J. Chem. Thermodynamics 44 (2012) 20–25

Contents lists available at SciVerse ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

Phase equilibrium measurements and the tuning behavior of new sII clathrate hydrates ☆

Woongchul Shin [a], Seongmin Park [a], Hyeyoon Ro [a], Dong-Yeun Koh [a], Jiwoong Seol [a], Huen Lee [a,b,]*

[a] Department of Chemical and Biomolecular Engineering (BK21 Program), KAIST, Daejeon 305-701, Republic of Korea
[b] Graduate School of EEWS, KAIST, Daejeon 305-701, Republic of Korea

ARTICLE INFO

Article history:
Available online 24 August 2011

Keywords:
Gas hydrate
sII hydrate
Pyrrolidine
Piperidine
Tuning clathrate hydrate

ABSTRACT

We suggest two types of new amine-type sII formers: pyrrolidine and piperidine. These guest compounds fail to form clathrate hydrate structures with host water, but instead have to combine with light gaseous guest molecules (methane) for enclathration. First, two binary clathrate hydrates of (pyrrolidine + methane) and (piperidine + methane) were synthesized at various amine concentrations. ^{13}C NMR and Raman analysis were done to identify the clathrate hydrate structure and guest distribution over sII-S and sII-L cages. XRD was also used to find the exact structure and corresponding cell parameters. At a dilute pyrrolidine concentration of less than 5.56 mol%, the tuning phenomenon is observed such that methane molecules surprisingly occupy sII-L cages. At the critical guest concentration of about 0.1 mol%, the cage occupancy ratio reaches the maximum of approximately 0.5. At very dilute guest concentration below 0.1 mol%, the methane molecules fail to occupy large cages on account of their rarefied distribution in the network. Direct-release experiments were performed to determine the actual guest compositions in the clathrate hydrate phases. Finally, we measured the clathrate hydrate phase equilibria of (pyrrolidine + methane) and (piperidine + methane).

1. Introduction

Clathrate hydrates are known to form three distinct structures of sI, sII, and sH via both artificial synthesis and natural occurrence [1,2]. The sI clathrate hydrates have received the greatest amount of attention due to active involvement of methane and carbon dioxide in their crystalline matrix, while the sH clathrate hydrates offer strong gas storage and transportation advantages due to their mild formation conditions [1,2]. While sI can be formed by a single guest such as CH_4 or C_2H_6, sH can be formed only with the coexistence of large organic guest molecules such as methylcyclohexane and a help gas such as CH_4 [3] and Xe [4]. On the other hand, the sII structure can be formed under the following guest selections of (1) relatively large hydrocarbons such as propane or *iso*-butane [1,2], (2) binary gaseous mixture such as CH_4 and C_2H_6 [5,6], (3) pure guest molecules such as pure O_2 [7], N_2 [8], or H_2 [9], (4) metastable C_2H_6 hydrate [10] using a coordinate compound, and (5) organic sII formers coexisting with small gaseous sI guest molecules [11–14]. For category (5), sII formers occupy the sII-L ($5^{12}6^4$) cage, while gas molecules only occupy the sII-S (5^{12}) cage. The sII structure comprises one CH_4 molecule per 8.5 H_2O molecules with a hydration number of 8.5 when the full CH_4 occupancy is achieved in sII-S cages [1,2]. Accordingly, the maximum CH_4 storage capacity of sII reaches approximately 70% to 80% of the capacities of sI ($n = 5.75$) and sH ($n = 6.8$). However, we must further recognize that nearly 40% of sII-S is filled with CH_4 when the remaining percentage empty, even when the powerful sII former of THF is used [15]. The degree of cage occupancy is, of course, significantly influenced by the molecular details of the organic sII formers used. Nevertheless, sII clathrate hydrates are likely to possess thermodynamic and kinetic advantages over sI and sH, but this will not always be the case. The pure sI CH_4 hydrate requires 13 MPa at $T = 288$ K to stabilize it, while the sII *tert*-butylalcohol and THF clathrate hydrates form at much lower pressures of 5.5 MPa [16] and 1 MPa [17], respectively. Moreover, most organic sII formers are highly soluble in water, but we note that the reported sH formers have limited water solubility, making it difficult for large guest molecules to be homogenously dispersed. Another interesting and unique feature is the appearance of the tuning phenomena, which only occurs in the sII structure. We found that large guest molecules exclusively occupy sII-L, while the real inclusion of small guest molecules in sII-L cannot occur. Nonetheless, at very dilute LGM concentrations, cage occupancy of CH_4 in both sII-S and sII-L can take place [16,18,19]. The tuning phenomena of the sII hydrogen hydrate was also confirmed by Lee *et al.* [20]. In the present study, we suggest the two new sII formers of pyrrolidine and piperidine, secondary amine compounds, and identify their tuning

---

☆ Paper for gas hydrate initiative

* Corresponding author at: Department of Chemical and Biomolecular Engineering (BK21 Program), KAIST, Daejeon 305-701, Republic of Korea.

E-mail address: h_lee@kaist.ac.kr (H. Lee).

0021-9614/$ - see front matter Crown Copyright © 2011 Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.jct.2011.08.018

patterns using the relevant NMR and XRD spectra. In addition, we measure the (liquid + hydrate + CH_4) phase equilibria of these two hydrate systems.

2. Experimental section

2.1. Materials

The CH_4 of 0.9995 mol fraction purity was purchased from Special Gas, Inc. High purity distilled water was obtained from a Millipore purification unit. Pyrrolidine (>0.99 mole fraction purity) was purchased from Aldrich, Inc. and piperidine (>0.99 mole fraction purity) was supplied by Daejung Chemicals & Metals Co., Korea.

2.2. Sample preparation

A liquid solution of (water + LGM), (LGM = large guest molecule) was frozen at atmospheric pressure and $T = 250$ K and was then ground with a 200 μm sieve in liquid nitrogen. Subsequently, the powdered sample was pressurized with 10 MPa of methane gas and matured at least for 5 days at $T = 273$ K.

2.3. Experimental measurements

A Varian (UnityNOVA600) 600-MHz solid-state NMR spectrometer was used. The powdered (~200 μm) samples were placed in a 2 mm o.d. zirconia rotor loaded into a variable temperature probe. All ^{13}C NMR spectra were recorded at a Larmor frequency of 100.6 MHz with MAS at ≈10 kHz, and the measurement temperature was fixed at 183 K. A pulse length of 2 μs and a pulse repetition delay of 10 s under proton decoupling were used with radiofrequency 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 $17.3 \cdot 10^{-6}$ at $T = 298$ 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 was used in which a CCD detector was equipped. It was cooled by liquid nitrogen. The samples were kept at $T = 93$ K during the measurements. The excitation source was an Ar-ion laser emitting a 514.53 nm line. The laser intensity was typically 30 mW. The PXRD patterns were recorded at $T = 123.15$ K on a Rigaku Geigerflex diffractometer (D/Max-RB) using graphite-monochromatized Cu Kα radiation ($\lambda = 0.15406$ nm) in the $\theta/2\theta$ scan mode. The XRD experiments were carried out in step mode with a fixed time of 3 s and a step size of 0.03° for $2\theta = 10°$ to 50°. The patterns obtained were calculated by the Checkcell program [21]. The equilibrium pressures and temperatures were determined by checking the routine PT trajectory consisting of hydrate formation and dissociation stages. The cooling rate was 0.5 K/h and the heating rate was 0.1 K/h. A 4-wire type PT-100Ω (±0.05% accuracy of full scale) and a PMP4070 device from Druck Inc. were used as temperature and pressure sensing devices. The direct-release experiments were conducted at $T = 296$ K and were repeated five times for reliability.

3. Results and discussion

Pyrrolidine and piperidine are secondary amine compounds. As shown in figure 1(a), pyrrolidine (C_4H_9N) has a pentagonal ring with four-carbon atoms and a nitrogen atom, while piperidine ($C_5H_{11}N$) has a hexagonal ring containing five-methylene units and a nitrogen atom. First, the two binary clathrate hydrates of (pyrrolidine + methane) and (piperidine + methane) were synthesized with sII stoichiometric amine concentration of 5.56 mol%. Their ^{13}C NMR spectra are shown in figure 1(b) together with those of sII (THF + methane) for more reliable identification. THF is the most common sII hydrate former. Three samples show a peak at $-4.5 \cdot 10^{-6}$ representing CH_4 molecules captured in sII-S. However, a significant peak of the CH_4 molecules in sII-L was not detected, which confirms that larger secondary guest molecules of tetrahydrofuran, pyrrolidine, and piperidine predominantly occupy most of the sII-L and firmly stabilize the polyhedral cage frameworks. The Raman spectra of the (pyrrolidine + methane) and (piperidine + methane) clathrate hydrates with amine concentration of 5.56 mol% are shown in figure 1(c), where a peak at 2915 cm^{-1} denotes the CH_4 in sII-S. There is no peak at 2905 cm^{-1}, which

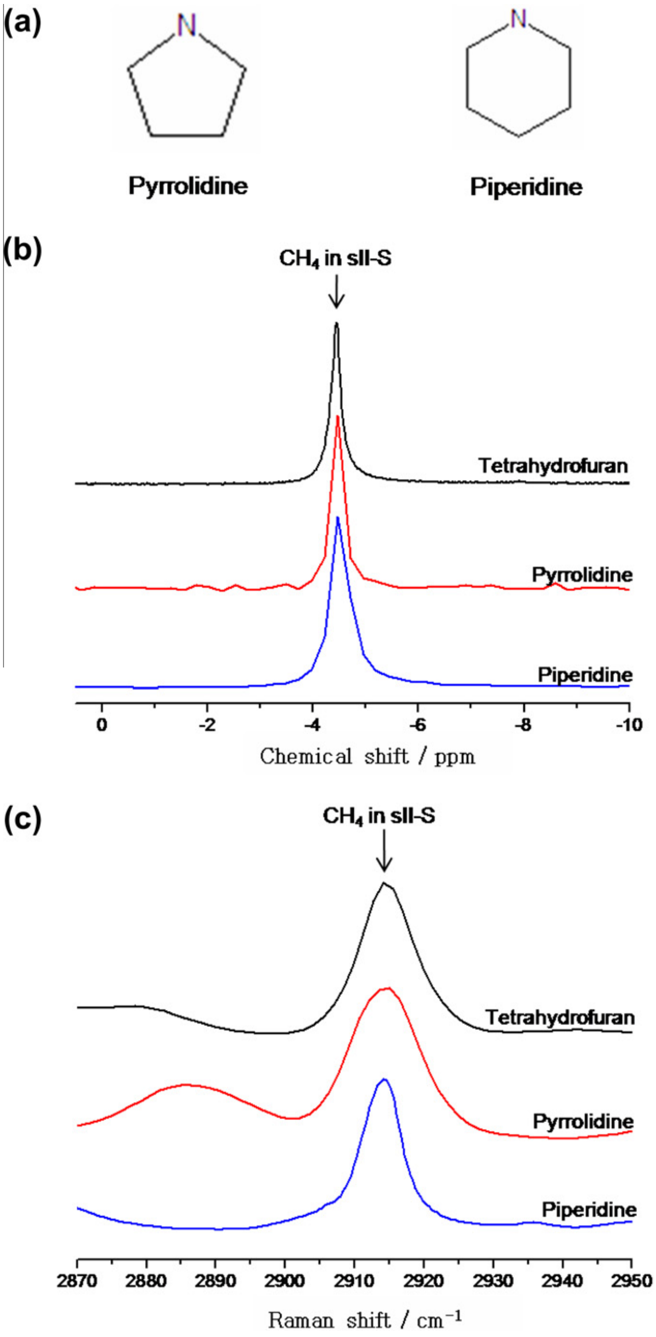

FIGURE 1. (a) Chemical structure of the new sII former, (b) ^{13}C NMR spectra of the (sII former + CH_4) binary clathrate hydrate, and (c) Raman spectra of the (sII former + CH_4) binary clathrate hydrate.