



Evaluating polymeric inhibitors of ethane clathrate hydrates



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ABSTRACT

Inhibitions of gas hydrates under severe conditions such as high subcooling temperature using kinetic hydrate inhibitors (KHIs) is practically challenging. However, KHIs are favorable than thermodynamic inhibitors (THIs) because of economical and environmental reasons. Therefore, fundamental understandings of polymers performance in high severity conditions are essential to rationally design effective KHIs for this type of application. In this paper, polyvinylpyrrolidone, polyethyloxazoline and low and high Mw of polyethylene glycol (200 MW and 20,000 MW) were investigated as kinetic ethane clathrate hydrates inhibitors. Performance was evaluated in terms of the induction time to nucleation and the total number of moles of ethane enclathrated in the hydrate. The induction time to nucleation was observed to scale in order of increasing performance as polyethylene glycol (20,000 MW), polyvinylpyrrolidone, polyethylene glycol (200 MW), and polyethyloxazoline. Polyethylene glycol leads to the lowest yield of ethane in the clathrate hydrate, while polyethyloxazoline and polyvinylpyrrolidone lead to similar high yields near the polymer-free system. The performance observed was supported by computational modeling using density functional theory (DFT), where infra-red (IR) band shifts were calculated for the polymer surrogates in hydrated forms. Additionally, bond distance, interaction energy, and atom charge of polymer surrogates molecules in the hydrated state were calculated. These calculations were correlated with the performances of polyvinylpyrrolidone and polyethyloxazoline as kinetic inhibitors of ethane clathrate hydrates.

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1. Introduction

Natural gas clathrate hydrates are solids in which water forms hydrogen bonded structures enclathrating natural gas guest molecules. The water is tetrahedrally coordinated to enable building of three-dimensional clathrate hydrate structures that vary with the size of guest molecules and formation conditions (i.e., pressure and temperature). Hydrate structures readily formed are known as sI, sII and sH (Kirchner et al., 2004). The small cage in sI is formed by linking twelve pentagons to form a pentagonal dodecahedra (5^{12}), while the large cage is a tetracapped dodecahedra ($5^{12}6^2$) having two

opposite hexagonal faces and twelve pentagonal faces (Barone and Chianese, 2009). Cage selection can be achieved by changing the guest molecules with the larger ones (e.g., propane) directing water structure to form the larger cages found in sII hydrate (i.e., $5^{12}6^4$).

Under gas and oil production conditions (high pressure and low temperature), natural gas clathrate hydrates are formed posing safety and operational issues. Several techniques are used to inhibit natural gas clathrate hydrate. One technique insulates and heats the pipelines so that the conditions of pressure and temperature where the natural gas clathrate hydrate is formed are not achieved (Mokhatab et al., 2007). Another technique is to dehydrate the fluids so that they contain no water. Two chemical-based processes are more relevant to the present work. These processes pump formulations into the pipelines to modify the properties of the fluids being delivered. The first process uses thermodynamic hydrate inhibitors, which change the thermodynamic conditions (i.e., pressure and temperature) at which the hydrates form. These types of solutions are typically ethylene glycol or methanol, which are

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introduced into the fluid being delivered at relatively high concentrations (up to 60–80 wt% of the water cut) (Masoudi et al., 2004). THIs were employed at early stages of the natural gas clathrate hydrate inhibition. Recently, the utilization of THI in offshore production has declined because of costs associated with the large volumes of additives, separations and environmental impact (Kelland, 2006). A second process called kinetic hydrate inhibitors, which occupies less than 1 wt% of the water cut, is often based on water-soluble polymer like polyvinylpyrrolidone and polyvinyl caprolactam (Reyes and Kelland, 2013). This process has shown greater advantage over the THIs method because of its low cost and moderate safety. The mechanism of these polymeric inhibitors consists of interacting with hydrate surface during the formation stage to delay the nucleation and crystal growth. The interactions believed to be through hydrogen-bondings and weak Van der Waals interactions (Reyes and Kelland, 2013).

Mechanisms of natural gas clathrate hydrate formation must be well understood to be inhibited by KHI chemical action. To date, this has been accomplished with molecular dynamic modeling (Jacobson et al., 2011). Modeling shows that natural gas clathrate hydrates form along a pathway wherein dissolved guest molecules (i.e., natural gas) quasi-equilibrate with an enriched guest separated phase (i.e., the nuclei). This phase changes irreversibly to become a structured natural gas clathrate hydrate (Jacobson et al., 2010). This modeling is in contrast to the labile cluster model where cages spontaneously enclathrate solvated guest molecules and assemble to form the hydrates (Sloan and Fleyfel, 1991), but it is similar to the model of Radhakrishnan and Trout (Radhakrishnan and Trout, 2002). Taking the most recent modeling work of Jacobson and coworkers as highly accurate (Jacobson et al., 2010), one way to inhibit natural gas clathrate hydrate would be to change the surface energy at the interface of the nuclei and the bulk solution, such that the surface area (along with the volume) of the nuclei decreases to disappearance. Another possible way to inhibit the natural gas clathrate hydrates would be to add into the system a polymer attracted to the nuclei core (i.e., a polymer more hydrophobic than the bulk solution) to disrupt the structuring process (Rodger, 2011). The simulated nuclei is also interesting, considering other work on the topic, such as the presence of the hysteresis effect when reproducing the clathrate hydrate in a system (Sefidroodi et al., 2013). This was claimed to be due to the presence of meta-stable clusters of hydrate while computational modeling shows that there are no meta-stables clusters present (Rodger, 2000).

In this paper, we aim to investigate the performance of polymeric inhibitors and their structure–property relationships under severe conditions of gas hydrates formation. In some gas fields, where the process conditions are considerably severe, high dosage of KHIs (around 2%) is used to provide protection against hydrate formation (Lavallie et al., 2009). However, under high subcooling temperature (above 8 °C) and at high pressure in the presence of sour gas, thermodynamic inhibitor is indispensable because KHIs cannot provide protection even if 5% is used (Kelland, 2006). Therefore, rational design of polymers based on fundamental understandings of polymer properties is required to develop high performance inhibitors. Here results are presented from investigating polymers as kinetic inhibitor of ethane clathrate hydrates under high subcooling temperature. The performance of the polymers is measured based on the induction time to nucleation, and the total number of moles of enclathrated ethane.

The ethane clathrate hydrate system forms an sI hydrate, the same structure formed in natural gases rich in methane (Subramanian et al., 2000; Kida et al., 2010), although modeling suggests some sII may also form along the pathway to the clathrate hydrate (Xu et al., 2011). A similar system has been investigated by Clarke and Bishnoi to understand decomposition of ethane

clathrate hydrate and by Morita and coworkers to investigate the packing of ethane into the hydrate cages (Clarke and Bishnoi, 2000; Morita et al., 2000). In Morita et al. work, a mixture of ethane, water, and liquid ethane was used at temperatures ranging from 290 to 324 K and pressures ranging from 200 to 4790 bar, unlike our present work which utilizes only ethane gas and water with one subcooling temperature (Morita et al., 2000). Clarke and Bishnoi work presents different approach of studying ethane clathrate hydrate decomposition in an isothermal and isobaric reactor, at temperatures ranging from 274.15 to 281.15 K and pressures between 5 and 11 bar (Clarke and Bishnoi, 2000). Both studies did not address the inhibition of ethane clathrate hydrate using polymeric inhibitors under severe conditions, and the contribution of polymer–water interactions to the inhibition performance.

In addition, the evaluated polymers as KHIs are investigated in this study using molecular computational modeling. The aim is to develop a computational method to understand the polymer–water interactions, and find a link between the modeled parameters and the experimental findings of ethane clathrate hydrates inhibitions.

2. Experimental

2.1. Materials

Polyethyloxazoline (50,000 MW), polyvinylpyrrolidone (40,000 MW), and polyethylene glycol (200 MW) were purchased from Sigma–Aldrich. Polyethylene glycol (20,000 MW) was purchased from Polysciences. Deionized water (DI) was obtained by Milli-Q system in our laboratory with $18 \text{ M}\Omega \text{ cm}^{-1}$ resistivity. All chemicals were used as received without further purification. The ethane gas purity is 99.5%.

2.2. Autoclave reactor for ethane clathrate hydrates formation

Investigation of ethane clathrate hydrates growth for evaluating polymer as KHI was conducted in a 3 L stainless steel Buechi-GlasUster autoclave reactor equipped with pressure and temperature data acquisition software. Schematic description of the experimental setup is presented in Fig. 1. Temperature moderation was performed by a Julabo cooling unit, which can readily cool the reactor to $263 \pm 1 \text{ K}$ by way of a 0.6 L reactor cooling jacket. Ethane and nitrogen were charged into the reactor by a valve at the reactor head. The reactor was also equipped with a pressure release port and a sapphire window for viewing ethane clathrate hydrates. The reactor was charged with a 33 wt% water cut (i.e., 1 L), and 3 wt% of the water cut was polymer. Ethane gas was charged into the vessel through the head valve in the reactor, and was kept purging for 5 min to remove the air. Then the pressure is increased to the target pressure ($15.7 \pm 0.2 \text{ bar}$). Once the pressure inside the reactor is stabilized, the temperature of the reactor was set at 275 K using the external chiller, and the stirring was immediately turned on. The reactor was operated at $300 \pm 20 \text{ rpm}$ stir rate. The pressure and temperature inside the reactor were kept recording during the experiment.

The ethane clathrate hydrates phase envelope, bubble points and ethane solubility were calculated with HYSYS-AspenTech software suite using Peng–Robinson equation of state (EOS) as a fluid package and Colorado School of Mines (CSM) model for the hydrate formation utility built-in function. The Peng–Robinson EOS is the most commonly applied fluid package for gas streams, and the CSM model was used instead of Ng–Robinson model because it has better prediction of hydrate formation for CH_4 and CO_2 gases under high pressures (Sun and Duan, 2005).

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