

## **NEW FINDINGS ON GUEST ENCLATHRATION IN STRUCTURE-H HYDRATES BY MEANS OF THERMODYNAMIC AND SPECTROSCOPIC ANALYSIS**

**Jong-won Lee**

**Department of Environmental Engineering  
Kongju National University  
275 Budae-dong, Cheonan-si, Chungnam, 330-717  
REPUBLIC OF KOREA**

**Hailong Lu, Igor Moudrakovski, Christopher Ratcliffe, John Ripmeester\***

**The Steacie Institute for Molecular Sciences  
National Research Council of Canada  
100 Sussex Drive, Rm 111  
Ottawa, Ontario, K1A 0R6  
CANADA**

### **ABSTRACT**

Among the three common gas hydrate structures, structure-H (sH) hydrate has been regarded as forming only in the laboratory since it was first reported in 1987. However, natural gas hydrate samples obtained from the Cascadia margin showed that sH hydrate can form naturally. Not only was the sH hydrate found in natural samples, but it was also discovered that n-alkanes such as n-pentane and n-hexane, considered to have too large molecular size to be sH hydrate formers, can act as co-guests of sH hydrates in mixtures with other sH hydrate formers. In this study, thermodynamic measurements and spectroscopic analysis of powder X-ray diffraction and  $^{13}\text{C}$  solid-state NMR methods, were performed for synthetic hydrate samples in order to identify the accommodation of n-alkanes with five or more carbon atoms. In addition, some new hydrate guests were found to form sH hydrates. From the present results, it is clear that, so far, our understanding of gas hydrates and guest enclathration needs to be revised and expanded in order to explain new findings.

*Keywords:* gas hydrates, spectroscopy analysis, structure-H hydrates, water-soluble formers

### **INTRODUCTION**

Gas hydrates, one class of inclusion compounds, are ice-like crystal compounds formed when small molecules are captured in the cavities of ordered three-dimensional hydrate frameworks [1]. The gas hydrates are known to have three distinct structures, that is, structure I (sI), structure II (sII) and structure H (sH). Depending on the hydrate structures formed, the types of cavities present and the distribution of those cavities in the unit cell

vary. While both sI and sII hydrates have one type of cavity ( $5^{12}$ ) in common, size and shape of large cavity ( $5^{12}6^2$  or  $5^{12}6^4$ ) distinguish one from the other. In case of the sH hydrate, there exist medium ( $4^35^66^3$ ) and large ( $5^{12}6^8$ ) cavities in addition to the common small ( $5^{12}$ ) one [2]. Because larger guest molecules to be captured in large cavities are too large to fill small or medium one, the second guest, called 'help gas', is required for filling small and medium cavities so as to

---

\* Corresponding author: Phone: +1 613 993 2011 Fax +1 613 998 7833 E-mail: john.ripmeester@nrc.ca

stabilize the whole structure. The sH hydrate can accommodate heavier hydrocarbons in the size range of 7.5-8.6 Å [3]. 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 gas hydrates formed from gas of biogenic origin are the sI form, whereas sII and sH hydrates have been conjectured to form from thermogenic gases [5] on the basis of gas analysis [6]. Accordingly, though the existence of sI and sII in nature has already been verified [7], it is thought that an sH hydrate can only exist in a laboratory environment until [8] Lu *et al.* presented thermodynamic and spectroscopic evidence for naturally occurring sH hydrate according to the compositional analysis of natural-gas hydrate samples recovered from the Cascadia margin [9]. In this sample, many heavier hydrocarbons including n-pentane and n-hexane are found to be contained, but the latter were not thought to be hydrate formers due to their large molecular sizes.

While investigating the application of the sH hydrate to energy storage for the first time, Khokhar *et al.* suggested the maximum limit of methane according to the hydrate structure formed [10]. In this report, sH hydrate was proposed to be an advantageous hydrate structure because it showed the largest storage capacity and low formation pressure, in case of mixed hydrates where methane molecules only occupied small or small/medium cavities. Since sH hydrate was found, many researchers have published phase equilibrium data with a variety of sH formers. Recently, Ohmura *et al.* [11] presented phase equilibrium and X-ray diffraction data for sH hydrate samples using methyl-substituted cyclic ethers and cyclic ketones, which have good solubilities in water compared with existing formers. Although many research works on the gas hydrate have been collected so far, there still exist some experimental results to be explained from a fundamental point of view.

In this report, one of the well-known sH-hydrate formers, 2,2-dimethylbutane is allowed to react

with CH<sub>4</sub> individually or as a mixture with n-pentane or n-hexane so as to check if heavier n-alkanes with C5 or C6 can be incorporated into the large cages of the sH hydrate. In addition, some cyclic ester and cyclic ketone substances were used to find new water-soluble hydrate formers. Synthesized samples were analyzed by means of thermodynamic and spectroscopic methods in order to identify the accommodation or molecular behaviors of new formers as well as large n-alkanes.

## EXPERIMENTAL

Methane gas of UHP Grade, supplied by Praxair, and distilled water were used for preparing all the hydrate samples in this study. 2,2-dimethylbutane, n-pentane, n-hexane, 2-methyl-tetrahydrofuran, cyclohexanone,  $\gamma$ -butyrolactone and  $\beta$ -butyrolactone were supplied by Sigma-Aldrich Co. and their nominal purities were 99+ mol%. All the materials were used without further treatment.

Hydrate-phase equilibria were measured by tracing the P-T trajectories from hydrate formation to dissociation. First 20.0 g of water and 4.0 g of hydrocarbons were added to the high-pressure cell. After assembling and pressurizing the cell up to the desired pressure with CH<sub>4</sub> gas, the cell was cooled to 273.15 K in a water bath. If the pressure drop due to hydrate formation reached a steady state, the bath temperature was slowly increased at a rate of about 0.2 K/h until complete dissociation. During the equilibrium measurements, temperature and pressure in the high-pressure cell were collected by means of a data acquisition system at intervals of 10 seconds. For preparing synthetic samples, ice ground into fine powders and cold hydrocarbons were loaded into the high-pressure cell. Then, 30.0 bar of CH<sub>4</sub> gas was introduced to the cell in order to prevent pure CH<sub>4</sub> hydrate (sI) from forming due to the reaction between ice and CH<sub>4</sub> gas. After observing the pressure drop due to hydrate formation, thermal cycling across 273.15 K was carried out twice to promote the conversion into hydrate. Finally, the cell was quenched in liquid nitrogen before opening the cell and taking hydrate samples for further microscopic analysis. Structural identification of the prepared samples was carried out on a Rigaku powder X-ray diffractometer equipped with an Anton Paar low-temperature controller that can be operated down to 83 K. CoK $\alpha$  radiation with a wavelength of 1.79021 Å was used and reflections were collected from 5.0 to 50.0° with a step size of 0.05 ° and a

step time of 5 seconds. During the diffraction measurements, the experimental temperature was kept at 85 K using liquid nitrogen.  $^{13}\text{C}$  NMR spectra were also obtained at 200 K for compositional investigations of the hydrate samples, by packing the 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  $^1\text{H}$  decoupling. The  $^{13}\text{C}$  NMR resonance peaks of adamantane, with assigned chemical shifts of  $\delta=38.56$  and 29.50 ppm at 298.15 K were used as the external chemical-shift reference.

## RESULTS AND DISCUSSION

### n-Pentane and n-Hexane as Co-guests

One of the well-known sH-hydrate formers, 2,2-dimethylbutane was selected to check if n-pentane or n-hexane could form sH hydrate in a mixture with other hydrate formers. When 2,2-dimethylbutane is allowed to react with  $\text{CH}_4$  individually and as a mixture with n-pentane and n-hexane, gas hydrates were formed successfully in both cases. Powder X-ray diffraction (PXRD) measurements were performed in order to verify the structure formed of the synthetic samples. All of the hydrate samples were found to have the sH-hydrate structure from a fit of the reflection patterns. The lattice parameters obtained were  $a=12.2664 \text{ \AA}$ ,  $c=10.0667 \text{ \AA}$  for 2,2-dimethylbutane +  $\text{CH}_4$  hydrate,  $a=12.1597 \text{ \AA}$ ,  $c=10.0731 \text{ \AA}$  for 2,2-dimethylbutane + n-pentane +  $\text{CH}_4$  hydrate, and  $a=12.2667 \text{ \AA}$ ,  $c=10.0754 \text{ \AA}$  for 2,2-dimethylbutane + n-hexane +  $\text{CH}_4$  hydrate. These values correspond to unit cell volumes of  $1311.75 \text{ \AA}^3$ ,  $1289.85 \text{ \AA}^3$ , and  $1312.96 \text{ \AA}^3$  for 2,2-dimethylbutane +  $\text{CH}_4$ , 2,2-dimethylbutane + n-pentane +  $\text{CH}_4$ , and 2,2-dimethylbutane + n-hexane +  $\text{CH}_4$  hydrates, respectively. The unit cell volumes of 2,2-dimethylbutane +  $\text{CH}_4$  and 2,2-dimethylbutane + n-hexane +  $\text{CH}_4$  hydrates are almost identical, while the value is slightly decreased by adding n-pentane to the system.

The composition of the hydrate samples and their structures can be identified using CP/MAS  $^{13}\text{C}$  NMR spectroscopy. As can be seen in Figure 1, all the spectra are consistent with the presence of sH hydrate, having a  $\text{CH}_4$  peak at  $-4.50 \text{ ppm}$ , which arises from  $\text{CH}_4$  in the  $5^{12}$  and  $4^35^66^3$  cavities of

the hydrate phase. In the downfield region of the spectra, four sharp peaks (at 8.66 ( $\text{C}_\delta$ ), 29.31 ( $\text{C}_\alpha$ ), 30.28 ( $\text{C}_\beta$ ), and 36.90 ( $\text{C}_\gamma$ ) ppm for  $(\text{C}_\alpha\text{H}_3)_3\text{-C}_\beta\text{-C}_\gamma\text{H}_2\text{-C}_\delta\text{H}_3$ ) are observed, which represent the four  $^{13}\text{C}$  resonances in 2,2-dimethylbutane. However, when n-pentane and n-hexane are added to the system, three additional peaks appear. CP/MAS NMR will not detect pure n-pentane and n-hexane as they have melting points of 143 and 178 K, respectively, as the liquid phase is invisible in CP/MAS NMR spectroscopy. Accordingly, 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.

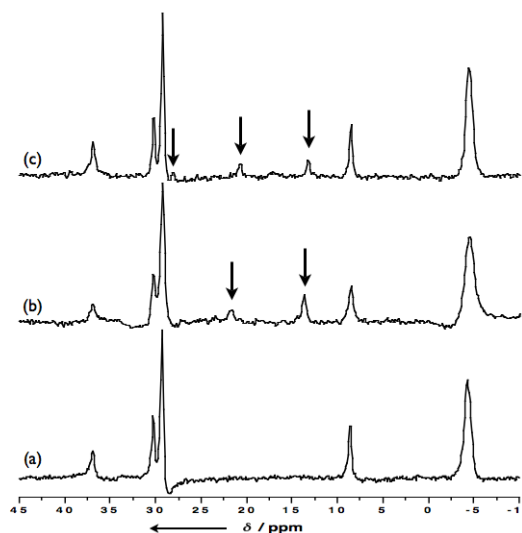


Figure 1 CP/MAS  $^{13}\text{C}$  NMR spectra of (a) 2,2-dimethylbutane +  $\text{CH}_4$ , (b) 2,2-dimethylbutane + n-pentane +  $\text{CH}_4$ , and (c) 2,2-dimethylbutane + n-hexane +  $\text{CH}_4$  hydrates at 200 K. The arrows in (b) and (c) indicate the additional peaks assigned to n-pentane and n-hexane, respectively, in the hydrate

Figure 2 shows a comparison of spectra for 2,2-dimethylbutane + n-hexane +  $\text{CH}_4$  hydrate obtained for the solid samples with two NMR measurement methods. As can be seen in this figure, the HPDEC method shows peaks in addition to the seven peaks obtained by the CP method, as now both solid hydrate and liquid phases become apparent. The three extra peaks at 14.70, 23.66, and 32.81 ppm represent three resonance peaks for liquid n-hexane, as excess n-hexane was used for their preparation. The other extra peak at 9.24 ppm indicates liquid 2,2-dimethylbutane in the sample, which means not all

of the hydrocarbon mixture was converted into hydrate.

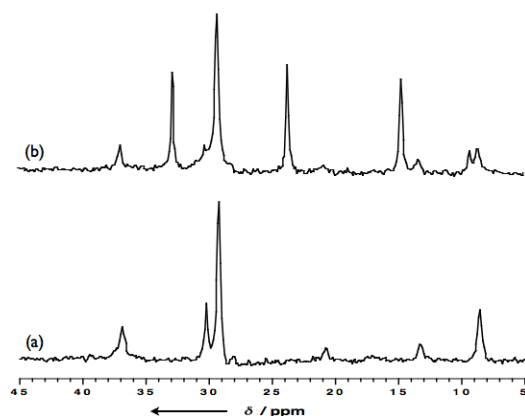


Figure 2  $^{13}\text{C}$  NMR spectra for 2,2-dimethylbutane + n-hexane +  $\text{CH}_4$  hydrate at 200 K by (a) CP/MAS and (b) HPDEC methods

Based on the peak areas of the NMR (HPDEC) spectra obtained, the amount of n-pentane and n-hexane in the large ( $5^{12}6^8$ ) cavity of sH hydrate was calculated. For 2,2-dimethylbutane + n-pentane +  $\text{CH}_4$  hydrate, n-pentane represents about 15.7 mol% of the heavy hydrocarbons in the hydrate phase, while n-hexane occupies about 8.3 mol% of the heavy hydrocarbons. Assuming that the total large cage occupancies of the large cavity are almost the same for both samples, the calculated amount values agree with the fact that n-hexane has a longer carbon chain, that is, it is more difficult to enter sH hydrate for the larger molecule. Hydrocarbons having five or more carbon atoms chains extended in an all-trans chain conformation are likely to be too large to fit in the large cages ( $8.62 \text{ \AA}$ ) of sH hydrate, although in other conformations, such as in methylcyclohexane where there is a five-carbon chain with one gauche interaction, fits quite comfortably. In the case of n-hexane, it is likely that the encaged conformer will have more than one gauche interactions in order to fit 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.

### New Water-soluble Hydrate Formers

Some hydrocarbons in the cyclic ester and cyclic ketone groups were tried as new water-soluble hydrate formers. As a result, 2-methyl-tetrahydrofuran,  $\gamma$ -butyrolactone,  $\beta$ -butyrolactone and cyclohexanone were found to form hydrates with  $\text{CH}_4$  gas. Hydrate phase equilibria of the 2-methyl-tetrahydrofuran (sH),  $\gamma$ -butyrolactone (sH) and cyclohexanone (sII) with  $\text{CH}_4$  systems are presented in Figure 3, in addition to pure  $\text{CH}_4$  hydrate measurement from the literature.

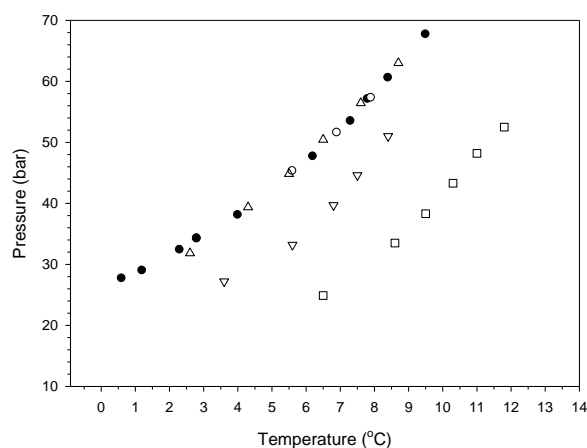


Figure 3 Hydrate-phase equilibrium data for 2-methyl-tetrahydrofuran ( $\Delta$ ),  $\gamma$ -butyrolactone ( $\nabla$ ), and cyclohexanone ( $\square$ ) hydrates with  $\text{CH}_4$ . Equilibrium points in the literature ( $\bullet$ ) and obtained experimentally ( $\circ$ ) are also included

While the phase equilibrium line of 2-methyl-tetrahydrofuran almost overlaps with that of pure methane hydrate, adding  $\gamma$ -butyrolactone or cyclohexanone shifts the equilibrium line to the promoted region. Although the equilibrium curve of the 2-methyl-tetrahydrofuran +  $\text{CH}_4$  system seems to overlap with that of pure methane hydrate, there exists small difference distinguishing those lines. That is, those equilibrium lines would have a different slope when plotted on the pressure axis on a log scale, and would intersect each other at around 278 K [10]. The largest shift of the hydrate equilibrium curve is achieved by addition of cyclohexanone, which is found to form a sII hydrate.  $\beta$ -

butyrolactone of the cyclic ester group is also found to be a new hydrate former (Figure 4). As shown in this figure,  $\beta$ -butyrolactone is found to form the sII hydrate on the basis of two characteristic peaks for the  $\text{CH}_4$  carbon atom at  $-4.20$  and  $-8.01$  ppm, while  $\gamma$ -butyrolactone form the sH hydrate with  $\text{CH}_4$  gas. In addition,  $\text{CH}_4$  carbon peak at  $-6.44$  ppm indicates that not all the ice particles are converted into hydrate phase and that some ice contents form sI  $\text{CH}_4$  hydrate due to its reaction with  $\text{CH}_4$  gas.

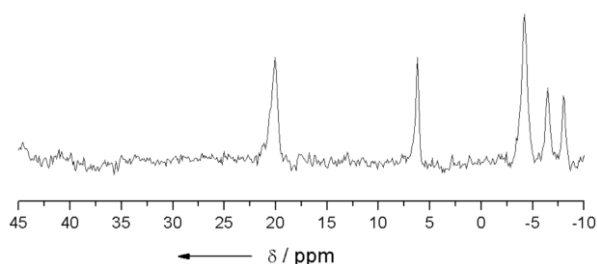


Figure 4 CP/MAS  $^{13}\text{C}$  NMR spectrum of  $\beta$ -butyrolactone +  $\text{CH}_4$  hydrate

From these results, the critical guest size determining the hydrate structure formed as sII or sH is thought to lie between the molecular sizes of this pair of chemicals. Similarly, the same conclusion can be drawn from the 2-methyl-tetrahydrofuran +  $\text{CH}_4$  and tetrahydrofuran +  $\text{CH}_4$  systems. While the tetrahydrofuran +  $\text{CH}_4$  system is known to form the sII hydrate, 2-methyl-tetrahydrofuran has one additional methyl group and becomes too large to fit the large cavity of the sII hydrate. Accordingly, the critical guest size can be estimated by comparing two pairs of hydrate formers as described above. In addition, the new hydrate formers show high solubilities (reasonably miscible with water) in liquid water so that hydrate formation can be faster than that of water-insoluble guests. Such a high solubility is thought to play an advantageous role when these formers are applied to practical hydrate-based processes.

## CONCLUSIONS

In this research, new findings on guest enclathration in sH hydrate are explored by means of thermodynamic and spectroscopic analysis. n-pentane and n-hexane, regarded as non-hydrate formers due to their inefficient cage filling properties are found to be able to act as co-guests in sH hydrate when they are used in a mixture with

other sH-hydrate formers. In addition, for some new hydrate formers having high solubility in water, thermodynamic phase equilibria and  $^{13}\text{C}$  NMR spectra are measured. High solubility of these formers can play an important role when they are applied to hydrate-based processes. The present results indicate that our understanding of gas hydrate and guest enclathration needs to be revised and expanded in order to explain new finding clearly and to utilize the gas hydrate efficiently in practical applications.

## REFERENCES

- [1] Sloan ED. *Clathrate hydrates of natural gas* 2<sup>nd</sup> edition. New York: Marcel Dekker, 1998.
- [2] Ripmeester JA, Tse JS, Ratcliffe CI, Powell BM. A new clathrate hydrate structure. *Nature* 1987;325:135-136.
- [3] Mehta AP, Sloan ED. Structure H hydrate phase equilibria of paraffins, naphthenes, and olefins with methane. *J. Chem. Eng. Data* 1984;39:887-890.
- [4] Ripmeester JA, Ratcliffe CI. Xenon-129 NMR studies of clathrate hydrates: new guests for structure II and structure H. *J. Phys. Chem.* 1990;94(25):8773-8776.
- [5] Brooks JM, Kennicutt MC, Fay RR, McDonald TJ, Sassen R. Thermogenic gas hydrates in the Gulf of Mexico. *Science* 1984;225(4660):409-411.
- [6] Sassen R, MacDonald IR. Evidence of structure H hydrate, Gulf of Mexico continental slope. *Org. Geochem.* 1994;23:1029-1032.
- [7] Davidson DW, Garg SK, Gough SR, Handa YP, Ratcliffe CI, Ripmeester JA, Tse JS, Lawson WF. Laboratory analysis of a naturally occurring gas hydrate from sediment of the Gulf of Mexico. *Geochim. Cosmochim. Acta* 1986;50:619-623.
- [8] Mehta AP, Sloan ED. Structure H hydrate phase equilibria of methane + liquid hydrocarbon mixtures. *J. Chem. Eng. Data* 1993; 38(4):580-582.
- [9] Lu H, Seo YT, Lee JW, Moudrakovski IL, Ripmeester JA, Chapman NR, Coffin RB, Gardner G, Pohlman J. Complex gas hydrate from the Cascadia margin. *Nature* 2007;445:303-306.
- [10] Khokhar AA, Gudmundsson JS, Sloan ED. Gas storage in structure H hydrates. *Fluid Phase Equil.* 1998;150-151:383-392.
- [11] Ohmura R, Matsuda S, Takeya S, Ebinuma T, Narita H. Phase equilibrium for structure-H hydrates formed with methane and methyl-substituted cyclic ether. *Int. J. Thermophys.* 2005;26(5):1515-1523.