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Unusual kinetic inhibitor effects on gas hydrate formation

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Abstract

Gas hydrate formation experiments were conducted with a methane–ethane mixture at 273.7 or 273.9 K and 5100 kPa and using water droplets or water contained in cylindrical glass columns. The effect of kinetic inhibitors and the water/solid interface on the induction time for hydrate crystallization and on the hydrate growth and decomposition characteristics was studied. It was found that inhibitors GHI 101 and Luvicap EG delayed the onset of hydrate nucleation. While this inhibition effects has been reported previously some unusual behaviour was observed and reported for the first time. In particular, the water droplet containing GHI 101 or Luvicap EG was found to collapse prior to nucleation and spread out on the Teflon surface. Subsequently, hydrate was formed as a layer on the surface. Catastrophic growth and spreading of the hydrate crystals was also observed during hydrate formation in the glass columns in the presence of the kinetic inhibitor. Finally, when polyethylene oxide (PEO) was added into the kinetic inhibitor solution the memory effect on the induction time decreased dramatically.

Keywords: Gas hydrates; Kinetic inhibitors; Water droplets; Morphology

1. Introduction

It is well known that gas hydrates may block hydrocarbon transportation lines. Therefore, various mitigation strategies have evolved which are classified either as thermodynamic or kinetic inhibition methods (Sloan, 1998). Thermodynamic methods use methanol and glycol (10–50% of the water phase), but are costly in offshore developments and onshore processing facilities (Dholabhai et al., 1992; Lovell and Pakulski, 2003). Kinetic inhibition methods are based on the injection of polymer-based chemicals at low dosages in the water phase (Fu, 2002; Huo et al., 2001; Koh et al., 2002). Kinetic inhibitors do not prevent the formation of hydrates but either delay their onset or modify them to reduce the agglomeration tendency (Englezos, 1996; Sloan, 1998). It is noted that in an analogous fashion antifreeze glycoproteins in the blood of Antarctic fish enable them to exist below 0 °C (Zeng et al., 2003; Marshall et al., 2004).

Gas hydrate formation is a complex multiphase crystallization process (Davidson, 1973; Englezos, 1993; Ripmeester, 2000; Koh, 2002; Sloan, 2003a,b). As such it is difficult to observe experimentally and various approaches have been followed to monitor hydrate formation and decomposition at different levels of detail (Sloan, 2003a,b). Morphology studies involve observations of hydrate formation at fluid/fluid interfaces and offer valuable information on the mechanistic aspects of crystal nucleation, growth, and decomposition (Maini and Bishnoi, 1981; Sugaya and Mori, 1996; Ohmura et al., 1999; Unchida et al., 1999, 2000; Servio and Englezos, 2003a,b; Ohmura et al., 2004, 2005; Lee and Englezos, 2005a).

These studies complement traditional gas uptake measurements (Englezos et al., 1987), structural investigations (Ripmeester, 2000; Udachin et al., 2002; Sloan, 2003a; Koh, 2002) and molecular simulations (Tse and Klug, 2002). Thus, it would be of interest to employ morphological observations in hydrate systems in the presence of kinetic inhibitors. One such study has been reported by Sakaguchi et al. (2003). In particular, the effect of two kinetic inhibitors

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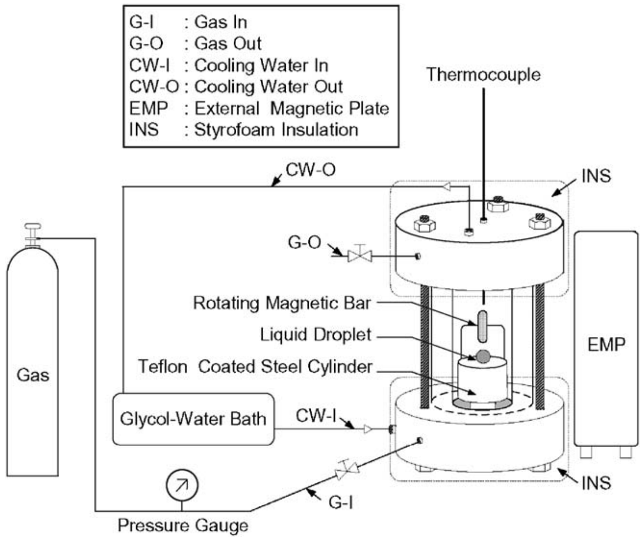

Fig. 1. Apparatus.

poly(*N*-vinylpyrrolidone) and poly(*N*-vinylcaprolactam) on structure II hydrates was studied with a model system involving HCFC-141b (CH_3CCl_2F) hydrate. It is noted that the kinetic inhibitor effects are usually studied in stirred vessels or flow loops (bulk systems).

In this work, we present the results from methane–ethane hydrate formation on water droplets containing kinetic inhibitors and in water enclosed in narrow cylindrical glass columns. A noteworthy property of the CH_4–C_2H_6 system is that although CH_4 and C_2H_6 are known to form structure I hydrate, the binary gas mixture forms structure II hydrate at certain compositions (Subramanian et al., 2000a,b). Kinetic inhibitor effects on gas hydrate formation of natural gas components in water in such systems have not been reported previously.

2. Experimental

Two types of gas hydrate formation experiments were conducted. In one arrangement, hydrate formation on three water droplets was observed. The second arrangement involved hydrate formation in water contained in narrow glass columns. The hydrate forming gas was a mixture with 89.4% CH_4 and the balance was C_2H_6.

A detailed description of the apparatus shown in Fig. 1 and the procedure is given elsewhere (Lee and Englezos, 2005a). Briefly, it consists of a crystallizer with a magnetic bar which rotates vertically to agitate the gas phase. The crystallizer is immersed in a cooling bath that contains a 50–50 wt% mixture of water and ethylene glycol. The hydrate crystals are monitored using a Nikon SMZ 2000 microscope fitted with digital camera. The procedure involves wiping the internal surface of crystallizer with a cotton cloth to remove moisture followed by injection of water droplets containing kinetic inhibitor on the Teflon surface of the crystallizer.

Table 1
Kinetic inhibitors

Product	Supplier
GHI 101	ISP technologies (Wayne, NJ, US)
Luvicap EG	BASF corporation (Charlotte, NC, US)
PVP	ALFA AESAR (Ward Hill, MA, USA)
NEL-411-31	ISP technologies

Table 1 presents the kinetic inhibitors used. Hydrate-forming gas was then added and withdrawn from the crystallizer in order to remove any residual air. When the temperature became stable the hydrate forming gas was fed and the magnetic stirring was started. This is time zero for the measurement of the induction time for hydrate formation.

Three cylindrical glass containers with a 6 mm diameter and 33 mm height containing 0.2 cm^3 of water or aqueous inhibitor solution were placed in the crystallizer. Experiments involved the formation of hydrates three times at 5100 kPa and 273.7 K. Following first or second formation the hydrate crystals were decomposed at 1 atm. However, the decomposition of hydrates formed for the third time was carried out at 1000 kPa instead of 1 atm. The water from the decomposed hydrates was kept at the decomposition pressure for one hour and was used for the subsequent hydrate formation.

Experiments were also carried out in two other cylindrical glass columns with a height of 40 mm and diameters equal to 3.5 and 10 mm. The amount of water added is given in Table 5. The procedure was similar to the one followed for the previous glass columns. The decomposition pressure was 1000 kPa. It is noted that the equilibrium hydrate formation pressure at 273.9 K is 1634 kPa.

3. Results and discussion

The experimental conditions and measured induction times for hydrate formation on water droplets are given in Table 2. As seen, the addition of a small amount (0.5 wt%) of inhibitors GHI 101 and Luvicap EG delayed the onset of nucleation. Inhibitor GHI 101 was the strongest. The induction time was much longer when water and small amount of GHI 101 was used. On the other hand PVP and NEL-411-31 did not delay the nucleation. PVP is known to be a weak kinetic inhibitor. For example it exhibited a small effect in methane hydrate formation experiments (Lee and Englezos, 2005b). It is also seen that 2-butoxyethanol by itself is not a kinetic inhibitor. However, this chemical is known to enhance the performance of kinetic inhibitors (Cohen et al., 1998a,b). In experiment 5 a small amount of polyethylene oxide (PEO) was also included but the induction time was same as that with GHI 101 alone. It was recently found that PEO has a synergistic effect with this kinetic inhibitor (Lee