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Formation Kinetics of Structure H Gas Hydrate

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Abstract: *This paper investigates the kinetics of structure H (sH) formation kinetics above and below the structure I (sI) formation equilibrium curve at temperatures of between 2°C and 6°C. Methane was used as a help gas and methylcyclohexane (MCH) was used as sH former. It was concluded that in the points above the sI formation equilibrium curve, at the first, the sI forms, and then converts to sH because of the low solubility of MCH in water. In the points under the sI equilibrium curve, at the first sH forms after a long induction time. The study also show the effect of the addition of hydroxymethylcellulose (in three concentrations of 0.05, 0.1 and 0.15 Wt%) on sH hydrate formation kinetics. With this additive, it was observed that the rate of sH formation increases.*

Keywords: *sH, sI, Formation Kinetics, Gas Hydrate*

1. Introduction

Gas hydrates are ice-like crystalline compounds formed when light gases come into contact with water at low temperatures and high pressures. Three crystallographic structures—I, II and H—are known for hydrates which differ in cavity size and shape. Gas hydrate has a reputation for being a new means of natural gas storage and transportation. Among the three structures, sH is the best candidate for this purpose because it forms in lower pressures the pressure required to form an sH hydrate is usually 30% to 80% of that required to form an sI methane hydrate.(Zheng, Fan, Liang, & Guo, 2004)) and it has a higher gas storage capacity.(Khokhar, Gudmundson, & Sloan, 1998).

At least two components are required for forming sH at a large molecule guest substance (LMGS) in the $5^{12}6^{8}$ cage and a help-gas like methane in 5^{12} and $4^{3}5^{6}6^{3}$ cages. Whereas so many researchers (Lederhos et al in 1992, Mehta and Sloan in 1994, Hütz and Englezos in 1996, Mooijer-van den Heuvel et al in 2000, Makino et al in 2004, Ohmura et al in 2005, etc.)

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have measured the equilibrium data points with different LMGSs, there is little information about the kinetics of sH gas hydrate.

Lee, Susilo and Englezos studied the kinetics of sH formation and decomposition in 2005. Methane was used as a help gas, and neohexane, *tert*-butyl methyl ether and methylcyclohexane (MCH) as the LMGS. It was concluded that both the rates of hydrate formation and the induction times are dependent on the magnitude of the driving force and the type of LMGS. When MCH was used as the LMGS, there was a long induction time and the rate of gas consumption had two different steps that are likely related to the structural differences or differences in the rate of filling the cavities.(Lee, Susilo & Englezos, 2005)

Susilo, Ripmeester and Englezos studied the methane conversion rate of ice into sH hydrate crystals in 2007. It was concluded that the rate of sH formation, with 200% LMGS synthesized at higher pressures, was much slower than the rate when synthesized at lower pressures. It is important to note that it is unclear whether the slower methane uptake rate is the result of higher occupancy or of the competition between the sI and sH hydrate formations. It could be that sI hydrate forms quickly at first, and then converts to sH hydrate at a slower rate. (Susilo, Ripmeester & Englezos, 2007).

Because the possibility of sI formation has been looked into in some studies discussing the formation of sH (Susilo et al. 2007), this study has tried to explore the kinetics of sH gas hydrate formation at temperatures of between 2°C and 6°C and different pressures at some points above and below the sI formation equilibrium curve. MCH was used as a sH former and methane was used as a help gas.

2. Materials used

The experiment materials in this work are presented in Table 1.

Table 1. Experiment materials used in this work

Component	Purity	Supplier
Methane	99.99%	Air product
Methyl cyclohexane (MCH)	>99.99%	Merck
Hydroxy methylcellulose (HMC)		Sigma Aldrich
Water		Distilled

3. Apparatus

Hydrate formation experiments are carried out in a high-pressure system. Fig. 1 shows the schematic diagram of the experimental set-up. The capacity of the cylindrical high-pressure 316 stainless-steel reactor, with a ¾-inch diameter, is 120 cm^3. There is a polyethylene shell around the reactor. A coolant (alcohol) is circulated from a refrigerated bath in the shell to keep the temperature constant. There are two valves in each side of the reactor for injecting the liquid substances and the gas. On one side of the reactor, there is a Druck PTX 1400 pressure transmitter with an accuracy of 0.1 bar; on the other side, a PT100 temperature sensor with an accuracy of 0.1 K. Both are connected into the high-pressure cell to measure the temperature and pressure of the cell. The sensors are connected to a data-logger and a personal computer to record the temperature and pressure as a function of time. A 45 rpm motor is attached to the reactor to rock it.

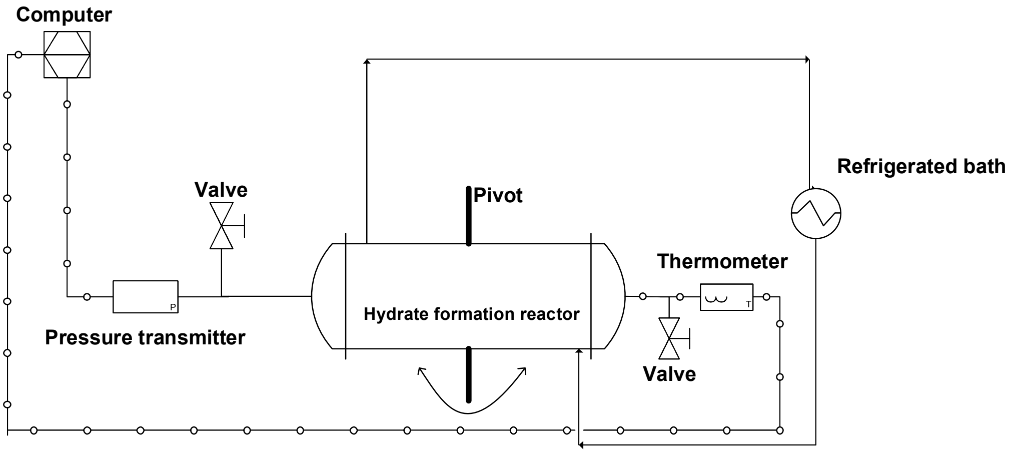

Fig. 1. Schematic diagram of the experimental apparatus

4. Procedure

The reactor was washed and rinsed with distilled water, and then it was evacuated. In each experiment, 40 cc of mercury (for better mixing), then 30 cc of water and then 10 cc of MCH were injected into the reactor with a syringe. (The volume of MCH is more than the stoichiometric amount.) Next, the circulator was turned on. When the temperature of the cell reached the desired level, the cell was pressurized with methane gas to a desired point. Over the course of the procedure, the temperature and pressure were recorded until a condition of equilibrium was achieved. After reaching equilibrium at the initial temperature and pressure, rocking of the cell was started. When the pressure was dropped and the temperature increased after rocking, the hydrate formed.

5. Results and discussion

The experimented points (some points with the initial conditions above the sI formation equilibrium curve, some under the curve) are shown in Fig. 2.

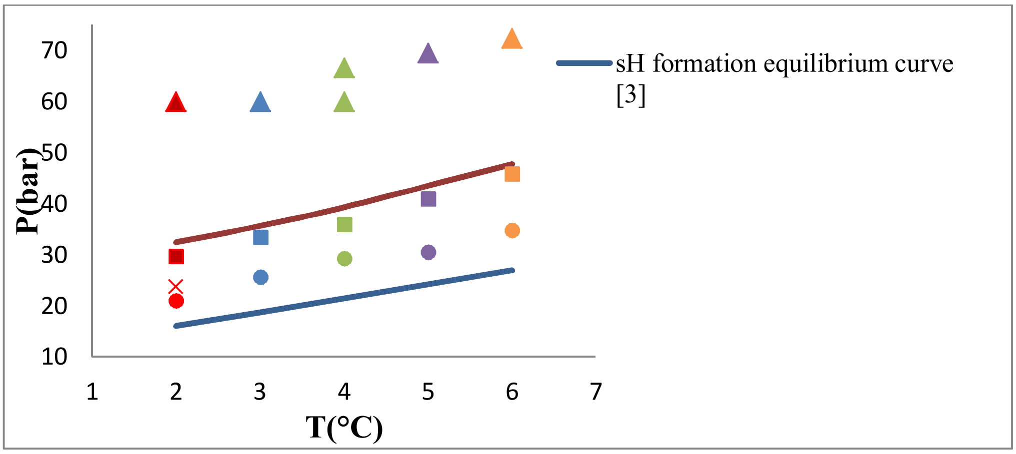

Fig. 2. Different Experimented conditions

5.1. Points at the top of the sI equilibrium curve

For all points above the sI equilibrium curve, the pressure drop curve has three parts. In the first part, with starting the mixing, a little methane gas dissolves in water and MCH. In the second part, pressure drops rapidly, and by the end of this part, pressure is close to the point of equilibrium. After several hours in the third part, another pressure drop occurs. The sH formation curve of one point above the sI equilibrium curve (initial condition: P=60 bar and T=2°C) is shown in Fig. 3.

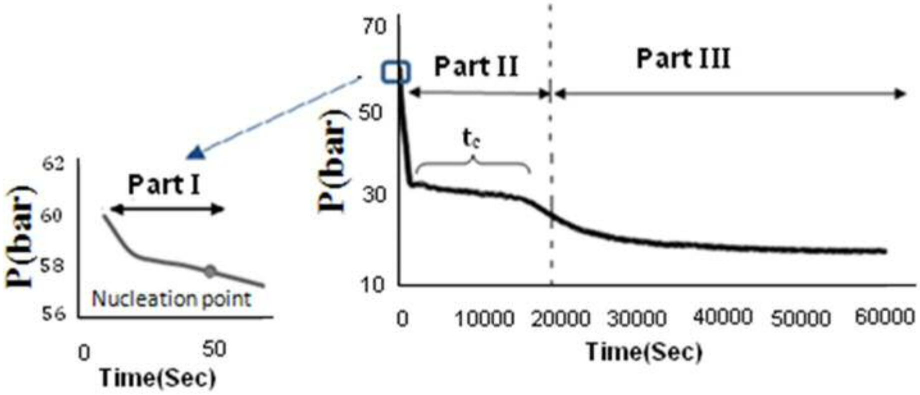

Fig. 3. sH gas hydrate formation curve in 2°C and 60 bar

The MCH that is used as the LMGS is a liquid hydrocarbon that has a low solubility in water. As such, it enters the water phase very slowly. Since sI can be stable with methane gas, in the absence of MCH and with the initial condition that is at the top of the sI formation equilibrium curve, the kinetic experiments of sI formation were conducted in the same conditions as those of sH experiments. In Fig. 4, sI and sH formation curves in 60 bar and 2°C are shown**.** The results of these two groups of experiments were compared, and it was concluded that the pressure at the end of part II in sH pressure drop curves is equal to the equilibrium pressure of sI formation in the same initial conditions.

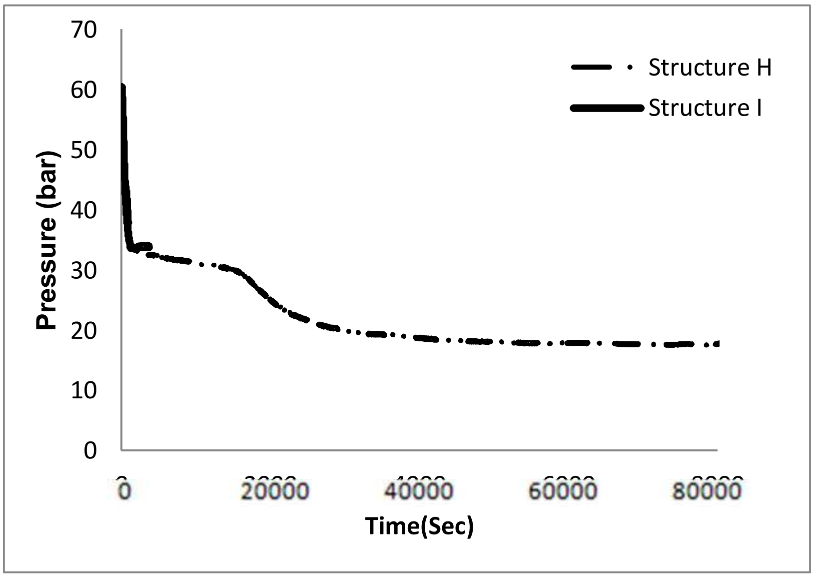

Fig. 4. sH and sI gas hydrate formation curves in 2°C and 60 bar

It seems that because of the low solubility of MCH in water, before entering it in the water phase, the cavities of sI form, and the fast pressure drop in part II is because of forming sI. After entering MCH in the water phase, because of the increased stability of sH, the cavities of sI convert to the cavities of sH. In Fig. 3, T is the time for converting the cavities of two structures into each other. After T in the third part, the pressure drops once more due to the filling of the other sH cavities. (This pattern was observed in all other experiments with other initial conditions, as shown in Fig. 2 with triangles.)

5.2. Points under the sI equilibrium curve

Experimented points under the sI equilibrium curve are shown with rectangles and circles in Fig. 2. The pressure drop curves for all these points have two parts. At the start of the mixing phase, a little methane gas dissolves in water and methyl cyclohexane, and a small pressure drop (3-4 bar) occurs. Following that, the pressure remains constant for several minutes (t'_c). t'_c is the time needed for entering MCH in the water phase and forming the nuclei of sH and particle agglomeration. In part II, the cavities of sH fill gradually, and the pressure drops again.

Under the sI equilibrium curve, sI can’t be stable; therefore, at the points with the initial conditions under the sI equilibrium curve, sI doesn’t form. In Fig. 5, the pressure drop at one point under the sI equilibrium curve (T=2°C, P=29.62 bar) is shown. (This situation was seen in all other experiments, with other initial conditions shown in Fig. 2 with rectangles and circles.)

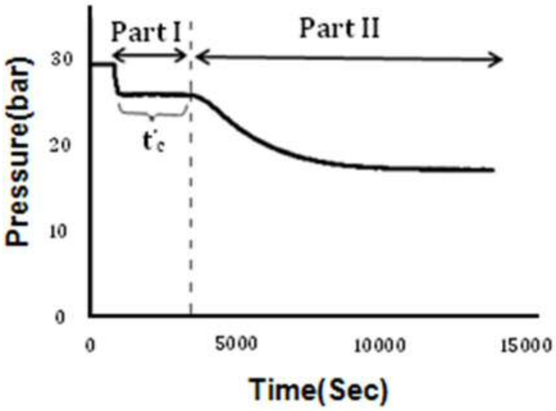

Fig. 5. sH gas hydrate formation curve in T=2°C, P=29.62 bar

It is expected that the lower the driving force, the longer the time that is needed for reaching the equilibrium. By comparing the results of the experiments with the initial conditions above and under the sI formation equilibrium curve, it can be understood that at the points above the curve, even in spite of the higher driving force, more time is required to reach the equilibrium. At these points, sI forms initially, and then is converted to sH, a process that takes a lot of time. But at the points with initial conditions under the sI equilibrium curve, sH forms after an induction time; therefore, the time required to reach the equilibrium at these points is less (Fig. 6).

By comparing the results of two points under the sI formation equilibrium curve, it can be understood that the less the initial pressure is, the higher the induction time and the lower the rate of formation (Fig. 6).

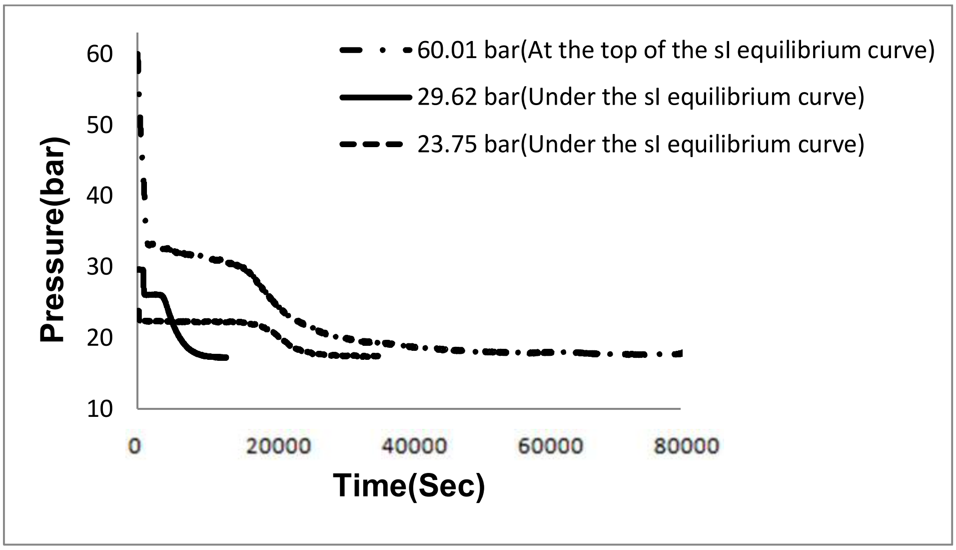

Fig. 6. sH gas hydrate formation curves in 2°C and different pressures

Table 2. Time of reaching the equilibrium for the points above and below the sI equilibrium curve in 2°C

Initial pressure (Bar)	Experimental position to Equilibrium Curve of sI	End Time (hr)
60.01	Above	17 hours
29.62	Under	3 hours
23.75	Under	10 hours

In all of the experiments that employed the initial conditions above or below the sI formation equilibrium curve, the phase of entering MCH in the water lasted for several hours. It was thus concluded that if another sH former that had a higher solubility in the water phase was used, or was used with an additive, the surface tension of the water would decrease and the rate of sH formation would increase. For examining this conclusion, HMC was used as an additive. HMC is a polymer that is made by substituting some hydroxyl groups in the structure of cellulose. Because of its mixed hydrophilic/hydrophobic structure, HMC will be preferentially absorbed during the air/water interface, and reduce the surface tension of the aqueous systems. (Wei, Cheng, Hou & Sun, 2008). The structure of this polymer is as follows:

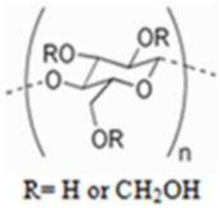

Fig. 7. Structure of HMC

HMC in three concentrations (0.05, 0.1 and 0.15 Wt%) was examined. The results are shown in Fig. 7. Clearly, because HMC decreases the interfacial tension of water, entering MCH and the conversion of two structures have happened at a higher rate and as a result, the rate of sH formation has increased.

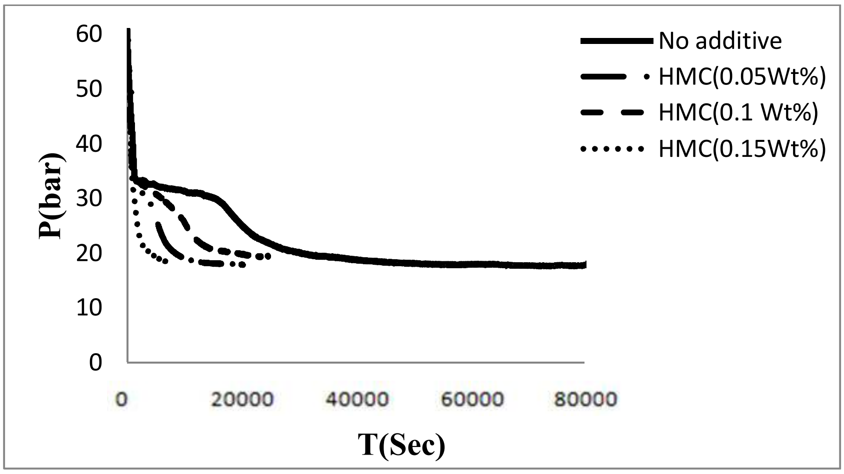

Fig. 9. Pressure drop versus time for HMC in different concentrations in 2°C

6. Conclusion

For the formation of sH gas hydrate with MCH or other sH formers that have low solubility in water, if the initial condition is above the sI formation equilibrium curve, sI forms at first, and then converts to sH; at the points under the curve, sH only forms after a long induction time. The rate of formation of a sH former with a higher solubility in water increases. Additives with the ability of reducing the interfacial tension of water, sH formers, can enter into the water phase at a higher rate and sH forms with a higher rate. By dissolving the HMC in water and reducing the interfacial tension of the water, the rate of hydrate formation increases.

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