Chemical Engineering Journal 258 (2014) 427–432

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

1-Propanol as a co-guest of gas hydrates and its potential role in gas storage and CO_2 sequestration

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HIGHLIGHTS

- We examine the enclathration of 1-propanol as a co-guest of gas hydrates.
- 1-Propanol forms cubic structure II hydrates with CH_4 and CO_2.
- 1-PrOH does not act as a notable hydrate promoter or an inhibitor for CH_4 hydrate.
- 1-PrOH functions as a significant thermodynamic hydrate inhibitor for CO_2 hydrate.

ARTICLE INFO

Article history:
Received 16 June 2014
Received in revised form 24 July 2014
Accepted 26 July 2014
Available online 5 August 2014

Keywords:
Gas hydrate
Gas storage
CO_2 sequestration
1-Propanol
Inhibitor

ABSTRACT

The inclusion of 1-propanol (1-PrOH) as a co-guest of gas hydrates in the presence of CH_4 and CO_2 and its potential role in gas storage and CO_2 sequestration were investigated focusing primarily on macroscopic hydrate phase equilibrium behavior and microscopic structural and cage filling characteristics. The powder X-ray diffraction (PXRD) patterns confirmed that both double CH_4 + 1-PrOH and double CO_2 + 1-PrOH hydrates are cubic structure II (sII) hydrates. 1-PrOH did not act as a remarkable thermodynamic hydrate promoter or inhibitor for CH_4 hydrate systems, though it did act as a significant thermodynamic hydrate inhibitor for CO_2 hydrate systems despite its participation as a co-guest in the hydrate lattices. The ^{13}C NMR results revealed that 1-PrOH was found in the large $5^{12}6^4$ cages of the sII hydrate along with CH_4 at lower 1-PrOH concentrations, and the chemical formulas for the double CH_4 + 1-PrOH hydrates were found to be $2.13\ CH_4 \cdot 0.53$ 1-PrOH $\cdot\ 17\ H_2O$ for the 1-PrOH 1.0 mol% solution and $1.85\ CH_4 \cdot 0.75$ 1-PrOH $\cdot\ 17\ H_2O$ for the 1-PrOH 5.6 mol% solution. The overall experimental results provide a better understanding of guest–host interaction, guest distributions, and structural transition in guest gas + 1-PrOH hydrates for the potential application of 1-PrOH in gas storage and CO_2 sequestration.

1. Introduction

Gas hydrates are non-stoichiometric crystal structures that can trap guest molecules in the well-defined host lattices built up from hydrogen-bonded water molecules. They have three distinct crystal types: structure I (sI), structure II (sII), and structure H (sH), which differ in sizes and shapes of the cages formed [1]. The chemistry of gas hydrates is an important issue in natural gas transportation because pipeline plugging due to gas hydrate formation can lead to serious safety problems and economic losses. The situation is even more serious in offshore oil and gas facilities where gas hydrates can block pipelines, which can result in major equipment damage, significant loss of production, and possible leakage of oil and gas [2].

CO_2, which is mainly produced from the combustion of fossil fuels, can be stored in the ocean or underground [3–5]. For ocean or geological sequestration, CO_2 should be transported from emission sources to storage sites through pipelines. Because CO_2 forms gas hydrates under milder conditions than CH_4, it is also expected that CO_2 hydrate formation and subsequent pipeline plugging can be major issues during CO_2 transportation [1].

Massive efforts have been made to prevent hydrate plugging in pipelines [2]. For flow assurance, the method currently favored for industrial use is inhibitor injection. These inhibitors alter the conditions under which hydrates may form, preventing hydrates from forming in the pipeline. Alcohols are the most commonly used thermodynamic inhibitors. They are known to disrupt the water's

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http://dx.doi.org/10.1016/j.cej.2014.07.110

hydrogen bonding network; thus, they inhibit the formation of gas hydrates without being trapped in the hydrate cages [2]. However, some researchers have recently reported that water-soluble alcohols, such as ethanol, propanols, and tert-butanol, form sII hydrates and act as guests of the hydrate structures in the presence of hydrophobic gases, such as CH_4 and CO_2 [6–18]. Furthermore, even methanol, the most widely used thermodynamic hydrate inhibitor, has recently been found to be able to be incorporated in the hydrate cages as a guest [19].

1-Propanol (1-PrOH), a secondary alcohol, was reported to form simple hydrates of cubic structure at temperatures much lower than the freezing point of water, but it also forms double 1-PrOH hydrates under the pressure of a help gas such as CH_4 [11,12,16–18,20]. The Raman spectrum and powder X-ray diffraction (PXRD) pattern of the double CH_4 + 1-PrOH hydrates indicated the formation of sII hydrates and the molecular dynamic simulations and thermodynamic modeling predicted the occupation of 1-PrOH in the large cages of sII hydrates under the pressurization of CH_4 [11,12,18]. However, the guest distribution and cage occupancy of each guest in sII double CH_4 + 1-PrOH hydrates have not yet been clearly revealed. In particular, the double hydrates of CO_2 + 1-PrOH have not yet been explored.

The enclathration of alcohols as guests in hydrate cages and their thermodynamic effects on hydrate equilibrium conditions are very crucial factors in flow assurance. This study examines the unique pattern and distribution of guest molecules in double 1-PrOH hydrates formed with either CH_4 or CO_2 as a help gas, focusing primarily on macroscopic hydrate equilibrium behaviors and microscopic analytical methods, such as ^{13}C NMR spectroscopy and PXRD. The three-phase hydrate equilibria (gas hydrate (H)–liquid water (L_W)–vapor (V)) for the ternary CH_4 + 1-PrOH + water and CO_2 + 1-PrOH + water mixtures at three different 1-PrOH concentrations (1.0, 5.6, and 10.0 mol%) were measured to examine the effect of 1-PrOH enclathration on the thermodynamic stability of the double hydrates. The crystal structures of both double CH_4 + 1-PrOH and double CO_2 + 1-PrOH hydrates were identified via PXRD. Accurate information on the guest distribution and cage occupancy of each guest in the CH_4 + 1-PrOH hydrates was examined via ^{13}C NMR spectroscopy.

2. Experimental

2.1. Materials

The CH_4 and CO_2 gases, which had stated purity values of 99.95% and 99.99%, respectively, were provided by PSG Gas Co. (Republic of Korea). 1-PrOH used in this study had a purity of 99.5%; it was purchased from Sigma–Aldrich (USA). Double distilled and deionized water was used. No further purification was carried out on any of the materials used.

2.2. Phase equilibrium measurements

An equilibrium cell with two sapphire windows was constructed for the hydrate phase equilibrium measurements. The cell, with an internal volume of approximately 200 cm^3, was made from 316 stainless steel and was immersed in the water bath. The windows were located at the front and the back of the cell in order to allow visual observation of phase transitions inside. An impeller type stirrer was used to agitate the cell content vigorously. The thermocouple used for temperature measurement has an accuracy of ±0.1 K for full ranges. The pressure transducer (S-10, 0–10.0 MPa, Wika, Germany) has an accuracy of ±0.25%, which was calibrated using a Heise Bourdon tube pressure gauge (CMM-137219, 0–10.0 MPa) with a maximum error of ±0.01 MPa in the full range.

An isochoric pressure search method with step heating was adopted for the H–L_W–V equilibrium measurement. The equilibrium cell was initially charged with approximately 90 cm^3 of 1-PrOH solution, and CH_4 or CO_2 was added until the target pressure was reached. Next, in order to nucleate hydrate crystals the cell temperature was decreased at a cooling rate of 1.0 K steps with a 60 min interval. A sudden pressure drop confirmed the formation of hydrates. This reduction in pressure was caused by the enclathration of gas molecules in the hydrate phase. After the completion of gas hydrate formation, the temperature was raised in 0.1 K steps with a 90 min interval, leading to an increase in cell pressure with corresponding hydrate dissociation. The H–L_W–V equilibrium point for each pressure condition could be determined by the intersection point between the hydrate dissociation line and the thermal expansion line in the pressure–temperature trace for formation and dissociation of CH_4 (or CO_2) + 1-PrOH hydrates. A schematic diagram of the experimental apparatus and a more detailed description of the experimental procedure were given in previous papers [21–23].

2.3. PXRD and ^{13}C NMR analyses

A Rigaku Geigerflex diffractometer (D/Max-RB) with graphite-monochromatized Cu Kα1 radiation (λ = 1.5406 Å) was used to identify the crystal structures of the double CH_4 + 1-PrOH and CO_2 + 1-PrOH hydrates. Prior to taking PXRD measurements, the gas hydrate samples were prepared in the equilibrium cell under high pressure and then were transferred to a liquid nitrogen vessel where they were finely powdered by grinding. The PXRD data were collected by step mode with a fixed time of 3 s and a step size of 0.02° for 2θ = 10–60° at 133.15 K. Analysis of the observed patterns was carried out using the Checkcell program.

The crystal structure and guest distributions of the double CH_4 + 1-PrOH hydrates were investigated using a Bruker 400 MHz solid-state NMR spectrometer (Bruker, Germany). The prepared hydrate samples were loaded in a zirconia rotor with 4 mm o.d. before being placed 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 at 243 K and atmospheric pressure. A pulse length of 2 μs and a pulse repetition delay of 10 s under proton decoupling were employed when a radio frequency field strength of 50 kHz corresponding to 5 μs 90° pulses was used. A chemical shift of 38.3 ppm at 300 K, corresponding to the downfield carbon resonance peak of adamantane, was used as an external chemical shift reference. A more detailed explanation of the PXRD and ^{13}C NMR analysis was provided in previous papers [24,25].

3. Results and discussion

3.1. PXRD

It has already been established that both pure CH_4 and pure CO_2 form sI hydrates [1]. However, the large molecular size of 1-PrOH means that its inclusion in hydrate lattices with pressurization of CH_4 or CO_2 can cause a structural transition of the sI hydrates to sII double hydrates [11,12]. In this study, the crystal structure of double 1-PrOH hydrates with CH_4 and CO_2 was determined using PXRD measurements. Fig. 1 presents the PXRD patterns of both the double CH_4 + 1-PrOH (5.6 mol%) hydrate and the double CO_2 + 1-PrOH (5.6 mol%) hydrate measured at 133.15 K. The double CH_4 + 1-PrOH hydrate was found to be a cubic (*Fd3m*) sII structure with a unit cell parameter of 17.29 Å, which is in good agreement with the value reported by Ohmura et al. [14]. The double CO_2 + 1-PrOH hydrate was also identified as a cubic (*Fd3m*) sII