Growth Kinetics Behaviors of Hydrate Film on Gas Bubble Suspending in Water with Inhibitors

Xin-Yang Zeng[1,2], Si Zhang [1,2,*], Guozhong Wu[4], Jiang Wang[4], Zhifeng Yang[1,3], Jing-Chun Feng[1,3,*]

1 Southern Marine Science and Engineering Guangdong Laboratory (Guangzhou), Guangzhou, 511458, P. R. China

2 South China Sea Institute of Oceanology, Chinese Academy of Sciences, Guangzhou 510301, P. R. China

3 Institute of Environmental and Ecological Engineering, Guangdong University of Technology, Guangzhou, 510006, P. R. China

4 Division of Ocean Science and Technology, Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, China

ABSTRACT

Gas hydrate formation on gas bubble prefers to exist in the deep-sea pipelines during the oil-gas transportation, resulting into the clogging of pipelines. The hydrate inhibitors are generally added to deal with the huge threat and challenge. This study provided the growth kinetics behaviors of hydrate film on gas ($CH_4 - C_3H_8$) bubble suspending in the water with the inhibitors (ethylene glycol: thermodynamic inhibitor of small molecular weight and LuviCap EG: kinetic inhibitor of big molecular weight, respectively) at extreme high undercooling degree (10 − 15 K), including the growth modes, the lateral growth rate, and the evolution of the morphology and mass transfer channels. The optical microscope was used to observe the kinetics growth phenomenon. Study showed the growth mode of pasty hydrate in the liquid phase instead of hydrated bubble when the inhibitor concentration increased to the critical 8000 ppm. For both inhibitors, the difference is that the craters embodied in the hydrate film were formed for LuviCap EG concentration from 500 to 4000 ppm. These craters were considered as the aggregative LuviCap EG molecules, which attached to the hydrate lattice in the lateral growth of hydrate film. Hence, the craters were a type of new mass transfer channels, accelerating the initial thickening growth of hydrate film. The craters quickly enlarged in the initial thickening and finally formed the uniform and coarse texture. The initial size and the enlarged rate of craters were determined by the concentration of LuviCap EG. In conclusion, the critical concentration indicated that the inhibitors should be added to more than 8000 ppm, which helps keep the good fluidity of oil-gas in the pipeline transportation. The morphology and kinetics behaviors of craters of new mass transfer channels on hydrate film on bubble shed light on the mechanism of hydrate formation in water with hydrate kinetics inhibitor, providing the theoretical basis of the hydrate anti-blockage mechanism for the oil-gas transportation in the deep-sea pipelines.

Keywords: gas hydrate, hydrate inhibitors, clogging of pipelines in oil-gas transportation, mass transfer channel, growth kinetics behaviors of hydrate film, hydrate morphology

1. INTRODUCTION

Gas hydrate plug formed during the hydrate exploitation and deep-sea oil-gas transportation has posed a huge threat and challenge to the safe of the marine energy sources, drawing extensive concern and study in the world (1-2). Adding thermodynamic inhibitor (THI) or kinetics inhibitors (KHI) in the pipeline is a straightforward solution to prevent hydrate formation. In the hydrate exploitation or oil-gas transportation, a large number of gas bubbles were produced (3-4). Gas bubbles provided a preferable site for the growth of gas hydrate. Therefore, the study on the kinetics of hydrate growth on gas bubbles is increasing (5-6). However, all these studies mainly focused on the hydrate growth in pure water, lacking the information on the hydrate growth in the solution with inhibitors. The growth kinetics behaviors of hydrate film on CH_4-C_3H_8 bubble suspending in water with inhibitors was studied in our experiment, including the critical concentration determining whether the hydrate film was formed on the bubble, the texture structure of hydrate film, and the relation of the lateral growth rate of hydrate film with inhibitor concentration. This study will help to
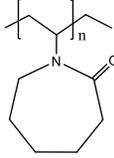
understand the effect of inhibitors on the oil-gas fluidity mechanism in the hydrate exploitation and pipeline transportation.

2. MATERIAL AND METHODS

Hydrate forming gas (95 mol% CH_4 + 5 mol% C_3H_8) used in this work were bought from Wen-Chuan Gas Ltd. Deionized water with a conductivity of less than 10^{-4} S·m^{-1} was used. Two types of inhibitors were used in this experiment (Table 1). Five groups of inhibitor solutions with different concentrations were made-up in the laboratory for MEG and LuviCap EG, respectively (Table 2). A high-pressure optical cell (Fig. 1a) was used in this experiment. Details of the cell referred to Peng et al. (7) and Li et al (8). Experiment methods referred to Zeng et al (9). The lateral growth rate and enlarged rate of mass transfer channels of films were acquired.

Table 1 Molecular structure and manufacturer of the inhibitors used in this study

Inhibitor	Molecular structure	Molecular weight (Da)	Solvent	Effective concentration	Manufacturer
MEG (THI)	$HO-CH_2-CH_2-OH$	62	-	-	Tianjin Yongda Chemical Reagent Company
LuviCap EG (KHI)	PVCap homopolymer	2000	Ethylene glycol	40 wt%	BASF

* THI and KHI refer to thermodynamic inhibitor and kinetic inhibitor, respectively.

Table 2 Solution with inhibitor made-in the laboratory

MEG solution		LuviCap EG solution	
Run	Mass fraction (ppm)	Run	Mass fraction (ppm)
1	500	6	500
2	1000	7	1000
3	2000	8	2000
4	4000	9	4000
5	8000	10	8000

3. RESULTS

The existence of critical concentration determining the formation of the hydrate films on the bubble was found. For thermodynamic inhibitor (ethylene glycol), the smooth film was formed on the gas bubble in the water solution of low inhibitor concentration (500 ppm). When the ethylene glycol concentration increased to between 1000 to 4000 ppm, a layer of flocculent hydrate closely surrounded the initial hydrate film (red circles in Fig. 1b, 1c and 1d). Besides, the thickness of the flocculent hydrate gradually increased (blue arrows in Fig. 1b, 1c and 1d). The hydrate on longer adhered to gas bubble to form the film when the inhibitor concentration in water further increased from 4000 to 8000 ppm (Fig. 1e). Therefor, it was speculated the critical concentration of hydrate film formation should be between 4000 and 8000 ppm. Similar phenomenon existed for the kinetics inhibitor (LuviCap EG) solution, i.e., the hydrate no longer adhered on the gas bubble to form the film in the water with 8000 ppm LuviCap EG (Fig.2). Contrast to the water solution with the ethylene glycol, the heterogeneous structure of the hydrate film was found, i.e., many craters was inlaid in the hydrate film at t_0 for 500, 1000, 2000 and 4000 ppm, respectively (Fig. 2a-2d). The heterogeneous structure vanished when the craters gradually enlarged and finally contacted each other with the thickening of the films according the local magnified texture of hydrate film (Fig. 3).

4. DISCUSSION

The critical concentration phenomenon of the formation of hydrate film on the gas bubble was associated with the inhibitor absorption. Both thermodynamic and kinetic inhibitors could adsorb to hydrate crystal lattices (10). The adsorption hindered the continuous growth of hydrate on the gas bubble, reducing the lateral growth rate of the film. The amount

of inhibitor molecules was enough (more than some critical value) so that the hydrate was surrounded by the
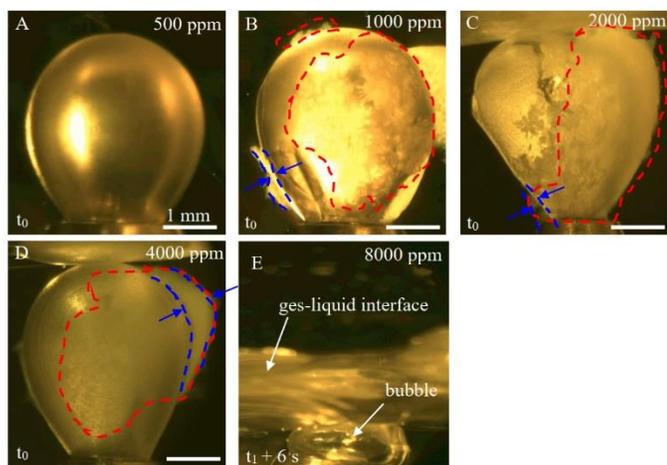

Fig. 1 Hydrate formation on gas bubble suspended in water with 500 (Run 1), 1000 (Run 2), 2000 (Run 3), 4000 (Run 4), and 8000 (Run 5) ppm MEG, respectively. t_0: the time of lateral growth end or thickening growth beginning; t_1: the initial time of hydrate formation at planar gas-liquid interface.
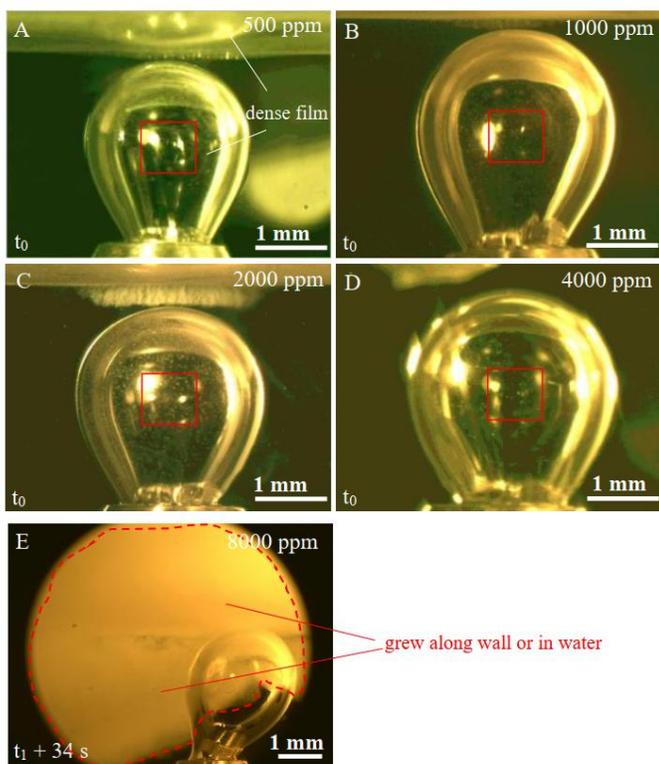

Fig. 2 Hydrate formation on gas bubble suspended in water with 500 (Run 6), 1000 (Run 7), 2000 (Run 8), 4000 (Run 9), and 8000 (Run 10) ppm LuviCap EG, respectively.

inhibitor molecules in the formation of hydrate. In this circumstance, the aggregation ability of hydrate was extremely weak. Accordingly, the scattered flocculent hydrate instead of the massive hydrate film was formed

when the inhibitor concentration was 8000 ppm in the experiments (Fig. 1e and 2e).

The heterogeneous structures (craters and smooth film) of hydrate films were due to the absorption and aggregation of some LuviCap EG molecules to the front edge of the film in the lateral growth. The film bypassed these absorptions and aggregations and continuously grew. The aggregations were called "craters" here. Them became a type of new mass transfer channels for the initial thickening of hydrate films. The evolution of channels was shot by the microscope (Fig. 3).
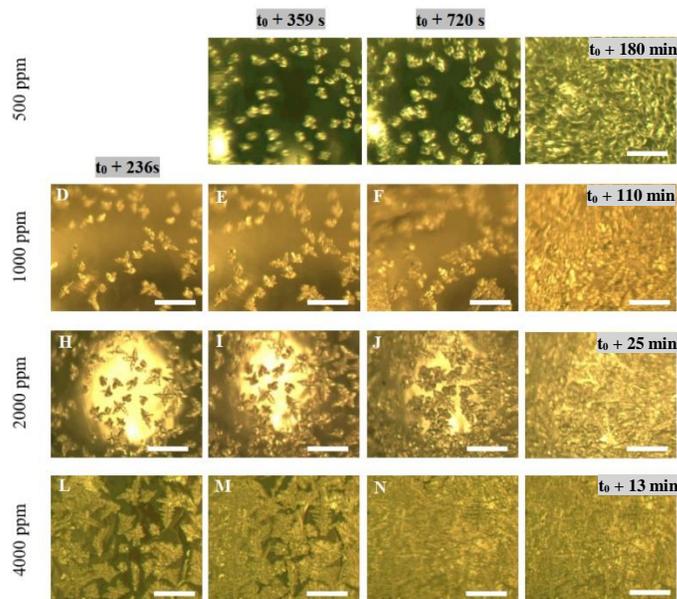

Fig. 3 Local magnified texture of hydrate film formed on gas bubble suspended in solution with 500 ppm (Run 6), 1000 ppm (Run 7), 2000 ppm (Run 8), and 4000 ppm (Run 9) LuviCap EG during thickening growth, respectively.

The transportation of the gas molecules or water molecules in the craters was easier than in the hydrate from one side to another of the film. Therefore, the further hydrate growth preferred in the craters in the initial thickening. The enlarged average rate and initial size of craters were expressed (Fig. 4). The initial area (S_{t0}) and the enlarged rate (V_e) are linearly related to the concentration.

5. CONCLUSIONS

The critical concentration determining the formation of the hydrate film on gas bubble was found in this paper. The critical concentration can be used as an important indicator of inhibitor amount added in oil-gas transportation. For example, in our experiment, more than 8000 ppm KHI should be added to guarantee the fluidity of oil-gas transportation. However, the clogging
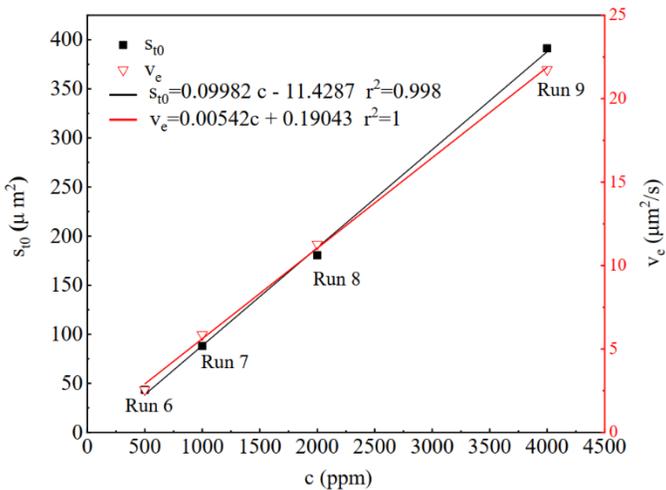
Fig. 4 Initial size (black) and average enlarged rate (red) of craters inlaid in hydrate films formed in solution with 500 ppm (Run 6), 1000 ppm (Run 7), 2000 ppm (Run 8), and 4000 ppm (Run 9) LuviCap EG, respectively.

mechanism of hydrates in pipeline were complicated and related many factors such as bubble velocity, gas-liquid ratio, subcooling, and gas composition et al. The further experiment should be conducted in the flow loop to verify or adjust the index of the critical concentration. Besides, a type of new mass transfer channels, the heterogeneous structures of hydrate films, were found. The enlarged rate and morphology evolution of craters in thickening shed light to the kinetics mechanism of hydrate formation on gas bubble in water with KHI. Further experiments should be designed to study the composition evolution of craters by Raman spectroscopy.

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