The Induction Period of Hydrate Formation in a Flow System*

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Abstract The appearance of turbidity due to large numbers of critical size hydrate nuclei may significantly affect the outgoing light intensity and the flow resistance in the pipe loop. The induction period of hydrate formation was determined by analyzing the experimental data—either based on the shading ratio data of laser detector or based on the pressure drop data of the flow system. The induction period of CCl_2F_2 (R12) in pure water and that of CH_4 in (tetrahydrofuran + water) systems were then measured with the above two methods. Experimental data show that the induction period depends on the driving force exponentially. Flow rate also has a significant influence on the hydrate nucleation. A new induction period model taking the driving force and liquid flow rate into account was proposed. And it is successfully applied to the calculation of the induction period, which is in good agreement with the experimental data obtained in this study.
Keywords hydrate, induction period, flow, laser, model

1 INTRODUCTION

The hydrate formation process is analogous to crystallization process. As in crystallization, the hydrate formation can be divided into nucleation and growth processes. Hydrate nucleation is a process of forming critical sized, stable hydrate nuclei. The induction period is the time elapsed during the nucleation process including formation of gas-water clusters and their growth to critical sized stable nuclei. In general, the induction period data are scattered and stochastic, and they cannot be predicted when the driving force is very small. Large driving force will make the nucleation much certainty so that the induction period can be determined. Hydrate growth is the process of growth of these stable nuclei, and comprehensive research results on the process are available[1−4].

Vysniauskas and Bishnoi[5] studied the influence of the history of water on the induction period for nuclei formation. There was no observable effect on the kinetics of hydrate growth, but the mean induction period varied with the source of water used. A lower mean induction period was observed when water obtained from thawed ice was used compared with that when hot tap water was used. The mean induction period was also lower when water obtained from dissociated hydrates was used. This was known as the memory effect. Sloan *et al.*[6−8] thought that an activation barrier was associated with the cluster coordination number transformation. The induction period was related to the number of cluster transfor-

mation and alternating structures also slowed hydrate kinetics considerably. Skovborg *et al.*[9] measured the induction time for methane, ethane and a mixture of the two gases. Natarajan *et al.*[10] investigated the induction phenomena in hydrate nucleation and reported the induction period for methane, ethane and carbon dioxide hydrates.

The induction period data reported in above literatures were usually obtained in stirred reactors. The obtained values of the induction period were always more than several hours or even several days, which were not in accord with the actual situation in a flow system. In this study, we use a flow loop device to measure the induction period for [CCl_2F_2 (R12)+ water] system and [CH_4 + tetrahydrofuran (THF)+ water] system before hydrate formation. New measurement methods for induction period are also proposed.

2 EXPERIMENTAL

2.1 Experimental setup

The flow loop system built by Sun *et al.*[11] was used to study the kinetics of hydrate in multiphase system and the schematic is shown in Fig. 1. The main body of this flow system is a transparent U-bend double pipe with 20 m in length (made by DB Robinson Corp., Canada). The ϕ25.4 mm inner tube can sustain a pressure up to 4.0 MPa. Coolant is circulating in the annulus of the double pipe through two fluid circulation baths (Neslab RTE 111D). Six thermocouples calibrated to ±0.1 K are installed along the

flow loop. Precision Heise pressure gauge (accurate to ±0.1%, scale from 0 to 1.0 MPa) is used to measure the pressure. The pipe loop is connected to a refrigerated mixing tank where gas hydrate is formed through gas-water contact. A centrifugal pump made in China is used to circulate the heterogeneous mixture through the pipe loop.

A laser granulometer (Model DP-01p, made by OMEC Co., China) is installed in the pipe loop for measuring the hydrate particle size distribution and shading ratio data. The laser light emitted from the emitter traverses through the measured section between two quartz glasses and captured by the receiver. The laser granulometer is capable of measuring particle sizes in the range of 10—1200 μm.

The pressure drop between the inlet and outlet of the pipe loop, points A and B in Fig. 1, is measured using a differential pressure transducer. A PC-based data acquisition system is setup for recording the particle diameter, particle concentration, and system temperature.
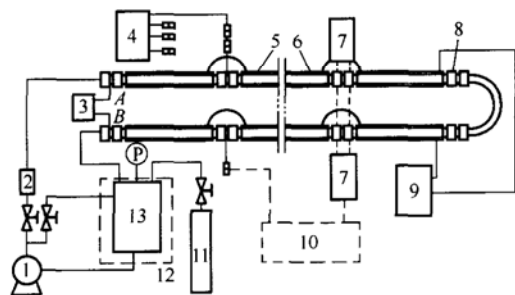

Figure 1   Schematic of the flow system
1—pump; 2—flow meter; 3—differential pressure transducer; 4—scanning thermometer; 5—cooling jacket; 6—inner tube; 7—laser scattering device; 8—swagelok union; 9—criculating bath; 10—data acquisition system; 11—gas cylinder; 12—cooling system; 13—mixing tank

2.2 Experimental methods

In the literatures, the induction period of hydrate was usually measured by analyzing the pressure recording line. An initial sharp decrease in pressure corresponding to the absorption of gas in the water is followed by a period with a more or less constant pressure. And then the equilibrium pressure is reached and the pressure remains constant in the cell until possible hydrate formation starts. As the hydrate grows, the pressure decreases sharply due to the consumption of gas. The induction period can then be determined from the above pressure line. In some cases, the change of pressure cannot be observed definitely.

Observing the appearance of turbidity in the liquid phase from windows in a reactor was another method to determine the induction period of hydrate in the literatures. Owing to the emergence of hydrate particles, the solution becomes translucent, but the size of a

critical hydrate nucleus is not visible to the naked eye. Only when the number of critical sized stable hydrate nuclei is very large, the turbidity can be observed.

In this paper, we propose two new methods to judge the induction period of hydrate formation in a flow system instead of the above two methods.

2.2.1 Shading ratio data analyzing method

The light intension weakens when a light traverses through the measurement zone. The outgoing light intensity I is then less than the incoming intensity I_0, and $(1 - I/I_0)$ is defined as the shading ratio, which is dependent on particle size as well as on particle concentration and length of light path. With a laser granulometer, the background scattering inherent in the system is measured to eliminate the influence of circulating water and saturated gas. The value of shading ratio is equal to zero at this time. When hydrate nuclei form, the shading ratio will change and be larger than zero. The induction time can then be determined from the shading ratio data. Although the laser granulometer cannot measure the critical hydrate nucleus, the appearance of turbidity due to large numbers of critical size hydrate nuclei can significantly affect the outgoing light intensity so that it can be determined by the laser granulometer.

2.2.2 Pressure drop data analyzing method

The pressure drop between the inlet and outlet of the pipe loop depends on the fluid property and its flow rate in the flow system. The pressure drop should keep constant without formation of hydrate. However, the flow resistance will increase with the formation of large numbers of critical size hydrate nuclei. Using a differential pressure transducer, the pressure drop can be measured and the induction period can then be determined from the sharp increase of the pressure drop.

2.3 Experimental steps

The experimental procedure of this study is described as follows:

(1) Clean the flow loop by flushing with a detergent solution and pure water and then evacuate it after draining.

(2) Charge a given amount of fluid into the mixing tank and the flow loop pipe.

(3) Turn on the refrigerator and cool the system to desired temperature. In this work, the experimental temperature was kept at 277.1 K throughout.

(4) Inject gas slowly into the mixing tank until the pressure is raised close to the hydrate equilibrium pressure. Pump the experimental fluid around the pipe loop so that the aqueous phase is saturated with gas and the system pressure remains constant.

(5) Measure the scattering background inherent in fluid and quartz glass to eliminate their influence on

the shading ratio measurements.

(6) Turn off the pump and increase the system pressure to assigned value (by injecting additional gas). Then turn on the pump again and circulate the fluid through the pipe loop at constant flow rate. The data of shading ratio and pressure drop between the inlet and outlet of the pipe loop are recorded by the laser granulometer and the differential pressure transducer at 10 s to 30 s intervals, respectively.

(7) The contact of gas with fluid in the mixing tank will lead to hydrate formation. The induction time experiment ends after formation of a great amount of hydrate.

We used shading ratio data analyzing method to measure the induction period for (R12 + water) system. When THF exists, the fluid is very turbid, so that pressure drop data analyzing method was used instead for (CH$_4$ + THF + water) system.

2.4 Experimental results

The hydrate kinetics for (R12 + water) system was studied using shading ratio data analyzing method. The scattering background was measured when the pressure was close to the hydrate equilibrium pressure to avoid the formation of hydrate. Thus when the system pressure is raised to experimental pressure, the solubility of gas in water will also rise. The outgoing light intensity I will then be a little lager than the incoming intensity I_0 because of the dissolution of gas. And the shading ratio $(1 - I/I_0)$ is a little lower than zero. The outgoing light intensity will decrease after the formation of hydrate nuclei. The induction period can then be determined from the shading ratio data changing from negative to zero. And the obtained induction period at different pressure and flow rate are listed in Table 1. It can be found that both the pressure and flow rate have significant influence on the induction period of hydrate formation. The induction period for (R12 + water) system can also be determined using pressure drop data analyzing method and similar data can be obtained.

For (CH$_4$ + THF + water) system, with the existence of THF, the induction period of hydrate formation is very short at high pressure and flow rate. In addition, shading ratio data analyzing method can not be used because of the turbidity of THF. Therefore, the operation condition at low flow rate (250 L·h^{-1}) was chosen to measure the induction period for (CH$_4$ + THF + water) system using pressure drop data analyzing method. Fig. 2 shows the change of pressure drop between the inlet and outlet of the pipe with time at different pressures. The pressure drop decreases slightly at the initial stage because of the dissolution of CH$_4$ and no hydrate nuclei exists in the solution. After a period of time, which is called as induction pe-

riod, the pressure drop then sharply increases due to the formation of large numbers of hydrate nuclei. The obtained induction period data for (CH$_4$ + THF+ water) system are also listed in Table 1. It can be seen that the induction period is in proportion to the pressure.

Table 1   The induction period of hydrate formation

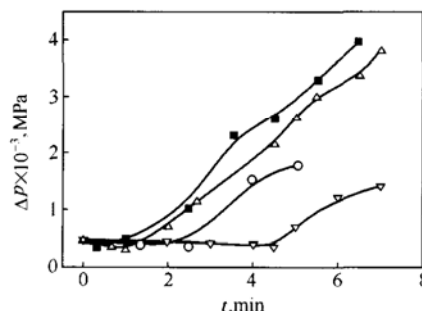|	p, MPa	Q, L·h^{-1}	t_{ind}, min
R12+ water	0.32	1400	0.6
	0.32	930	2.0
	0.32	550	2.5
	0.32	300	6.5
	0.24	1400	2.5
	0.24	930	3.6
	0.24	550	5.5
	0.24	300	14.3
CH$_4$ + THF + water	0.45	250	4.6
	0.50	250	2.5
	0.64	250	1.0
	0.80	250	0.5

Figure 2   Variation of pressure drop with time
($Q = 250$ L·h^{-1})
p, MPa: ■ 0.80; △ 0.64; ○ 0.50; ▽ 0.45

3   MATHEMATICAL MODEL

The induction period t_{ind} can be given as

$$t_{ind} = t_{tb} - t_{eq} \tag{1}$$

Here t_{tb} is the turbidity time when the solid hydrates grow in the solution. t_{eq} is the solubility time when gases dissolute into the liquid and the aqueous solution is not yet saturated. During the experiments, the appearance of the turbidity is quite sudden while a clear solution switches to a translucent one. In this paper, t_{tb} is determined from shading ratio data or pressure drop data.

As in crystallization studies, the rate of hydrate nucleation, R, may be expressed in a form of power law given below

$$R = k(S - 1)^n \tag{2}$$

where k and n are constants and S is supersaturation of gas in liquid. Since the induction period is inversely related to the rate of nucleation, then

$$t_{ind} = \alpha / R^r \tag{3}$$

where α and r are proportionality constants. The value of r is usually different from unity since the dependence of induction period on the nucleation rate may be non-linear. From Eqs. (2) and (3), we obtain

$$t_{\text{ind}} = \frac{\alpha}{k^r}(S-1)^{-nr} \qquad (4)$$

Natarajan et al.[10] defined the driving force for hydrate nucleation as the difference between the fugacity of the dissolved gas in the liquid and the three-phase equilibrium fugacity. Thus $(S-1)$ in Eq. (4) can be replaced by $(f_g^V/f^{eq}-1)$. The induction period is then described by the following equation

$$t_{\text{ind}} = K\left(\frac{f_g^V}{f^{eq}} - 1\right)^{-m} \qquad (5)$$

where K and m are constants.

In this paper, the experimental data are obtained in a flow loop system. The induction period is dependent on system pressure and liquid flow rate. A flow rate parameter is introduced to the induction period model, which is as follows

$$t_{\text{ind}} = K\left(\frac{f_g^V}{f^{eq}}\sqrt{Q/Q_0} - 1\right)^{-m} \qquad (6)$$

where Q is liquid flow rate and Q_0 is a referent flow rate. And Q/Q_0 shows the influence of agitation in a flow system. The three-phase equilibrium fugacity f^{eq} is calculated by the hydrate model proposed by Chen and Guo[12].

The model parameters K and m for (R12 + water) system are regressed from experimental data and the values are 32.028 and −2.083, respectively. The comparison of experimental data for hydrate induction period with calculated results is shown in Fig. 3. As shown in Fig. 3, the induction period decreases with the increase of system pressure at the same flow rate. And the induction period decreases at higher flow rates because of the increase of gas/liquid contact area and stronger turbulence, but the effect of flow rate weakens when flow rate is more than $1000\,\text{L·h}^{-1}$.

Figure 4 shows the experimental data and the calculated results for (CH$_4$ + THF + water) system at different system pressures. The induction period model parameters, K and m, are 22.406 and −2.604, respectively. It can be found that the induction period depends on the driving force exponentially.
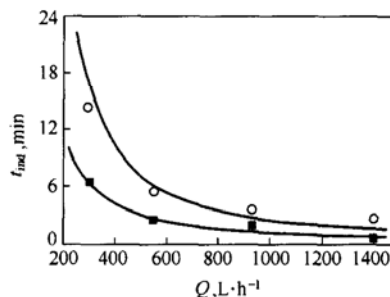

Figure 3   Variation of the induction period with flow rate and system pressure for (R12 + water) system
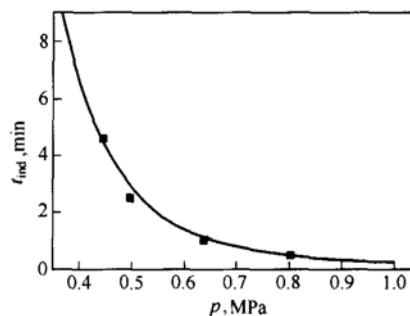■ 0.32 MPa; ○ 0.24 MPa; —— calculated

Figure 4   Variation of the induction period with system pressure for (CH$_4$ + THF + water) system
$(Q = 250\,\text{L·h}^{-1})$
■ exp. data; —— calculated

The measurement of induction period using the two new methods can eliminate the deviation by direct observation from naked eye. Different from those induction period data obtained in a reactor, the induction period data in this paper were measured in a flow system, which was much suitable to the operation condition of pipeline in situ.

4   CONCLUSIONS

A transparent flow loop device was built to study the kinetics of hydrate formation. Shading ratio data analyzing method and the pressure drop data analyzing method were proposed to measure the hydrate formation induction period in a flow system. The hydrate kinetics for (R12 + water) system and (CH$_4$ + THF + water) system were studied using the above two methods, respectively. The experimental data showed that the induction period was related to the system pressure and flow rate. A new model for induction period was proposed taking the driving force and liquid flow rate into account.

NOMENCLATURE

f^{eq} the three-phase equilibrium fugacity, MPa
f_g^V the fugacity of the dissolved gas in the liquid, MPa
I the outgoing light intensity
I_0 the incoming intensity

K constant in Eq. (5)
k constant in Eq. (2)
m constant in Eq. (5)
n constant in Eq. (2)
p pressure, MPa
Q liquid flow rate, $L \cdot h^{-1}$
Q_0 referent flow rate, $L \cdot h^{-1}$
R the rate of hydrate nucleation
r proportionality constant in Eq. (3)
S supersaturation of gas in liquid
t_{eq} the solubility time, min
t_{ind} the induction period, min
t_{tb} the turbidity time, min
α proportionality constant in Eq. (3)

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