In situ observations by magnetic resonance imaging for formation and dissociation of tetrahydrofuran hydrate in porous media☆

Jiafei Zhao, Lei Yao, Yongchen Song⁎, Kaihua Xue, Chuanxiao Cheng, Yu Liu, Yi Zhang

Key Laboratory of Ocean Energy Utilization and Energy Conservation of Ministry of Education, Dalian University of Technology, Dalian, 116024, P.R. China

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Abstract

Tetrahydrofuran (THF) hydrate has long been used as a substitute for methane hydrate in laboratory studies. This article investigated the formation and dissociation characteristics of THF hydrate in porous media simulated by various-sized quartz glass beads. The formation and dissociation processes of THF hydrate are observed using magnetic resonance imaging (MRI) technology. The hydrate saturation during the formation is obtained based on the MRI data. The experimental result suggests that the third surface has an effect on hydrate formation. THF hydrate crystals lean to form on the glass beads and in their adjacent area as well as from the wall of the sample container firstly. Furthermore, as the pore size diminishes, or as the formation temperature decreases, the nucleation gets easier and the formation processes faster. However, the dissociation rate is mostly dependent on the dissociation temperature rather than on the pore size.

Keywords: Tetrahydrofuran hydrate; Porous media; Formation; Dissociation; MRI

1. Introduction

Clathrate hydrates are equilibrium crystal structures that are formed when certain components of natural gas (e.g., methane, carbon dioxide, propane) and volatile liquids (e.g., certain alcohols, tetrahydrofuran) in molecules become permanently enganged by water molecules [1]. Water molecules form a framework containing relatively large cavities through hydrogen bonding. Gas molecules, whose diameter is less than the size of the cavity, can occupy the cavities. Because of the nonbonded interactions between the encaged gas molecules and water lattice, the hydrate structure is thermodynamically stabilized. There are three prominent structures that hydrates crystallize in — structures I, II and H — depending on the nature and size of the guest molecules [2].

Hydrates are of interest for a number of different applications including as a potential source of energy, as a potential greenhouse gas storage medium, for gas transportation, desalination, refrigeration and for flow assurance in oil and gas pipelines where they may form solid plugs and lead to less production [3]. Although the physical properties and thermodynamics of hydrates are known to an acceptable degree for most engineering applications, the kinetics still remains a scientific curiosity. Most hydrates form at high pressure and low temperature, so specialist equipment is generally needed to form and study them. Among numerous compounds known as hydrate formers, tetrahydrofuran (C₄H₈O, hereafter THF) has long been used as a proxy of methane in laboratory studies [4–6]. The main advantages of THF are as follows: (I) ability to remain in the liquid state under atmospheric pressure; (II) complete miscibility in liquid water, which enables relatively rapid, homogeneous formation of THF hydrate and close control on hydrate saturations; and (III) ability to form a structure II hydrate at atmospheric pressure and easily achieved temperatures, making the experiments easier [7–10]. No highly mobile and compressible gases are released during the dissociation of THF hydrate, so the poroelastic complication can also be avoided [11].
The THF/water solution allows hydrate crystals to form and grow anywhere within it. If it is composed of THF and water at a molar ratio of 1:17 (or 19% by weight), THF forms a structure II hydrate with water and the melting point of the solution is raised to approximately 4.4°C [4]. The mass transfer process can be eliminated from the process of crystal growth, thereby offering a more simplified system for studying hydrate growth. In such a system, the rate of crystal growth is considered to be determined by the transfer of heat generated at the surfaces of growing crystals to the surrounding solution and to the reaction at the surfaces [12]. Pinder [13] found that hydrate formation rate was controlled by the diffusion rate of the hydrate film, not by the heat transfer. Larsen [14] suggested that the crystal growth is mainly determined by the heat transfer unless the heat transfer is much increased by some means. Bollavaram et al. [15] suggested that the surface-reactive restraints could not be overlooked even if the heat transfer is much increased. The third surface also has an effect on hydrate nucleation. Large areas of interactive surface and possible surface ordering have an impact on the thermodynamic and kinetic characteristics of hydrate formation [16,17]. Since the porous media have a large specific surface area, a strong surface tension and capillary condensation phenomenon, they also have an impact on hydrate phase equilibrium [18]. Even the 3-Å molecular sieve powder can shorten THF hydrate nucleation time and promote hydrate growth [19].

Several experimental techniques have been used to measure hydrate formation and dissociation processes, including ultrasonic detection, electrical resistance measurement, laser interferometry and visual microscopy [20,21]. Magnetic resonance imaging (MRI) has been shown to be an effective tool for observing the formation and dissociation of THF hydrate [9]. The MRI signal is strong for THF/water solution, but not detected above the background noise for solid hydrate. So it can be used to determine the spatial distribution of hydrate and nonhydrate phases, hydrate saturation and the rate of hydrate formation and dissociation.

In this study, in situ observation by MRI of the formation and dissociation of THF hydrate in various-sized quartz glass beads is presented. The saturations during the process were measured. The work also provides an improved basic understanding of the processes and corresponding dynamics.

2. Experiments

2.1. Apparatus and materials

Five different diameters of quartz glass beads (AS-ONE, Co., Ltd, Japan) — BZ-4 (3.962–4.699 mm, average 4.5 mm), BZ-3 (2.500–3.500 mm, average 3.0 mm), BZ-2 (1.500–2.500 mm, average 2.0 mm), BZ-1 (0.991–1.397 mm, average 1.2 mm) and BZ-04 (0.350–0.500 mm, average 0.4 mm) — were used to simulate the porous media. The porous media exhibited almost the same porosity of around 35%. THF (Tianjin Damao Chemical Reagent Factory, Tianjin, China) with a minimum purity of 99.0% and deionized water were mixed at a mass ratio of 19:81 which corresponds to 1:17 on a molar basis in our experiments.

Hydrate formation and dissociation were achieved by controlling the temperature of the coolant continuously circulating through the MRI cell around the exterior of the sample. The experimental system is illustrated in Fig. 1. Fluorinert FC-40 (3M, St. Paul, MN, USA) was used as the coolant because it contains no imageable hydrogen and has low dielectric properties to minimize RF losses. The temperature controller was an F25-ME-type circulator (Julabo, Inc., Germany) with a temperature control range from −28°C to 200°C and a precision of ±0.01°C. THF solution was pumped into the sample container by a JB-80-type manual pump (Haian Oil Scientific Research Apparatus, Co., Ltd, Jiangsu, China).

A cross-sectional diagram of the temperature-controlled cell used inside the MRI is shown in Fig. 2. The part imaged by MRI was made up of polyimide. The other parts were made of titanium and the two were joined by a tapered thread. The glass bead samples were sealed in the inner sample container and the coolant, FC-40, was pumped from the bath through the sleeve around the sample container and back to the bath, giving a good control of the sample temperature and a quick response to temperature changes.

A Varian 400-MHz NMR (Varian, Inc., Palo Alto, CA, US) was used to monitor the formation and dissociation of THF hydrate. It operated at a resonance of 400 MHz, 9.4
T, to measure hydrogen. A spin-echo multislice (FSEMS) pulse sequence was used with a repetition time of 500 ms and an echo time of 10.14 ms. Images were all collected with 256 points for read out and phase encoding. Field of view was set to 40×40 mm, giving a voxel size of 0.156×0.156 mm. Furthermore, the thickness of the MRI slices is 100 μm.

2.2. Procedure

The quartz glass beads were saturated by the stoichiometric THF/deionized water solution. Temperature was held at −4.0°C, −3.0°C, −2.0°C, and −1.0°C, respectively, by circulating the coolant in the THF hydrate formation cycle.

In the formation process, the crystal nucleation is difficult since the nucleation in the liquid phase interior needs a great deal of energy input to overcome the surface barrier. Therefore, the initiation of the nucleation is important. In this work, all of the samples were gently shaken in the same way after cooling for 1 min to promote nucleation, but there was no shaking thereafter.

A strategy was used to ensure the formation of THF hydrate instead of ice under our experimental condition. The method used in this research was to raise the temperature to 3°C (still under the THF solution equilibrium temperature of 4.4°C) after the solution was completely converted to solid and to keep the temperature for 5 h. If the crystals melt, the resultant is considered to be ice; otherwise, the product is THF hydrate. In our experiments, the crystals did not show any obvious change, which confirmed the formation of THF hydrate.

For the dissociation cycle, temperature was raised to 5.5°C in BZ-3 and BZ-04 or to 8°C in BZ-4, BZ-2, BZ-1 and BZ-04 are shown in Fig. 3. The black area in the images represents the glass beads and hydrate phase, while the white area is the nonhydrate phase (aqueous THF solution). When the only signal observed in the images was background noise, indicating that the liquid phase was all converted to solid, THF hydrate formation was completed.

The nucleation process of THF hydrate is different from that of the common gas hydrate. Since THF can be completely soluble in water, nucleation of THF hydrate with no external medium added is a homogeneous process and anywhere in the solution could be a nucleation spot. But porous media have a large specific surface area and a strong surface tension, so they have an influence on hydrate formation. In our experiments, the hydrate started forming from the wall of the sample. This might be due to the fact that the wall of the sample container reached the required formation temperature first. It was also found that the THF hydrate crystals formed on the glass beads and in their adjacent area first. It seemed that hydrate growth was influenced by porous media and the crystals leaned to form on them.

Furthermore, the mean MRI signal intensities of the samples during the formation processes are shown in Fig. 4. With the growth of THF hydrate, the signal intensity decreases.

The hydrate saturation can be calculated from the MRI data. Two methods are commonly used to determine the porosity of porous media [16,17]. First, the ‘bulk method’ is based on the mean signal related to that of the entire sample volume. For this method, it is assumed that the

Fig. 2. Cross-sectional diagram of the MRI cell. (1) Coolant inlet or outlet; (2) thermocouple; (3) sealing o-ring; (4) high-pressure joint; (5) inner sample container; (6) sleeve; (7) sieve; (8) pressure pad.
response of the MRI signal has a linear relation to the water saturation. Second, the ‘distribution shape method’ is based on the shape of the probability distribution obtained from the signal for each mapped voxel. For this method, the threshold needs to be found from the probability distribution. In this work, the bulk method.

Fig. 3. MR images of THF hydrate formation processes at −2.0°C in various-sized quartz glass beads.
was used to avoid any subjectivity. Thus Eq. (1) was used to calculate the hydrate saturation in the formation process.

\[ S_i = \frac{I_0 - I_i}{I_0} \times 100\% \] (1)

Where \( S_i \) is the hydrate saturation at \( t=i \) minutes, \( I_0 \) is the mean MRI intensity of the imaging plane at \( t=0 \) min and \( I_i \) is the mean MRI intensity of the imaging plane at \( t=i \) minutes. In our experiments, the hydrate saturation in BZ-2 reached about 24% in 7 min, about 54% in 10 min, about 72% in 33 min and 87% in 50 min.

The time when hydrates could be observed in MR images with the set resolution (hereafter, hydrate appearance time) is shown in Fig. 5. The smaller the size of the glass bead is, or the lower the formation temperature is, the shorter the time to start hydrate formation. Fig. 5 also suggests that, as the formation temperature gets higher, the differences between the nucleation rates of hydrate forming in different pore sizes became more obvious. The formation of THF hydrate in pure THF/water solution with no glass beads was also measured in the present study. It took about 30 min at \(-4.0^\circ\text{C}\) and about 70 min at \(-2.0^\circ\text{C}\) to start the formation. It confirms the significance of the existence of the third surface to the crystal nucleation. Porous media increase the contact surface and reduce the surface energy and the chemistry potential barrier that the nucleation must overcome. Thus, the nucleation becomes easier.

The entire formation time (hydrate appearance time not included) in different quartz glass beads is shown in Fig. 6. It suggests that THF hydrate formation rate is also faster in porous media with a smaller pore size at a lower temperature. For the pure THF/water solution, it took about 75 min at \(-4.0^\circ\text{C}\) and about 85 min at \(-2.0^\circ\text{C}\) to complete the hydrate formation of the same amount. This result does not agree with our previous work. The previous work was not undertaken with an in situ MRI monitoring. The formation process was observed through the visual window first, and then the sample was imaged using MRI for further study. For the small glass beads, the hydrate crystal was not easy to observe unless it grew larger. This might lead to the mistaken conclusion that a larger pore size shortens the formation time in the previous work.

The pure THF/water hydrate formation in the test tube was also tried. However, no obvious phenomenon was observed within 2 days. It is not quite known why pure THF hydrate could be formed in the MRI cell but could not be formed in the test tube. It appears that the shape and the smoothness of the sample container caused the difference.

![Fig. 4. The mean MRI signal intensities of the samples during the formation processes.](image)

![Fig. 5. Hydrate appearance time in various-sized quartz glass beads as a function of temperature.](image)

![Fig. 6. The entire formation time in various-sized quartz glass beads as a function of temperature.](image)
Moreover, experiments on THF hydrate formation above 0°C (under an equilibrium temperature of 4.4°C) were also carried out. It took a longer time to start and complete the entire formation and the experimental result also showed the tendency suggested above.

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3.2. THF hydrate dissociation

The bath temperature was raised to 3°C after the entire formation process was completed, and it was held there for 5 h. No obvious change was observed. Then the temperature was increased to 5.5°C in BZ-3 and BZ-04 and to 8°C in BZ-4, BZ-2 and BZ-1, and the hydrate dissociation process began. Images were also collected by MRI during the dissociation cycle, as shown in Fig. 7. The images slowly gained in intensity with time.

Baldwin et al. [9] found that the MRI intensity across the stone plug uniformly increased with the time during dissociation. They thought that the unexpected uniformity could be the result of the slow warming process and of the heat transfer properties of the rock matrix. They suggested that the dissociated portion would be observed as a ring beginning from the outer edge of the sample at a faster warming rate. The same phenomenon was also found in our experiment. But a ring of stronger intensity at the outside edge of the sample could also be observed.

The entire dissociation time in BZ-3 and BZ-04 at 5.5°C is shown in Fig. 8. It took about 46 min in BZ-3 and 43.5 min in BZ-04 to complete the dissociation at 5.5°C. The entire dissociation time in BZ-4, BZ-2 and BZ-1 at 8°C is shown in Fig. 9. It took about 24 min in BZ-4, 25.5 min in BZ-2 and 24 min in BZ-1 to dissociate entirely. It seems that the dissociation time is mainly dependent on the dissociation temperature rather than on the sizes of the glass beads under our experimental situation. No obvious dissociation time difference was observed for different formation temperatures and different diameters. This result does not quite agree with the fact that smaller glass beads have larger contact areas and therefore cause a faster heat transfer to the hydrate. It might be caused by the present high dissociation temperature, so the difference was not obvious. For the pure THF hydrate, it took about 110 min at 5.5°C and 65 min at 8°C to complete the total dissociation of the same amount of hydrate. It suggests that even at the present dissociation temperature the glass bead size does have an impact if large, to a certain extent.

4. Conclusions

An experimental investigation on THF hydrate formation and dissociation in porous media was carried out using MRI. Based on the experimental results, the following conclusions can be drawn:

(1) Since porous media provide a large specific surface area and contact area, they can promote THF hydrate nucleation and formation compared with the situation without porous media.

(2) THF hydrate crystals start to form on porous media and in their adjacent area as well as from the wall of the sample container. The smaller the pore size is, or the lower the formation temperature is, the faster the nucleation and the shorter the entire formation time. As the formation temperature gets higher, the effect of the porous media became more obvious.

(3) For the dissociation cycle, the dissociation time is mostly dependent on the dissociation temperature rather than on the size of the glass beads. The impact of the glass bead size on the dissociation might be obvious at a lower temperature.

Further studies should consider THF hydrate dissociation in various-sized glass beads at different temperatures to investigate the dissociation characteristics and the effect of glass bead size. The structure of the porous media should also be explored in detail as it may affect the THF hydrate formation and dissociation.
References