Journal of Natural Gas Science and Engineering 46 (2017) 873–883

Contents lists available at ScienceDirect

Journal of Natural Gas Science and Engineering

journal homepage: www.elsevier.com/locate/jngse

Gas hydrates inhibition via combined biomolecules and synergistic materials at wide process conditions

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ARTICLE INFO

Article history:
Received 16 March 2017
Received in revised form
31 May 2017
Accepted 14 July 2017
Available online 1 September 2017

Keywords:
Gas hydrates
Flow assurance
Kinetic inhibitors
Thermodynamic inhibitors
Amino acids
Synergetic compounds

ABSTRACT

The motive of this research to present a systematic study in context of implementation of gas hydrate inhibitors that are obtained via naturally occurring amino acids (L-Alanine, Glycine, L-Histidine, L-Phenylalanine and L-Asparagine). These materials are tested for methane (CH_4) hydrate inhibition purposes from both thermodynamically and kinetically perspectives at wide process conditions. In this presented work, all studied amino acids have been tested at both 1 wt % as low dosage inhibitors as well as at higher concentrations up to 5 wt %. Furthermore, Polyethylene-oxide (PEO) and Vinyl Caprolactum (VCap) were used at 1 wt % in studied aqueous solutions as synergetic compounds to enhance the inhibition performance for CH_4 hydrate inhibition. Gas hydrate experiments were carried out by using rocking cell apparatus, from which pressure, temperature equilibrium data were obtained at recorded time and these data were translated into inhibitor performance evaluation from both thermodynamics and kinetic inhibition perspectives. This study includes the discussions of the effect of solubility limitation of studied amino acids, the effect of inhibitor concentration effect on the thermodynamic shift of the hydrate equilibrium curve, the role of side chain in amino acids in kinetic hydrate inhibition, the hydrophobic interactions of alkyl chain in water for synergistic point of view. The results showed that the suitability of amino acids combined with synergistic materials for high kinetic inhibition performance, which provided an additional time shift up to 35 h in hydrate formation at moderate process conditions up to 55 bars, specifically when L-Alanine was used.

1. Introduction

Natural gas exists in abundant quantities and being replaced coal for power generation in both industrial and residential applications due to its clean nature. Moreover, chemical process industries utilize natural gas as a starting material to produce syngas in various processes such as gas to liquid (GTL) and ethylene processes, where natural gas is the source of hydrogen gas (Park et al., 2015). The consumption of natural gas has been increased dramatically in the past couple of decades (Brown et al., 2014). Typical natural gas production starts by drilling either at the seafloor or at onshore reservoirs and once the gas reservoir is tapped the gas is transported through the pipelines to a larger distribution pipe networks or direct to the gas processing facilities. During the course of gas transmission through the pipelines, there is a risk of gas hydrate cluster formation inside the pipeline and at other process equipment at low temperature and high pressure conditions (Kvamme et al., 2016; Aman and Koh, 2016), which leads to blockage in the pipelines and hinders the transportation of the flow the gas causing substantial economic losses and even catastrophic pipeline failures that might result in complete operation shutdowns.

Gas hydrates are crystalline and ice-like structures, which are

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https://doi.org/10.1016/j.jngse.2017.07.034

formed by the coexistence of water molecules and gas hydrate former molecules (e.g. methane, ethane etc …). The favorable process conditions for the gas hydrate cages to occur is low temperatures and high pressures, which leads the formation of a network of hydrogen bonds (HO–H) in which gas hydrate former molecules are trapped and encapsulated within three-dimensional frameworks. The X-ray determination (Loveday et al., 2001; Koh, 2002) reveals that gas hydrate clusters mainly found in three types of molecular arrangements, cubic structure I (sI), cubic structure II (sII) and hexagonal structure H (sH), and the hydrate cage type depends upon the shape and/or size of the host gas or hydrate former gas molecule. For instance, CH_4, CO_2 and C_2H_6 leads to sI type hydrates, whereas C_3H_8 and iso-C_4H_{10} molecules leads to sII type hydrate cage structure (Sloan, 2003). In order to prevent hydrate formation inside the gas transmission pipelines and provide flow assurance, gas hydrate inhibitors have been injected into the pipelines. Hydrate inhibitors are typically charged or polar compounds such as electrolytes, alcohols and glycols, which are classified as thermodynamic hydrate inhibitors. Amongst those typical inhibitors, methanol and mono-ethylene glycol have been proven to be the most effective ones (Jager et al., 2002). On the other hand, unlike thermodynamic inhibitors, kinetic hydrate inhibitors (typically water-soluble polymers) do not show significant shifting effect on the pressure (P) and temperature (T) hydrate equilibrium curve towards the hydrate safe region. Nevertheless, they show the effect of time delay for the growth of hydrate crystals in which the hydrate inhibition is applied (Kelland, 2006). Some surfactants act as anti-agglomerates via forming aggregates leaving the hydrate particles as tiny particles and hinder their growth within the pipeline (Kumar et al., 2015). Such conventional inhibitors injected in large quantities during pipeline operations and the risk of toxic materials spillage to the surrounding aquatic system is high and dangers the habitat. Therefore, in order to prevent environmental hazards due to the excessive usage of high toxic nature chemicals in the pipelines, environmentally benign chemicals have been searched by both academia and industry in order to replace the toxic ones. It is also aimed to reduce the cost of the intervention in the case pipeline is under the hydrate formation risk by reducing the amount of the used chemicals as well as reduce or eliminate the cost of the recovery of the injected chemicals to the pipeline. Search for alternative thermodynamic and kinetic inhibitors such as urea (Muromachi et al., 2015), chitosan (Xu et al., 2010), proteins (Kelland, 2006) and synthetic bio-molecules have been used as gas hydrate inhibitors in recent years as being alternative inhibitors in order to tackle above-mentioned challenges (Naeiji et al., 2014; Roosta et al., 2016; Shatat et al., 2013; Sa et al., 2011).

Amino acids are model compounds of proteins and they are also found in genetic coding as the fundamental building blocks known life forms in our planet (Riyazuddeen et al., 2012). Among 500 known amino acids, only 20 of those appear in genetic coding and these synthesized amino acids are frequently used in animal feed additives, flavor enhancers, cosmetics ingredients and medicinal products (Ivanov et al., 2013). Moreover, amino acids were also used as corrosion inhibitors and due to their negligible negative impact on aquatic systems (Barouni et al., 2008; Hluchan et al., 1988; Dehdab et al., 2016). Chemically, amino acids have zwitterion, which contains carboxylic (-COOH) and ammonium (-NH_2) groups attached to the center C atom, and yet some amino acids also contain an additional carboxylic acid, amide, phenyl, imidazolium and alkyl chains. These additional groups determine the nature of amino acid such as acidity/basicity or hydrophilicity/hydrophobicity. Amino acid molecules in water accessing zwitterion-ion, zwitterion-water-dipoles, ions-water-dipole interactions with water molecule as well as other ions present in aqueous systems (Riyazuddeen and Altamash, 2009, 2010, 2011, 2012). The electrostatic force of attraction capability of an amino acid can have an effect on liquid water structure and might lead to a prevention of hydrogen bonding during the hydrate cage formation around the hydrate former and guest gas molecule. Raman spectroscopy technique has been proven that, hydrophilic or hydrophobic moieties disrupt or strengthening the water structures (Sa et al., 2015). Sloan and Koh (Hydrate Formation, 2007) also postulated that hydrogen bonding and electrostatic interactions lower the activity coefficient of water, and thus thermodynamic inhibition takes place.

Natural gas consists of complex multi-component gas mixtures and as documented elsewhere (IPCC reports; Zavala-Araiza et al., 2015; Tariq et al., 2016) methane (CH_4) is the major constituent of natural gas reservoirs. In this work, rather than dealing with complex multi component gas mixtures, which can lead to different hydrate cage formations, CH_4 has been studied as a representative model for natural gas to study gas hydrate inhibition performance of amino acids. Having said that, in the case of actual pipeline conditions gas hydrates are formed in both sI and sII type; in this proof of concept experimental work, methane is used and only sI type of hydrate formation is observed. A number of researchers presented their reports using amino acids as inhibitor for kinetic, thermodynamic studies for CO_2, CH_4 and tetrahydrofuran gas hydrates (Naeiji et al., 2014; Roosta et al., 2016; Sa et al., 2011, 2016). This study provides a detailed study of thermodynamic and kinetic methane hydrate inhibition performance together by using Glycine, L-Alanine, L-Histidine, L-Phenylalanine and L- Asparagine amino acids as inhibitors at both low and high doses at various process conditions that includes pressures between 40 and 120 bars. Moreover, a combined synergized behavior of amino acids was also studied for enhanced kinetic inhibition purposes by adding 1 wt% of water soluble polymer/monomer (polyethylene oxide/vinyl caprolactum) into the L-Alanine Glycine and L-Histidine solutions at above-mentioned pressure ranges.

2. Experimental section

2.1. Materials

CH_4 gas with the purity of 99.9% was purchased from Buzware Scientific and Technical Gases, Doha (Qatar). Amino acids and synergents were purchased from Sigma-Aldrich and the details of the purities, structures and molar masses of these samples are provided in Table 1. All the aqueous samples were prepared in Millipore quality distilled water (Milli-Q, Millipore, resistivity 18.2 MΩ cm) by weighing on an Mettler Toledo XS105 electronic balance with a precision of ± 0.00001 g.

2.2. Apparatus and methods

Rocking cell is an assembly of five cells parallel working at a same skid (RC-5) has been purchased from PSL SystemtechniK GmbH, Germany. RC-5 assembly is capable of operating at pressures up to 200 bar (2900 psi) and has temperature rating of −10 °C to 60 °C. Each high-pressure rocking cell has a volume of 40.13 cm^3 and it encapsulates a stainless steel ball with the diameter of 17 mm, which moves back and forth and provides agitation within the cell. There are total 5 rocking cells installed on a metal plate and the assembly is submerged in a cooling-heating bath for thermostating purposes. The mixing inside the cells is carried out by rocking with a pre-defined frequency of 10 rocks/min and with the rocking angle of 30° (Qureshi et al., 2016). Cells were pressurized directly with cylinder pressure of gas in the range of 30–120 bars at different desired pressure intervals and pressures within the cells