Fuel 164 (2016) 237–244

Contents lists available at ScienceDirect

Fuel

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

Enclathration of *tert*-butyl alcohol in sII hydrates and its implications in gas storage and CO_2 sequestration

Eunae Kim [a], Seungmin Lee [b], Ju Dong Lee [b], Yongwon Seo [a,*]

[a] *School of Urban and Environmental Engineering, Ulsan National Institute of Science and Technology (UNIST), Ulsan 689-798, Republic of Korea*
[b] *Offshore Plant Resources R&D Center, Korea Institute of Industrial Technology, Busan 618-230, Republic of Korea*

HIGHLIGHTS

- We examine the effects of *tert*-butyl alcohol (tBA) on CH_4, CO_2, and N_2 hydrates.
- tBA forms sII hydrates with CH_4, CO_2, and N_2 by enclathrating tBA in sII large cages.
- tBA functions as a thermodynamic hydrate promoter for both CH_4 and N_2 hydrates.
- tBA acts as a thermodynamic hydrate inhibitor for CO_2 hydrates.
- tBA can be used for CH_4 storage and CO_2 sequestration.

ARTICLE INFO

Article history:
Received 30 April 2015
Received in revised form 14 July 2015
Accepted 5 October 2015
Available online 22 October 2015

Keywords:
tert-Butyl alcohol
Gas storage
CO_2 sequestration
Gas hydrate

ABSTRACT

The inclusion of *tert*-butyl alcohol (tBA) as a co-guest of clathrate hydrates in the presence of CH_4, CO_2, and N_2 was investigated for its potential role in gas storage and CO_2 sequestration. The ^{13}C NMR, Raman spectroscopy, and powder X-ray diffraction revealed that the guest gas (CH_4, CO_2, and N_2) + tBA + water systems form sII hydrates. The enclathration of tBA molecules in the sII large ($5^{12}6^4$) cages resulted in significant thermodynamic stabilization of the CH_4 + tBA and N_2 + tBA hydrates. However, the hydrate phase equilibrium curves of the CO_2 + tBA hydrates were shifted to inhibited regions despite the participation of tBA molecules as a co-guest in the sII hydrate lattices. tBA was found to function as a thermodynamic promoter for both CH_4 and N_2 hydrates, whereas it functioned as a thermodynamic inhibitor for CO_2 hydrate. The overall experimental results provide a better understanding of the thermodynamic behaviors, structural transitions, and guest distributions of the guest gas (CH_4, CO_2, and N_2) + tBA hydrates for the potential use of tBA in gas storage and CO_2 sequestration.

1. Introduction

Clathrate hydrates are non-stoichiometric crystalline compounds which capture guest molecules of appropriate sizes and shapes in the cages constructed by hydrogen-bonded water molecules [1]. There are three representative structure types of clathrate hydrates: sI, sII, and sH, which consist of cages that are of different sizes and shapes. For each unit cell, sI hydrates consist of two small (5^{12}) and six large ($5^{12}6^2$) cages, sII hydrates consist of sixteen small (5^{12}) and eight large ($5^{12}6^4$) cages, and sH hydrates consist of three small (5^{12}), two medium ($4^35^66^3$), and one large ($5^{12}6^8$) cages [1]. In general, small sized gas molecules such as CH_4 and CO_2 form sI hydrates, and larger guests such as C_3H_8 and tetrahydrofuran (THF) or much smaller guests such as N_2 and O_2 form sII hydrates. Large liquid hydrocarbon molecules such as methylcyclopentane and neohexane form sH hydrates in the presence of small help gases such as CH_4 and H_2S [1].

Clathrate hydrates have various technological applications, such as natural gas storage/transportation, CO_2 sequestration, and desalination [2–19]. However, clathrate hydrates can lead to major problems in the gas and petroleum industries by blocking pipelines, which induces many safety concerns and tremendous financial losses [20–23]. Pipe plugging can also occur in the process of the transportation of CO_2 to the sequestration sites because CO_2 can form gas hydrates at relatively mild pressure conditions. To prevent these problems, extensive efforts have been made to develop hydrate inhibitors: thermodynamic inhibitors, kinetic inhibitors, and anti-agglomerants [22,23]. Many petroleum industries introduced thermodynamic hydrate inhibitors into the pipelines, because this is the most convenient method to avoid hydrate formation. The addition of thermodynamic hydrate inhibitors in

---

* Corresponding author. Tel.: +82 52 217 2821; fax: +82 52 217 2819.
E-mail address: ywseo@unist.ac.kr (Y. Seo).

http://dx.doi.org/10.1016/j.fuel.2015.10.005
0016-2361/

large enough quantities moves the equilibrium conditions needed for hydrate formation into unfavorable regions of low temperatures and high pressures [22].

Among the well-known thermodynamic inhibitors, alcohols and glycols are the most investigated additives. Methanol, which is the most representative thermodynamic inhibitor, interrupts the hydrogen bonding between water molecules and prevents clathrate hydrate formation without being incorporated into the cages [22]. However, recent studies demonstrate that some alcohols, such as ethanol, 1-propanol and 2-propanol can be enclathrated in the hydrate lattices when CH_4 or CO_2 is present. This indicates that alcohols can thermodynamically promote or inhibit the clathrate hydrate formation, and thus, can play a significant role in gas storage and CO_2 sequestration by functioning as co-guests of clathrate hydrates [24–36].

Among the simple alcohols, *tert*-butyl alcohol (tBA) has the most hydrophobic characteristics and was reported to form sII hydrates under the pressurization of CH_4 [37]. However, the possibility of tBA to form clathrate hydrates in the presence of CO_2 and N_2, thermodynamic behaviors of the guest gas (CH_4, CO_2, and N_2) + tBA hydrates, and guest distributions of each guest molecule in the guest gas + tBA hydrates have not yet been clearly examined. Considering the molecular size, tBA molecules are expected to be enclathrated in the large ($5^{12}6^4$) cages of the sII hydrates, and therefore, can promote or inhibit gas hydrate systems.

The precise nature of the guest gas (CH_4, CO_2, and N_2) + tBA clathrate hydrates were therefore investigated in this research. Particular attention was given to macroscopic thermodynamic phase behaviors and microscopic analyses to elucidate structural transitions, cage occupancies of each guest, and guest distributions for potential applications of tBA to gas storage and CO_2 sequestration. The accurate three-phase (clathrate hydrate (H)–liquid water (L_W)–vapor (V)) equilibria of the guest gas (CH_4, CO_2, and N_2) + tBA clathrate hydrates were measured at two different tBA concentrations (1.0 and 5.6 mol%) to examine the thermodynamic effects of tBA on clathrate hydrates. The structure identification and determination of cage occupancies for each guest molecule in the CH_4 + tBA hydrates were performed via ^{13}C NMR and Raman spectroscopy. The crystal structures of both CO_2 + tBA and N_2 + tBA hydrates were examined via powder X-ray diffraction (PXRD) and Raman spectroscopy.

2. Materials and methods

2.1. Materials and apparatus

CH_4 (99.95%), CO_2 (99.99%) and N_2 (99.99%) gases were supplied by PSG Gas Co. (Republic of Korea). *tert*-Butyl alcohol (tBA) with a purity of 99% was purchased from Sigma–Aldrich Co. (USA). Double-distilled and deionized water was used. All materials were used without further purification.

The experimental apparatus used for the hydrate phase equilibrium measurements and sample preparation for microscopic analyses was specifically designed for accurate measurement of the pressure and temperature during the hydrate formation and dissociation processes. A high-pressure cell, which is made of 316 stainless steel with an internal volume of 250 cm^3, was immersed in a water bath. The temperature of the water bath was regulated by an external circulator (RW-2025G, JEIO Tech, Republic of Korea) with a programmable controller. Two sapphire windows at the front and back sides of the high-pressure cell allowed visual observation of the phase transitions occurring inside the equilibrium cell. An impeller-type stirrer was used. A thermocouple with an accuracy of ±0.1 K was placed in the cell, and it was calibrated using an ASTM 63C mercury thermometer (Ever Ready Thermometer, USA). A pressure transducer (S-10, Wika, Germany) with an uncertainty of 0.01 MPa was used, and it was also calibrated using a Heise Bourdon tube pressure gauge (CMM-140830, 0–20.0 MPa, maximum error of ±0.02 MPa).

2.2. Hydrate stability condition measurements

An isochoric method with step heating and cooling was adopted to perform hydrate phase equilibrium measurements. First, the equilibrium cell was filled with 80 cm^3 of tBA solution (1.0 and 5.6 mol%). To flush out any residual air from inside the cell hydrate forming gas was used three or more times before each run of the experiment. After the equilibrium cell had been sufficiently pressurized with the hydrate forming gas, the system temperature was cooled to a temperature lower than the expected equilibrium temperature. Thermal contraction caused the cell pressure to decrease as the temperature was lowered in increments of 1.0 K/h. A sudden drop in pressure was then observed due to hydrate crystal growth after nucleation. After the pressure became constant, the temperature was slowly increased at a rate of 0.1 K/90 min. The equilibrium cell pressure similarly increased as the hydrate was dissociated. The cell pressure continued to increase slightly even after the hydrate had completely dissociated. This was due to thermal expansion. The H–L_W–V equilibrium points at each pressure level were worked out with reference to the intersecting points of the hydrate dissociation line and thermal expansion line.

2.3. Microscopic analyses

A Bruker 400 MHz solid-state NMR spectrometer from the Korea Basic Science Institute (KBSI) was used in order to determine the structure and guest distributions of the CH_4 + tBA hydrates. For the sample preparation, the formed hydrates were finely powdered in liquid nitrogen and placed into a 4 mm o.d. Zr rotor that was put into the variable-temperature (VT) probe. All ^{13}C NMR spectra were recorded at a Larmor frequency of 100.6 MHz with magic angle spinning (MAS) between 2 and 4 kHz, in an environment of 243 K atmospheric pressure. A pulse length of 2 μs and a pulse repetition delay of 10 s under proton decoupling were applied, and a radio-frequency field strength of 50 kHz corresponding to 5 μs 90° pulses was used. The downfield carbon resonance peak of adamantane, which was assigned to a chemical shift of 38.3 ppm at 300 K, was used as an external chemical shift reference.

For Raman measurements, the clathrate hydrate samples were finely powdered and pelletized into cylinder form with a diameter of 1.0 cm and a height of 0.3 cm. Raman spectra were obtained using a Raman spectrometer (alpha 300R, WITech, Germany) that was equipped with a 1800 grooves/mm holographic grating and a thermoelectrically cooled CCD detector. The excitation source was a He–Ne laser with a wavelength of 532 nm and an intensity of 20 mW. By regulating the flow rate of liquid N_2 vapor, the temperature was kept constant at 170 K.

The PXRD patterns of the clathrate hydrates were recorded at 140 K using an X-ray diffractometer (Rigaku Geigerflex, D/Max-RB), which was equipped with a graphite-monochromatized Cu Kα1 radiation source ($\lambda = 1.5406$ Å). The PXRD patterns were recorded in a step mode with a fixed time of 3 s and a step size of 0.02° for $2\theta = 5–55°$. The patterns that were obtained were analyzed by the ChekCell program to identify the structures of the CO_2 + tBA and N_2 + tBA hydrates. More detailed descriptions of the experimental procedures are presented in our previous studies [15,16,38–41].