

n-Pentane & n-Hexane as Coguests of sH Hydrates in the Mixture with 2,2-Dimethylbutane and Methane

Jong-won Lee¹⁾, Hailong Lu, Igor L. Moudrakovski
Christopher I. Ratcliffe, John A. Ripmeester²⁾

Key words : n-pentane(n-펜탄), n-hexane (n-헥산), gas hydrate (가스 하이드레이트), structure H (구조 H), natural gas (천연 가스), NMR spectroscopy (NMR 분광법)

Abstract : n-Pentane and n-hexane, previously regarded as non-hydrate formers, are found to form structure H hydrate in mixtures with 2,2-dimethylbutane. Even though they are thought to be too large to fit into the largest cage of the structure H hydrate, powder XRD and NMR measurements show that they form gas hydrates in mixtures with other sH hydrate former. These findings are of fundamental interest and also will impact the composition and location of natural gas hydrates and their potential as global energy resource and climate change materials.

1. Introduction

Gas hydrates are ice-like solid materials formed when small molecules are captured in the cavities of ordered three dimensional hydrate frameworks.¹⁾ As a large amount of the Earth's natural gas supply is known to be trapped in hydrate deposits that occur globally under the permafrost and in marine sediment on the continental margins,²⁾ intensive research has been performed to explore and assess this potential new energy source for eventual utilization. It is well known that gas hydrates are classified into three main structures, known as cubic structure I (sI), cubic structure II (sII), and hexagonal structure H (sH). Amongst hydrocarbon molecules, methane and ethane form sI or sII hydrates, whereas C3 and C4 hydrocarbons, often in the presence of C1 and C2 hydrocarbons, form sII hydrates.¹⁾ The sH hydrate, identified by Ripmeester et al. in 1987, can accommodate heavier hydrocarbons up to C8, such as cycloalkanes, methylcycloalkanes, and methyl-substituted n-alkanes, in the largest cavity ($5^{12}6^8$) of the structure.^{3,4)} For sH

hydrates, it is necessary to fill the small cavities (5^{12} , $4^35^66^3$) with an help gas, such as methane, to form a stable structure. However, n-alkanes with five or more carbon atoms were identified as not being able to stabilize the sH hydrate, and it was conjectured that they may not fill the large cage efficiently.⁴⁾ Because the amount, and location, of natural gas stored in hydrate form strongly depends on the nature of the hydrate, the structural, compositional, and stability characteristics of the hydrate become critical in evaluating a hydrate for its potential as an energy source and climate-change agent. So far, analysis of natural-gas hydrate samples has shown that most natural hydrates formed from gas of biogenic

1) Dept. of Environmental Engineering, Kongju National University

E-mail : maruhill@kongju.ac.kr

Tel : (041) 550-0396 Fax : (041) 552-0380

2) Steacie Institute for Molecular Sciences, National Research Council of Canada

E-mail : john.ripmeester@nrc.ca

Tel : (+1) 613-993-2011 Fax : (+1) 613-998-7833

origin are the sI form, whereas sII and sH hydrates have been conjectured to form from thermogenic gases⁵⁾ on the basis of gas analysis;⁶⁾ a sII hydrate has been identified directly only once. Accordingly, though the existence of sI and sII hydrates in nature has already been verified, it is thought that an sH hydrate can only exist in a laboratory environment.⁷⁾ Recently, according to the compositional analysis of natural-gas hydrate samples recovered from Cascadia, there was evidence of hydrates that contained heavier hydrocarbons, including n-pentane and n-hexane. However, as the latter were not considered to be hydrate formers,^{1,8)} their presence in the natural hydrate⁹⁾ suggests that they may in fact contribute to hydrate formation in the presence of other sH-hydrate formers.

2. Experimental

Sample preparation: ice (5.0 g) was ground into a fine powder and placed in a high-pressure cell (internal volume: approximately 20.0 cm³) with either a pure 2,2-dimethylbutane (1.0 g) or a liquid mixture of 2,2-dimethylbutane and n-pentane or n-hexane (1 mL). To prevent the ice powders from melting, the liquid mixture was cooled in a freezer at 253.15 K before addition. After filling the cell with ice and the liquid mixture, the cell was kept in a water bath kept at a constant temperature of 271.15 K. Then, CH₄ gas was slowly introduced up to 30.0 bar so as not to form pure CH₄ hydrate from the reaction between the ice and CH₄ gas. When the pressure drop because of the hydrate formation was observed after 1 day, the temperature was increased to 274.15 K to promote the conversion of water into hydrate. To convert additional water into hydrate, this thermal cycling procedure was performed twice.

Structural identification of the prepared samples was carried out on a Rigaku powder X-ray diffractometer equipped with an Anton Paar low-temperature controller. This apparatus has a maximum capacity of 12 kW and can be operated down to 83 K. CoK α with a wavelength of 1.79021 Å was used as the radiation source and reflections were collected from 5.0 to 50.08 with a step size of 0.058 and a step time of 5 s. During the diffraction measurements, the experimental temperature was kept at about 85 K using liquid nitrogen. For compositional investigations, ¹³C NMR spectra were obtained at 200 K by packing the hydrate samples in a 7-mm diameter Zirconium rotor, which was loaded into the variable

temperature(VT) probe of a Bruker DSX400 solid-state NMR spectrometer. All spectra were recorded at a Larmor frequency of 100.6 MHz with magic angle spinning (MAS) at 2.0 kHz with cross-polarization (CP) or from single-pulse free induction decays with ¹H decoupling. The ¹³C NMR resonance peaks of adamantane, with assigned chemical shifts of $\delta = 38.56$ and 29.50 ppm at 298 K were used as the external chemical-shift reference.

3. Results and Discussions

2,2-Dimethylbutane is one of the well-known sH-hydrate formers, and its phase equilibria with CH₄ gas have been reported under various conditions.⁷⁾ When 2,2-dimethylbutane is allowed to react with CH₄ individually or as a mixture with n-pentane or n-hexane, gas hydrates are formed successfully in each case. To verify the structure of the synthetic samples, powder X-ray diffraction (XRD) measurements were performed (Figure 1).

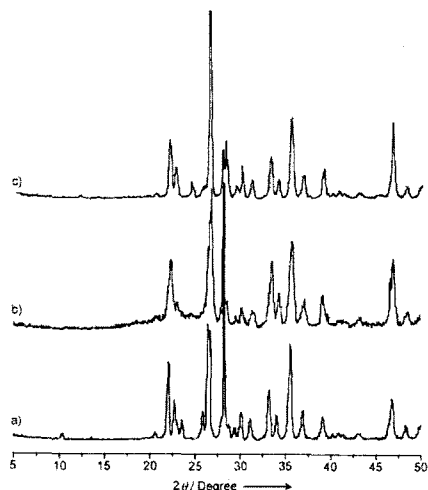


Fig. 1 Powder XRD patterns of a) 2,2-dimethylbutane + CH₄, b) 2,2-dimethylbutane + n-pentane + CH₄, and c) 2,2-dimethylbutane + n-hexane + CH₄ hydrates at 85 K.

The lattice parameters, obtained from a fit of the reflections indexed according to the sH-hydrate structure (P6/mmm), are $a = 12.2664$ and $c = 10.0667$ Å for the 2,2-dimethylbutane + CH₄ hydrate, $a = 12.1597$ and $c = 10.0731$ Å for the 2,2-dimethylbutane + n-pentane + CH₄ hydrate, and $a = 12.2667$ and $c = 10.0754$ Å for the 2,2-dimethylbutane + n-hexane + CH₄ hydrate. These

values correspond to unit-cell volumes of 1311.75, 1289.85, and 1312.96 cm³ for 2,2-dimethylbutane + CH₄, 2,2-dimethylbutane + n-pentane + CH₄, and 2,2-dimethylbutane + n-hexane + CH₄ hydrates, respectively. The unit-cell volumes of 2,2-dimethylbutane + CH₄ and 2,2-dimethylbutane + n-hexane + CH₄ hydrates are almost identical, whereas the value is slightly decreased by the addition of n-pentane to the system.

The composition of the hydrate samples and their structures can be identified using cross-polarization/magic angle-spinning (CP/MAS) ¹³C NMR spectroscopy. All of the spectra were consistent with the presence of an sH hydrate (Figure 2), with a CH₄ peak at δ = 4.50 ppm, which arises from CH₄ in the 5¹² and 4³5⁶3³ cavities of the hydrate phase. This observation agrees with the structural identification from powder XRD studies. In the down field region of the spectra, four sharp peaks (δ = 8.66 (C_δ), 29.31 (C_α), 30.28 (C_β), and 36.90 ppm (C_γ) for (C_αH₃)₃-C_β-C_γH₂-C_δH₃) are observed, which represent the four ¹³C NMR resonances in 2,2-dimethylbutane.

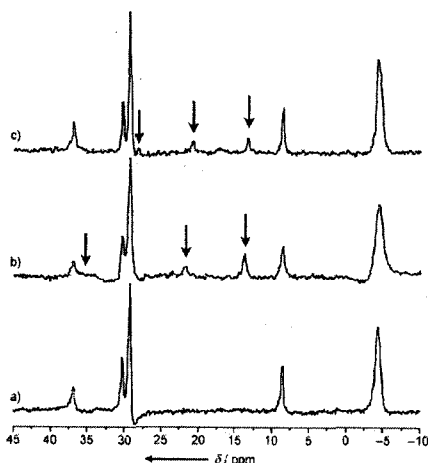


Fig. 2 CP/MAS ¹³C NMR spectra of a) 2,2-dimethylbutane + CH₄, b) 2,2-dimethylbutane + n-pentane + CH₄, and c) 2,2-dimethylbutane + n-hexane + CH₄ hydrates at 200 K. The arrows in (b) and (c) indicate the additional peaks assigned to n-pentane or n-hexane, respectively, in the hydrate cages.

However, when n-pentane and n-hexane are added to the system, three additional peaks appear. Because the melting points of n-pentane and n-hexane are 143 and 178 K, respectively, CP/MAS NMR spectroscopy will

not detect these hydrocarbons if they are not present in the solid hydrate, as the liquid phase is invisible with this technique. Hence, we can conclude that the additional peaks in the mixed hydrates can indeed be assigned to n-pentane and n-hexane in the hydrate cages. NMR spectra for pure n-pentane and n-hexane at 200 K are shown (Figure 3).

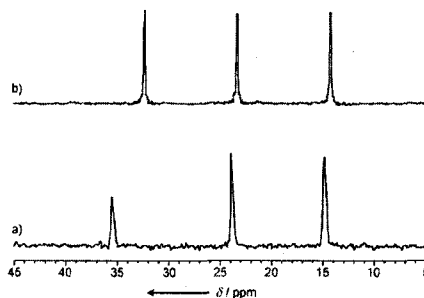


Fig. 3 HPDEC ¹³C NMR spectra of a) n-pentane and b) n-hexane at 200 K.

As mentioned earlier, these chemicals exist as liquids at this temperature, and the NMR spectra were obtained with a high-power decoupling (HPDEC) method. Three sharp peaks are observed for each hydrocarbon. The observed chemical shifts of n-pentane (δ = 14.89 (C_α), 23.95 (C_β), and 35.54 ppm (C_γ) for C_αH₃-C_βH₂-C_γH₂-C_βH₂-C_αH₃) are slightly different from those of n-hexane (δ = 14.11 (C_α), 23.22 (C_β), and 32.28 ppm (C_γ) for C_αH₃-C_βH₂-C_γH₂-C_γH₂-C_βH₂-C_αH₃). Figure 4 shows a comparison between the spectra of the 2,2-dimethylbutane + n-hexane + CH₄ hydrate obtained by the two NMR methods from solid samples.

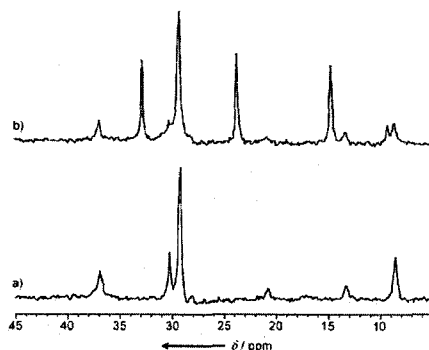


Fig. 4 ¹³C NMR spectra for 2,2-dimethylbutane + n-hexane + CH₄ hydrate at 200 K by a) CP/MAS and b) HPDEC methods at 200 K.

As expected, the HPDEC method shows other peaks in addition to the seven obtained by the CP method, as now both the peaks for the solid and liquid phases become apparent. The three extra peaks at $\delta = 14.70$, 23.66, and 32.81 ppm represent liquid n-hexane in the samples, as excess n-hexane was used for their preparation. The other extra peak at $\delta = 9.24$ ppm indicates liquid 2,2-dimethylbutane in the sample, which means not all of the hydrocarbon mixture was converted into the hydrate. We note that the use of these two methods in obtaining the spectra is essential in this case, as we need to distinguish the enclathrated form from the liquid guest.

Based on the peak areas of the CP/MAS NMR spectra obtained, the amount of n-pentane and n-hexane in the large ($5^{12}6^8$) cavity of the sH hydrate was calculated. n-Pentane represents about 15.7 mol% of the heavy hydrocarbons in the hydrate phase of the 2,2-dimethylbutane + n-pentane + CH_4 hydrate, whereas n-hexane represents about 8.3 mol% of the heavy hydrocarbons in the 2,2-dimethylbutane + n-hexane + CH_4 hydrate. Assuming that the total large-cage occupancies of the large cavity are almost the same for both samples, the calculated values agree with the fact that n-hexane has a longer carbon chain, that is, it is more difficult for a larger molecule to enter the sH hydrate.¹⁾ Hydrocarbons with five or more carbon-atom chains extended in an all-trans chain conformation are likely to be too large to fit in the large cages (8.62 Å) of an sH hydrate, although in other conformations, such as methylcyclohexane in which there is one gauche interaction, the five-carbon chain fits quite comfortably. This behavior is also reflected in the unit-cell volumes, for which the volume is somewhat smaller for the pentane-containing inclusion than for the other two compounds studied. In the case of n-hexane, it is likely that the encaged conformer will have more than one gauche interaction to fit into the cage. We note that at this stage it is not possible to say whether the compositions are determined by thermodynamics (overall stability) or kinetics (rate at which the right conformer presents itself for inclusion). Certainly, one can assume that even if the n-alkanes were able to form thermodynamically stable sH compounds without co-guests, nucleation might be a problem as the concentration of the correct conformers may well be too low.

4. Conclusion

It is clear that special attention must be paid to sH hydrates made from hydrocarbon mixtures as it is not necessarily obvious which guest molecules may be found in the hydrate lattice. This observation is also true for phase equilibrium studies—only a direct measurement will confirm which hydrocarbons are present as guests.

References

- [1] E. D. Sloan, *Clathrate Hydrates of Natural Gas*, 2nd ed., Marcel Dekker, New York, 1998.
- [2] K. A. Kvenvolden, 1988, "Methane hydrate - A major reservoir of carbon in the shallow geosphere", *Chem. Geol.* 71, pp 41-51 ; K. A. Kvenvolden, 1995, "A review of the geochemistry of methane in natural gas hydrate", *Org. Geochem.* 23, pp 997-1008 ; D. Grauls, 2001, "Gas hydrate: Importance and applications in petroleum exploration", *Mar. Pet. Geol.* 18, pp 519-523.
- [3] J. A. Ripmeester, J. S. Tse, C. I. Ratcliffe, B. M. Powell, 1987, "A new clathrate hydrate structure", *Nature* 325, pp 135-136 ; K. A. Udachin, C. I. Ratcliffe, G. D. Enright, J. A. Ripmeester, 1997, "Structure H hydrate: A single crystal diffraction study of 2,2-dimethylpentane.5(Xe,H₂S).34H₂O", *Supramol. Chem.* 8, pp 173-176.
- [4] J. A. Ripmeester, C. I. Ratcliffe, 1990, "Xenon-129 NMR studies of clathrate hydrates: New guests for structure II and structure H", *J. Phys. Chem.* 94, pp 8773-8776.
- [5] J. M. Brooks, M. C. Kennicutt, R. R. Fay, T. J. McDonald, R. Sassen, 1984, "Organic gas hydrates in the Gulf of Mexico", *Science* 225, pp 409-411.
- [6] R. Sassen, I. R. MacDonald, 1994, "Evidence of structure H gas hydrate, Gulf of Mexico continental slope", *Org. Geochem.* 2, pp 1029-1032 ; D. W. Davidson, S. K. Garg, S. R. Gough, Y. P. Handa, C. I. Ratcliffe, J. A. Ripmeester, J. S. Tse, W. F. Lawson, 1986, "Laboratory analysis of a naturally occurring gas hydrate from sediment of the Gulf of Mexico", *Geochim. Cosmochim. Acta* 50, pp 619-623.
- [7] A. P. Mehta, E. D. Sloan, 1993, "Structure H hydrate phase equilibria of methane + liquid hydrocarbon mixtures", *J. Chem. Eng. Data* 38, pp 580-582.
- [8] A. P. Mehta, Ph.D. thesis, "A thermodynamic investigation of structure H clathrate hydrate", Colorado School of Mines (USA), 1996.
- [9] A. P. Mehta, J. A. Ripmeester, "Structural characterization of hydrate formation in Black Oil and condensate systems", *Proc. 4th Int. Conf. Gas Hydrates*, Yokohama, Japan, 2002, pp 580-585.