki *et al.* (2018) measured an equilibrium pressure of CH_3D hydrate, but that of $^{13}CH_4$ has not been studied yet. Fractionation of hydrogen isotope of methane during the formation of methane hydrate has been reported by Hachikubo *et al.* (2007) that δ D of hydrate-bound methane becomes several ‰smaller than that of residual methane. This result suggests that the equilibrium pressure of CH_3D hydrate is larger than that of CH_4 hydrate, and Ozeki *et al.* (2018) demonstrated the difference between these equilibrium pressures. Since Hachikubo *et al.* (2007) showed no isotopic fractionation in methane $\delta^{13}C$, the equilibrium pressures of $^{12}CH_4$ and $^{13}CH_4$ hydrates are thought to be almost the same. In this study, we measured the equilibrium pressures of $^{13}CH_4$ hydrate to check the difference from that of $^{12}CH_4$ hydrate.

Methane hydrate samples were synthesized in small pressure cells (volume: 5 mL). Fine ice powder (1g) was put in a pressure cell, and introduced $^{13}CH_4$ (purity: 99.5%, Taiyo-Nissan). Clathrate hydrate was formed by melting the ice powder at the temperature of 273.2K under high pressure of methane. We also prepared normal methane (purity: 99.99% for methane, but 98.9% for $^{12}CH_4$, Takachiho Chemical Industry Co. Ltd.) hydrate as a reference, using the same preparation method. These pressure cells were placed in a temperature-controlled liquid bath, and measured their equilibrium pressures from 269.5K to 277.9K.

The difference in equilibrium pressure between $^{13}CH_4$ and normal methane (mainly $^{12}CH_4$) hydrates was smaller than the measurement error. This results agree with the previous report by Hachikubo *et al.* (2007).

References

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