Equilibrium pressure of clathrate hydrates composed of isotopologue methane

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Methane is composed of carbon and hydrogen. Because these components have isotopes, $^{12}CH_4$ (98.9%), $^{13}CH_4$ (1.1%), and CH_3D (0.013%) exist in nature. Since their molecular weight differs with each other, physicochemical properties of them are also different with each other. Pure methane hydrate is "mixed-gas hydrate" of their isotopologues. Equilibrium pressure of pure methane hydrate was first reported more than a half century ago; however, those of $^{13}CH_4$ and CH_3D hydrate have not been studied yet. Fractionation of hydrogen isotope during the formation of methane hydrate has been reported by Hachikubo *et al.* (2007) that δD of hydrate-bound methane becomes several ‰smaller than that of residual methane in the formation process. This result suggests that the equilibrium pressure of CH_3D hydrate is larger than that of CH_4 hydrate. In this study, we measured the equilibrium pressures of CH_3D hydrate and confirmed the difference between them.

Methane hydrate samples were synthesized in small pressure cells (volume: 5mL). Fine ice powder (1g) was put in a pressure cell, and introduced CH_3D (purity: 98%, 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 273.2K to 277.2K.

The equilibrium pressure of CH_3D hydrate was about 0.07MPa larger than that of CH_4 hydrate, and the results agreed with the previous report by Hachikubo *et al.* (2007).

Reference

Hachikubo A, Kosaka T, Kida M, Krylov A, Sakagami H, Minami H, Takahashi N, Shoji H (2007) Isotopic fractionation of methane and ethane hydrates between gas and hydrate phases. Geophys Res Lett 34: L21502. doi:10.1029/2007GL030557

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