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Experimental Investigation of Methane Hydrate Formation in the Presence of Two-Phase Aqueous-Hydrocarbon Fluid

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INTRODUCTION

Gas hydrates are crystalline compounds that are stabilized when gas molecules with particular size are surrounded by water molecules under the equilibrium temperature and pressure [1]. In addition, blockage of natural gas pipelines related to hydrate formation has made the industry focus on understanding hydrate formation condition and how it can be prevented [2]. Moreover, there are many reasons make hydrate kinetic studies so sophisticated. For example, main component of hydrate structures, i.e. gas and water molecules, are present in different phases, and the suitable molecule contacts are affected by mass transfer coefficients. In some limited studies, parameters such as water to gas ratio [3], stirring rate and cooling rate [4] were taken into consideration. It was founded by Lee and his coworkers [5] that cooling rate has not any significant effects on thermodynamic equilibrium of methane hydrate through sediments. On the contrary, hydrate formation kinetics were significantly influenced by cooling rate.

Moreover, it is hypothesized that the presence of liquid hydrocarbon interferes in both nucleation and growth of hydrate formation. In this study, the effect of liquid hydrocarbon on methane hydrate kinetics was investigated. Firstly, hydrate formation was carried out under the two different cooling rates as the blank tests. Then, comparative tests were done in the presence of liquid hydrocarbon.

EXPERIMENTAL

MATERIALS AND APPARATUS

Methane gas with 99.99% purity, distilled water and liquid gas condensate were used in hydrate formation tests. A 750-ml stirred reactor equipped with a programmable water bath was applied. A pressure transducer (0.1%) and a PT-100 (0.5 °C) were used for measurement of reactor pressure and temperature respectively. Finally, measured data were recorded by data logger during time.

EXPERIMENTAL PROCEDURE

Firstly, distilled water and liquid hydrocarbon were loaded in reactor according to Table 1. Then, stirrer was switched on (500 rpm), and reactor was pressurized using methane up to 130 bar at 30 °C (the condition out of methane hydrate zone). Afterwards, temperature of water bath was cooled from 30 to 5 °C with constant cooling rate, and then it was kept constant at 5 °C (in the methane hydrate zone). Finally, based on the reactor temperature and pressure profile, hydrate formation was monitored for each test.

Table 1: Tests Characteristics.

Run	Hydrocarbon volume (ml)	Aqueous volume (ml)	Cooling rate (°C/h)
1	0	300	10
2	0	300	5
3	150	150	10
4	225	75	10
5	150	150	5
6	225	75	5

RESULTS AND DISCUSSION

In Fig. 1, the pressure and temperature changes of blank tests under the cooling rate of 10 °C/h (run 1) are typically shown. Two phases of liquid and gas are stable out of hydrate zone, and temperature decrease results into gas compression and gas solubility. Methane hydrate equilibrium curve is extracted from HWHYD software [6]. As shown in Fig. 1-A, once operating condition of reactor (P-T) passes methane hydrate equilibrium curve during cooling step, it is probable that hydrate nuclei form through the bulk of aqueous phase followed by hydrate crystal growth. However, gas compression is present relative to the fluid temperature in the reactor at any moment. In addition, as shown in Fig. 1-B, hydrate formation macroscopic growth is distinguished due to a simultaneous pressure drop with a temperature peak. Neglecting very low methane solubility in water, the moles of gas entering hydrate structure is calculated using Equation 1.

$$\Delta n = \left(\frac{PV}{ZRT}\right)_0 - \left(\frac{PV}{ZRT}\right)_t \qquad (1)$$

In the above equation (Equation 1), P, V, T and R denote for reactor pressure, volume of gas phase, reactor temperature and universal gas constant respectively. Also, Z is calculated using Peng-Robinson equation of state. Subscript 0 is representative of the local zero time based on the onset of hydrate growth, and subscript t denotes for the end time of the test. Here, the end time is considered as 10 hours after the observation of the onset of hydrate formation.

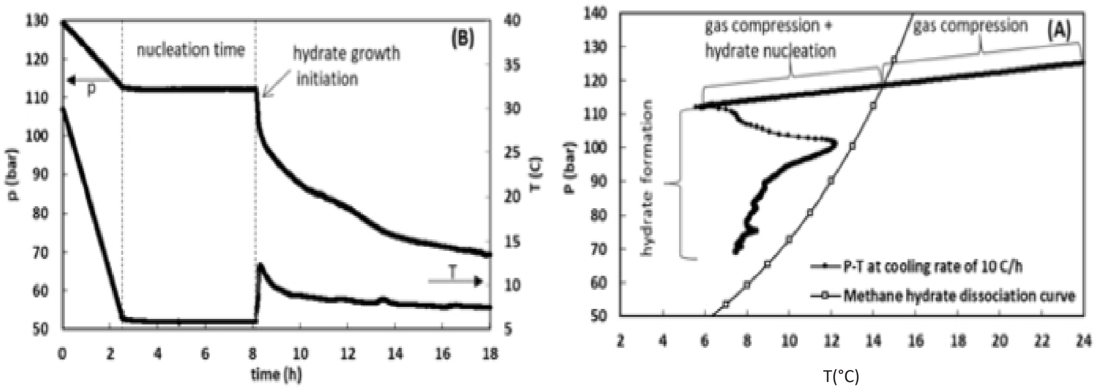

Figure 1: (A) P-T of blank test (run 1) vs. methane hydrate equilibrium curve and (B) P and T profiles under the cooling rate of 10 °C/h.

Pure methane forms sI structure including 5.75 water molecule per 1 gas molecule [1]; therefore, the water to hydrate conversion percentage based on the ideal stoichiometry of hydrate is calculated by Equation 2.

$$\text{Conversion} = \frac{(\Delta n \times 5.75 \times 18.02)}{m_{water}} \qquad (2)$$

The summarized results of blank tests are given in Table 2. It is observed that hydrate growth initiates after the 5.7 hours when the temperature of bath is kept constant at 5 °C for cooling rate of 10 °C/h (run 1). This is called induction time, i.e. although operating temperature and pressure are at the hydrate zone, they remain constant and no macroscopic hydrate growth is detected. For cooling rate of 5 °C/h (run 2), hydrate growth initiates during constant cooling rate step at 7.9 °C of reactor temperature. Furthermore, this temperature is marked to represent the onset of hydrate formation and is called induction temperature.

Although the hydrate kinetic rates are similar for initial 4 hours after the onset of hydrate formation, gas mole consumption increases more for cooling rate of 5 °C/h in comparison with 10 °C/h. Finally, it results in more water to hydrate conversion. The effect of cooling rate on hydrate quality is observed in Fig. 2.

Table 2: Summarized blank tests results.

Run	1	2
Cooling rate (°C/h)	10	5
Induction Temperature (°C)	6.6	7.9
Induction time (h)	5.7	-
Hydrate gas consumption (mole)	1.22	1.36
Water to hydrate conversion (%)	42.1	47.0

Figure 2: Methane hydrate picture formed under the cooling rate of 10 °C/h (top (or above) image) and 5 °C/h (down (or below) image) at the blank tests.

TESTS IN THE PRESENCE OF LIQUID HYDROCARBON

The summarized results of the tests are given in Table 3. In the presence of liquid hydrocarbon with the volume ratio of 1:1 to water, the induction time decreases from 5.7 to 0.3 hours for cooling rate of 10 °C/h, and the induction temperature increases from 7.9 to 11.0 °C for cooling rate of 5 °C/h.

An increase in the water/hydrocarbon volume ratio results into less water to hydrate conversion. It is suggested that droplets of water disperse in bulk of liquid hydrocarbon while the water interface to gas increases, and hydrate is formed around each droplet until the formation of hydrate layer like a barrier separates water from gas and prevents more hydrate formation. As a result, water to hydrate percentage decreases from 42.1 to 40.1 and from 25.7 to 20.7, for cooling rate of 10 and 5 °C/h respectively. The presence of liquid hydrocarbon decreases the time of hydrate completion (duration of hydrate growth) significantly. On the other hand, when the water/hydrocarbon volume ratio increases, duration of hydrate growth decreases more.

CONCLUSIONS

In hydrate formation mechanism, water-gas contact plays an interesting role, and the parameters, which affect it, may control the hydrate formation. Moreover, it is observed that the presence of liquid hydrocarbon causes that (1) the onset of hydrate formation is shifted, (2) water to hydrate percentage is decreased, and (3) duration of hydrate growth is decreased. Furthermore, water-hydrocarbon volume ratio has the significant effect on macroscopic hydrate formation kinetic. Finally, an increase in the water-hydrocarbon volume ratio results in more decrease in water to hydrate percentage and duration of hydrate growth.

Table 3: Summarized results of the tests in the presence of liquid hydrocarbon.

Run	3	4	5	6
Cooling rate (°C/h)	10	10	5	5
Water : hydrocarbon	1 : 1	3 : 1	1 : 1	3 : 1
Induction Temperature (°C)	6.7	9.9	11.0	7.0
Induction time (h)	0.3	-	-	0.0
Hydrate gas consumption (mole)	0.61	0.29	0.38	0.15
Water to hydrate conversion (%)	42.1	40.1	25.7	20.7
Hydrate completion time (h)	4.0	1.5	2.5	0.5

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