The Synergism of PEG to Kinetic Hydrate Inhibitor

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ABSTRACT

The inhibiting effect of Inhibex 301 for the CH₄ + C₂H₆ + C₃H₈ gas mixtures + brine systems was assessed using a high pressure sapphire cell. The onset time of hydrate formation was determined by visual observation. The hydrate onset time of Inhibex 301 was prolonged apparently by the addition of polyethylene glycol (PEG). The subcooling of Inhibex 301 was improved dramatically after PEG was added. PEG is thought to be synergic with Inhibex 301 in the hydrate inhibition.

KEY WORDS: gas hydrate; kinetic inhibitor; assessment; PEG; synergism.

INTRODUCTION

In oil and gas industries, pipelines and production facilities might be blocked by gas hydrate, which is a kind of crystalline compounds formed by gas and water. It is well known that gas hydrate is stable at high pressure and low temperature. The temperature in offshore pipelines is usually low and the pressure is high enough to form gas hydrate. In order to reduce the risk of hydrate plug in pipelines, several methods are used (Sloan and Koh, 2008). The most popular method adopted at the present is the addition of thermodynamic inhibitors into the pipelines. The thermodynamic inhibitors could elevate the formation conditions, either lower the formation temperatures at given pressure or increase the formation pressure at given temperature. Methanol and glycols are two typical thermodynamic hydrate inhibitors which are widely used in oil and gas industries. The concentration of methanol and glycols may reach 50 wt % on the free water basis. Toxicity of methanol limits its application for environmental concerns. Moreover, the thermodynamic inhibitors are costly (Sloan and Koh, 2008). The costs make a critical burden on oil and gas industries.

For the pipelines in deep marine environment, the risk of hydrate plug increases because of lower temperature. For the purpose of the avoidance of the costly thermodynamic hydrate inhibitors, oil and gas industry has been making variety efforts to seek new hydrate inhibitors for decades. Low dosage hydrate inhibitors (LDHIs) were then developed and the concentrations of LDHIs are typically lower than 1.0 wt %. There are two kinds of LDHIs based on the inhibit mechanisms: the kinetic hydrate inhibitors (KHI) and anti-agglomerates (AAAs) (Kelland, 2006). The KHI interferes with the nucleation and the growth of hydrate crystals. In contrast, the AAAs do not retard the formation of hydrate particles, but preventing them from agglomerating and accumulating into large masses. Most of the KHI are polymers or copolymers (Larsen et al., 1998; Arjmandi et al., 2002; Moon et al., 2005; Lee and Englezos, 2006; Zeng et al., 2006). The first breakthrough in KHI is the discovery of poly vinylpyrrolidone (PVP) which was found delaying the formation of THF hydrates (Sloan, 1995, 1999). Afterwards, Gaffix VC-713 from ISP was found to have better performance than PVP. Poly vinylcaprolactam was thought as the key monomer in VC-713. Most of the ISP patents were applied based on VCap polymer (Bakeev et al., 2000, 2001, 2002). Some commercial kinetic hydrate inhibitors were also developed by ISP. Inhibex 301 is one of the new products developed by the ISP Corporation to substitute Inhibex 713.

In this work, the inhibiting effect of Inhibex 301 for the CH₄ + C₂H₆ + C₃H₈ gas mixtures + brine system was assessed by visual observation method. The inhibition effect of polyethylene glycol (PEG) on hydrate growth was experimentally measured. Inhibex 301 combined with PEG showed good performance in kinetic hydrate inhibition. The effect of the synergism of PEG to Inhibex 301 at different ratio is experimentally determined.

EXPERIMENTAL APPARATUS AND PROCEDURES

Since KHI retard the nucleation and the growth of hydrate, the onset time of hydrate particles is the most critical parameter which indicating the inhibiting effect of KHI. Moreover, the growth characteristic of hydrate particles also implies the retarding effect of KHI during the hydrate growth process. The onset time of hydrate formation is defined as the time taken from the beginning of gas dissolving into the aqueous phase to the first very tiny detectable hydrate crystals appearing in the aqueous phase or on the cell wall. In this work, the onset time was determined by visual observations in a fully visible sapphire cell.

Experimental apparatus

Schematic of the apparatus used in this work is shown in Fig. 1. The key part of the apparatus is a transparent sapphire cell (2.54 cm in inner diameter and 10 cm in length). The details of this apparatus were described elsewhere (Sun et al., 2003; Zhang et al., 2006). In brief, the transparent sapphire cell was housed in an air-bath and equipped with a