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Thermodynamic inhibition of 4-methylmorpholine while forming sH hydrate with methane

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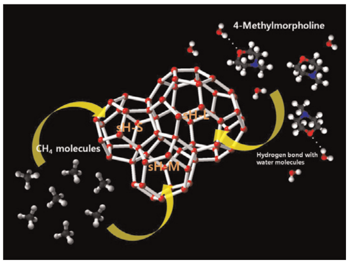
HIGHLIGHTS

- 4-methylmorpholine as a new large-molecule guest substance of structure H hydrate.
- Thermodynamic inhibition effect of 4-methylmorpholine at various concentrations.
- The ratio of the molecular diameter to cage diameter is 0.87.
- Explanation for enclathration behaviors of 4-methylmorpholine.

GRAPHICAL ABSTRACT



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ABSTRACT

4-methylmorpholine (4-mMPL), a nitrogen-containing heterocyclic compound, is an organic base which acts as a proton acceptor. In this study, we characterized structure H (sH) clathrate hydrates with 4-mMPL by measuring the hydrate-phase equilibria and a series of microscopic analyzes (powder X-ray diffraction, solid-state ^{13}C NMR and Raman spectroscopy). 4-mMPL was found to have lower dissociation temperature at a given pressure compared to that of pure CH_4 hydrate, simultaneously with a co-guest in sH hydrates (hexagonal P6/*mmm*). Such a change of thermodynamic stability is attributed to an oxygen atom in the molecular structure of 4-mMPL, which prevents hydrogen-bonding among water molecules. The ratio of the molecular diameter to cage diameter is 0.87, implying that the guest molecules can fit into cavities without distortion. The thermodynamic and chemical characteristics of 4-mMPL can be extended to other guest species in order to explain molecular behaviors related to inherent mechanisms of hydrate stability and host-guest interactions.

1. Introduction

Clathrate hydrates, or gas hydrates, are non-stoichiometric crystalline compounds formed by physical interactions (van der Waals force) between water and guest molecules (Sloan and Koh, 2008). Hydrogen-bonded networks of four-connected water molecules can entrap a large number of different types of small molecules (< 10 Å) into polyhedral cages, which contain various

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combinations of faces (Jeffrey, 1984). Because the molecules encaged in the cavities are unbound to the host framework, the guests are free to vibrate and rotate, but possess limited translational motion (Sum et al., 2009). Clathrate hydrates are of considerable interest to both science and engineering fields, particularly with respect to potential gas storage applications (Chatti et al., 2005; Struzhkin et al., 2007), a new source of natural gas (Makogon et al., 2007), and sequestration of CO_2 in the deep ocean (Teng et al., 1997). In general, the three most common structures, termed structures I, II and H, are known to exist for gas hydrates mainly depending on the molecular size of the accommodated guest species (Sloan and Koh, 2008). Among these families, hexagonal structure H (sH) hydrates, which were first discovered by Ripmeester et al. (1987) and subsequently detected in nature by Sassen and MacDonald (1994), have stimulated diverse researches on large-molecule guest substances (LMGSs). And finally Lu et al. (2007) provided direct evidence for the natural occurrence of sH hydrates containing more than 13 different hydrocarbon guest molecules, which are recovered from Barkley canyon, on the northern Cascadia margin (Chapman et al., 2004). These include common petroleum molecules such as i-C_5 and others with diameters as large as 7.5–8.6 Å (Khokhar et al., 1998), which are too large to be enclathrated in the cages of structure I (sI) and structure II (sII) hydrates. The formula for the unit cell of sH hydrates is $3S \cdot 2M \cdot 1L \cdot 34H_2O$, and consists of three 5^{12} cages, two $4^35^66^3$ cages, and one large $5^{12}6^8$ cage. Many LMGSs that form sH hydrates, such as tert-butyl methyl ether (TBME), methylcyclohexane (MCH), methylcyclopentane (MCP), and neohexane (NH) have been suggested (Ripmeester and Ratcliffe, 1990). A large number of studies have been carried out to identify phase equilibrium conditions, formation kinetics, and structural characteristics (Lee et al., 2010; Seo et al., 2010). Moreover, new LMGSs enclosed in sH hydrates with CH_4 gas are being explored for gas storage application and separation media, since sH hydrates commonly have superior storage capacity and thermodynamic stability compared to sI and sII hydrates (Shin et al., 2011; Jin et al., 2013; Strobel et al., 2008). Recently, the gas hydrate has become one of the major issues in flow assurance, as it may block flowlines during the production and transportation of petroleum fluids (Sloan, 2005). To deal with this severe problem, some hydrate research has focused on identifying stable regions for safe production, and searching for hydrate inhibitors that shift the equilibrium phase boundary of gas hydrates into the inhibited region so that the operational conditions can reside outside the hydrate formation region (Gbaruko et al., 2007; Ostergaard et al., 2005).

In this study, 4-methylmorpholine (4-mMPL) was tested and analyzed for binary sH hydrates with high-pressure CH_4 gas. 4-mMPL is a nitrogen-containing organic base with intermediate strength, which can be readily protonated. We investigate the equilibrium pressure-temperature relationships to identify stability regions with the new hydrate former. In addition, microscopic analyzes for 4-mMPL+CH_4 hydrate samples were performed to characterize crystal structures and molecular behaviors by means of powder X-ray diffraction (PXRD), solid-state ^{13}C NMR methods, and Raman spectroscopy.

2. Experimental details

2.1. Materials

CH_4 of 99.95 mol% purity was purchased from the Special Gas Company (Daejeon, Korea). High purity distilled water was obtained from a Millipore purification unit. 4-Methylmorpholine (ReagentPlus, 99%) was purchased from Aldrich.

2.2. Sample preparation

The hydrate samples were synthesized from aqueous 4-mMPL solutions of various concentrations and slowly frozen at 243.0 K. The frozen solutions were ground into fine powders with a 200 μm sieve in liquid nitrogen. Then, the powdered sample was placed in a high-pressure cell and pressurized with CH_4 gas up to 10 MPa at 243.0 K. The high-pressure cell was stored at 243.0 K for 5 days. After forming the hydrate samples, the high-pressure cell was cooled down to liquid nitrogen temperature, and the pressure was slowly released.

2.3. Experimental Measurements

To determine the equilibrium condition of the clathrate hydrate, the non-isothermal method was implemented using an impeller-type stirring cell. The thermal cycle includes the following two steps: a cooling step, in which the system temperature is decreased from 293.0 K to a temperature below hydrate formation, ranging from 263.0 K to 273.0 K (1.0 K/h), and a heating step, in which the system temperature is brought back to the initial temperature (0.1 K/h). A P–T hysteresis during the thermal cycle for measuring equilibrium conditions of gas hydrates is shown in Fig. S1. A four-wire-type PT-100 Ω (±0.05% accuracy of the full scale), and a PMP4070 device from Druck Inc. in the range of 0–20 MPa were used as temperature and pressure sensing devices, respectively. A schematic diagram of the experimental apparatus is shown in Fig. 1. The PXRD pattern was obtained at 93.0 K on a Rigaku D/Max-RB diffractrometer using graphite-monochromatized CuK_α radiation ($\lambda = 0.15406$ nm) in the $\theta/2\theta$ scan mode. The PXRD experiments were carried out in step mode with a fixed time of 2 s and a step size of 0.03° for $2\theta = 5.00°$ to 55.01°. The patterns obtained were calculated by the Checkcell program (Laugier and Bochu, 2002). A Varian (Agilent VNMRS600) 600-MHz solid-state NMR spectrometer was used. The powdered (~200 μm) samples were placed in a 4.0 mm o.d. zirconia rotor loaded into a variable temperature probe. All ^{13}C NMR spectra were recorded at a Larmor frequency of 150.9 MHz with MAS at about 5 kHz, and the measurement temperature was fixed at 203.0 K. A pulse length of 5 μs and a pulse repetition delay of 10 s under proton decoupling were used with a radio-frequency field strength of 50 kHz, corresponding to a 5 μs 90° pulse. The downfield carbon resonance peak of hexamethyl benzene (HMB), assigned a chemical shift of 17.3 ppm at 298 K, was used as an external chemical shift reference. To obtain CH_4 signals of a higher intensity, a gaseous mixture of $^{13}CH_4$ and $^{12}CH_4$ was used. For Raman measurements, a Horiba Jobin-Yvon LabRAM HR UV/Vis/NIR high-resolution dispersive Raman microscope equipped with an electrically cooled (203.0 K) CCD detector placed in liquid nitrogen was used. The samples were kept at 93.0 K during the measurements. The excitation source was

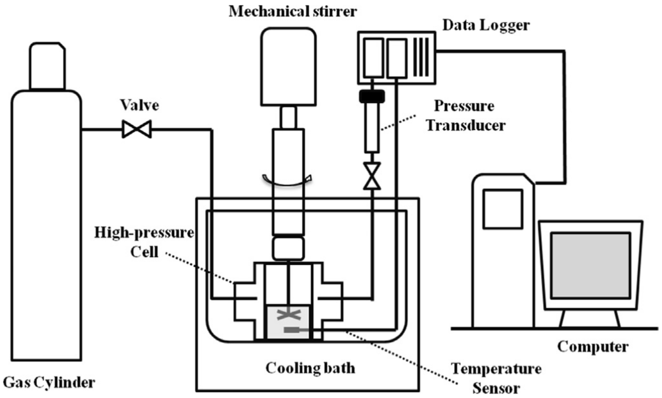

Fig. 1. Schematic diagram of the experimental apparatus.