



Characterization of kinetics of hydrate formation in the presence of kinetic hydrate inhibitors during deepwater drilling



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ARTICLE INFO

Article history:

Received 9 October 2014

Received in revised form

3 December 2014

Accepted 5 December 2014

Available online 10 December 2014

Keywords:

Analysis method

Kinetics of hydrate formation

Kinetic hydrate inhibitor

Lactam

Deepwater drilling

Dynamic condition

ABSTRACT

An analysis method to characterize the kinetics of gas hydrate formation in downhole dynamic conditions was introduced by combining two plots, one is the pressure versus temperature plot, and the other is pressure and temperature versus time plot. By means of the combined method, the induction time, hydrate growth period and catastrophic formation period could be identified. The typical kinetic hydrate inhibitors (KHIs) which were all vinyl lactam polymers, were chosen for testing, including PVCap (Polyvinyl caprolactam), PVPC (vinyl pyrrolidone/vinyl caprolactam) and VVA (vinyl pyrrolidone/vinyl caprolactam/AMPS). The kinetics of hydrate formation in bentonite mud containing the typical KHIs were experimentally investigated under 3000 m deepwater drilling condition. The results show that these KHIs are more efficient in preventing hydrate growth than nucleation, which means the inhibition mechanism of vinyl lactam KHI polymers is growth inhibition. As the concentration increases, the inhibition effect of these KHIs on hydrate growth gets stronger, thus the delay of catastrophic hydrate formation gets longer, while the induction time can only increase slightly.

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1. Introduction

Gas hydrate formation is a serious safety assurance concern in oil and gas industry, especially in deepwater drilling operations (Barker and Gomez, 1989; Zamora et al., 2000; Kelland and Iversen, 2010). Gas hydrate formation occurs easily in the condition of high pressure and low temperature in deep sea, and cause blockage in pipelines or/and Blow Out Preventers, which would lead to serious safety problems. At present, there have been several ultra-deep water wells drilled in water depth greater than 3000 m. Taking The Gulf of Mexico and The South China Sea for example, at a water depth of 3000 m, the pressure at the seabed is up to 30 MPa, and the temperature is as low as 2–4 °C, where hydrate formation is a prominent problem for drilling operations. Practices show that adding hydrate inhibitors into drilling fluids is an efficient path to control hydrate formation during deepwater drilling. It is known that thermodynamic hydrate inhibitors (THIs) including sodium chloride, methanol and glycol are the most popular hydrate inhibitors in oil and gas industry (Yousif, 1996; Ebeltoft et al., 1997; Talaghat, 2014a,b). However, a high concentration of THIs may be

required for deepwater drilling, which would lead to high cost, high drilling fluid density, and raise logistical and environmental concerns. Kinetic hydrate inhibitors (KHIs) were thought to be a better alternative for hydrate control in deepwater drilling with low environmental impacts and low costs. The typical commercial KHIs are mainly vinyl lactam polymers containing five-membered lactam rings or/and seven-membered lactam rings, such as PVP (polyvinyl pyrrolidone), PVCap (polyvinyl caprolactam), vinyl pyrrolidone/vinyl caprolactam copolymer, and some lactam terpolymers. KHIs cannot avoid hydrate formation, but can hinder hydrate nucleation or/and growth by adsorbing to nucleation sites or/and growth sites (Yang and Tohidi, 2011; Fernando and Kelland, 2013). In deepwater drilling operations, either of the two inhibition effects can reduce or even eliminate the risk of hydrate blockages. At present, there have been lots of reports on the development and property evaluation of KHIs, while the effects of these polymers on kinetics of hydrate formation under downhole dynamic conditions are in need of further study for deepwater drilling applications. It is considered that such research would help to get a better understanding of how KHIs actually work in deepwater drilling operations, and then make a better use of KHIs to minimize the impact of hydrate formation during deepwater drilling.

The hydrate inhibition performance or features of KHIs have been studied with various analysis methods. The performance of

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KHIs in deepwater drilling fluids with clays was studied by plotting the gas consumption as a function of time (Kelland et al., 2008). The process of hydrate formation was investigated according to the sign of pressure drop in the isothermal method, but nucleation may occur without being detected (Villano and Kelland, 2011). The hydrate nucleation time could be identified under static condition using a high pressure micro-differential scanning calorimeter (Daraboina et al., 2013). The kinetics of gas hydrate formation with the presence of PVP, modified starch and surfactants were experimentally studied based on the gas consumption rate (Talaghat, 2013; Karimi et al., 2014). An experimental study on the inhibition mechanisms of KHIs using ultrasonic test technique suggested that, three periods of gas hydrate formation could be identified, PVCap could prevent hydrate growth while VP/BA could prevent hydrate nucleation (Yang and Tohidi, 2011). However, due to the restrict of experimental apparatus and methods, there is still a lack of experimental evidence about the kinetics of hydrate formation in the presence of KHIs in downhole dynamic conditions during deep or ultra-deep water drilling. Moreover, a majority of previous works published on this subject were conducted without added bentonite, while in drilling operations, bentonite was used to prepare drilling fluids for rheology and filtrate control. In addition, there would be drilling cuttings suspended in drilling fluids, and bentonite is usually used to simulate drilling cuttings in laboratory studies. Therefore, experiments should be carried out under a dynamic condition with bentonite to simulate the real downhole conditions during deepwater drilling, and a corresponding research method is also needed.

In this work, with a simulating apparatus for the measurement of hydrate formation, an analysis method to characterize the kinetics of hydrate formation in dynamic drilling conditions was introduced by combining two plots, one is the pressure versus temperature plot, and the other is pressure and temperature versus time plot. By means of the combined analysis method, three KHI polymers, PVCap (polyvinyl caprolactam), PVPC (vinyl caprolactam/vinyl pyrrolidone copolymer) and a ternary polymer inhibitor VVA (vinyl caprolactam/vinyl pyrrolidone/AMPS terpolymer) were selected, and the kinetic processes of natural gas hydrate formation in bentonite muds containing these KHIs were studied under 3000 m deepwater drilling condition.

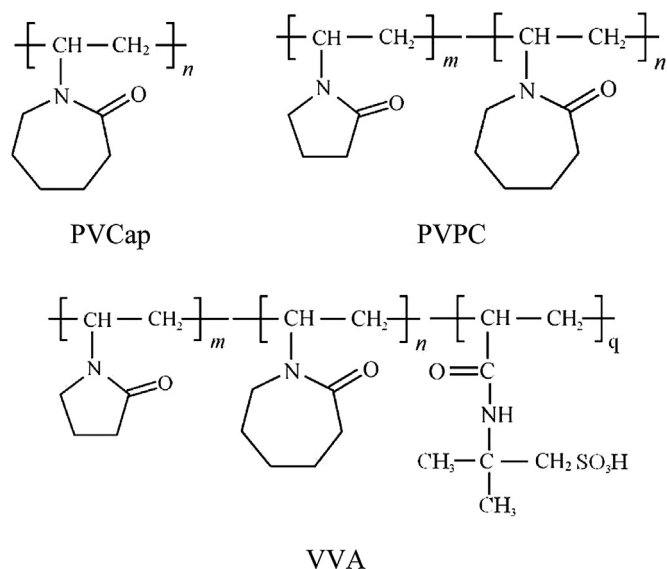


Fig. 1. Structures of KHI polymers tested.

2. Experimental section

2.1. Materials

PVCap, PVPC and VVA were synthesized in our laboratory (Zhao et al., 2013). All these inhibitors are vinyl lactam polymers, and the polymer structures are given in Fig. 1. The Fourier transform infrared spectra (FT-IR) of these polymers were recorded by a NEXUS FT-IR spectrometer (Thermo Nicolet Corporation), as shown in Fig. 2. For these polymers, the band at 2940 cm^{-1} indicated the $-C-H$ stretching vibration, the band at 1650 cm^{-1} indicated the $-C=O$ stretching vibration, the band at 1540 cm^{-1} indicated the $-N-C=O$ stretching vibration. For VVA, the band at 1200 cm^{-1} and 1049 cm^{-1} indicated the stretching vibration of sulfo group. The impurity of these KHI polymers is diethyl ether, which was used in purification. Sodium bentonite was obtained from Huawei bentonite company China, and was determined to have a cation exchange capacity of $70\text{ mmol}/(100\text{ g})$. The standard natural gas which forms structure II hydrates was used in all experiments, and the composition is given in Table 1.

2.2. Apparatus and procedure

A simulating apparatus was designed to evaluate the inhibition property of hydrate inhibitors, as illustrated in Fig. 3. It can simulate the condition of high pressure and low temperature in deep and ultra-deep sea. The high pressure autoclave is made of stainless steel, and the total volume is 750 mL, this relative large volume could reduce the stochastic effect for hydrate nucleation (Villano and Kelland, 2011), thus ensuring experimental repeatability. The autoclave is equipped with a stirrer mechanism, which can be regulated to keep a constant speed in the range 0–1000 rpm, and the torque is monitored in real time using torque sensor. The operating temperature is controlled by a circulator bath through a

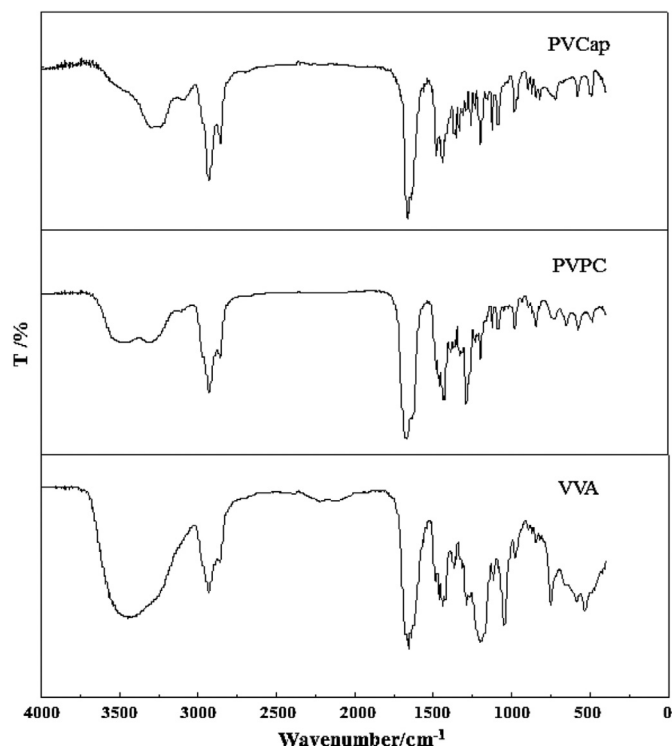


Fig. 2. FT-IR spectra of KHI polymers tested.

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