



Synergetic effects of polyacrylamide and nonionic surfactants on preventing gas hydrate formation



Khadijeh Rostami Khodaverdiloo, Amir Erfani, Kiana Peyvandi*, Farshad Varaminian

School of Chemical, Gas and Petroleum Engineering, Semnan University, Semnan 35131_19111, Iran

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ABSTRACT

The aim of this work is to conduct an experimental investigation on the synergetic influence of polyacrylamide (PAM), some non-ionic surfactants and polymers on the ethane hydrate formation kinetics. The surfactants and polymers used in the experiments belong to the family of nonylphenol ethoxylates (NPE), lauryl alcohol ethoxylates (LAE), polyvinylpyrrolidone (PVP), polyethylene glycol (PEG) and ethylene oxide/propylene oxide copolymer (EO/PO). All experiments have been performed in an isochoric batch reactor under high pressure conditions. It is found that synergism of PAM and surfactants exhibits strong inhibition of ethane hydrate at experimental subcooling temperature of 10.5 °C. The experimental studies prove that the synergism of a very low dosage of PAM and surfactants not only delays the induction time but also dramatically lowers the hydrate formation rate.

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1. Introduction

Gas Hydrates are crystalline solids in which the guest molecules (usually gas) with suitable sizes, are trapped in cages formed due to hydrogen bonding between the water molecules (host). Since the Van Der Waals forces exist between the hydrate former (guest) molecules and the cavities of water, the structure of gas hydrate becomes thermodynamically stable under suitable thermodynamic conditions (usually elevated pressures and/or low temperatures). According to the size of cavities and the molecules of hydrate former, three main structures of gas hydrate containing structure I (sI), structure II (sII) or structure H (sH) can be formed (Khosharary et al., 2015; Mohebbi et al., 2012).

In recent years, to investigate the hydrate formation process, two main groups of studies have been done: (1) thermodynamics of hydrate formation (2) kinetics of hydrate formation. Major progresses have been obtained in the realm of hydrate formation thermodynamics since 1934, but many challenges exist in studying the kinetics of hydrate formation, for instance, recognizing the mechanism of hydrate formation or inhibition kinetics. Furthermore, the study of hydrate formation kinetics is of importance for many applications such as transportation and storage of natural

gas, refrigerant hydrate formers as phase change materials, water desalination and gas separation. On the other hand, due to some major safety and operational problems associated with hydrate formation in hydrocarbon transportation pipelines, the chemical treatment for preventing hydrate is also required. Beside hydrate formation in pipelines, problems associated with hydrate formation in drilling operations are also important. Nowadays the industry is concerned with safe deep water drilling operations more than any time. It is known that the conventional way of gas hydrate inhibition is using thermodynamic inhibitors, for example, methanol. The high cost and environmental problems of thermodynamic inhibitors due to high required concentration of thermodynamic inhibitors are the main problems of using thermodynamic inhibitors; therefore, development of low dosage hydrate inhibitors (LDHI) which are environment-friendly have been an intriguing topic for researchers and industry.

Low dosage hydrate inhibitors are classified into the kinetic inhibitors (KI) and anti agglomerants (AA). While the kinetic inhibitors prevent hydrate formation by prolonging induction time of hydrate formation, anti-agglomerants inhibit pipeline plugging. Environmental aspects of commercial LDHIs have encouraged researches to look for more environmentally friendly LDHIs (Peng et al., 2009; Mohebbi et al., 2012).

The amount of the kinetic inhibitor used is generally ranging from 0.01% to 0.1% with the molecular weight ranging from several thousands to millions (Wu et al., 2007). First generation of kinetic

* Corresponding author.

E-mail address: k_peyvandy@semnan.ac.ir (K. Peyvandi).

inhibitor was Polyvinylpyrrolidone (PVP), a commercially available water soluble polymer with lactam rings. It was imagined that a polymer with lactam rings is an efficient gas hydrate kinetic inhibitor. Three other commercially available polymers with lactam rings were tested and proved to be more effective. These three polymers were known as second generation kinetic inhibitors. Names and acronyms of these polymers are Polyvinylcaprolactam (PVCAP), terpolymer, N-vinylpyrrolidone/N-vinylcaprolactam/N-di methylaminoethylmethacrylate (VC-713) and N-vinylpyrrolidone-co-N-vinylcaprolactam (VP/VC). The size of the lactam ring in kinetic inhibitors is similar to five and six member of hydrate structure. Due to the electro negativity of nitrogen and oxygen in amide group of lactam ring, it can adsorb on the hydrate crystal and sterically block the hydrate growth. According to the investigation of Koh et al. (2002), it was shown that gas hydrate formation generally occurs at the gas–liquid interface. This study also revealed that polymeric kinetic inhibitors are capable of controlling both surface and bulk nucleation.

In recent years, several investigations have been conducted on the gas hydrate inhibitors. Makogon and Sloan (2002) utilized molecular dynamics and Monte Carlo simulations to investigate mechanism of kinetic inhibitors; they suggested that inhibition mechanism consist of two main components. First, the lactam ring of the inhibitor adsorbs on the hydrate crystal surface by hydrogen bonding so that the crystal only can grow around and between the polymer strands. Furthermore, kinetic inhibitors satirically block non-polar solutes (such as methane) from entering a hydrate cavity. It has been shown that polymeric kinetic inhibitors are effective for SI and SII. It has been also concluded that adsorption of polymers on hydrate crystal surface is practically irreversible and as showed by experiments, this adsorption is fairly rapid. It is noteworthy that in their study it was observed that a weak interaction between exists hydrate former solute (a non polar gas), and hydrophobic part of the polymer which affect adsorption of methane in hydrate cavity. Different polymers had different effects on the methane adsorption. The largest decrease in methane adsorption was caused by PVCAP. In their study, the effect of monomer size on inhibitor's effectiveness was carried out. It was concluded that the size of 160 °Å is the optimized value.

Peng et al. (2009) studied kinetic effects of VC-713 terpolymer. They studied the influence of this kinetic inhibitor on the nucleation and the lateral growth rate of methane hydrate separately. They concluded that the effect of VC-713 on the nucleation of the methane hydrate is limited. This kinetic inhibitor significantly inhibited the lateral growth of methane hydrate. Duchateau et al. (2012) determined the interfacial properties of kinetic hydrate inhibitors (KHIs) and their performance by using a high-pressure pendant drop tensiometer. They determined surface activity of various KHIs and their influences on the rheological properties of the water/gas interface in and outside the hydrate stability zone (HSZ). They have uncovered that inside the HSZ, the variation rate of the dilatational elastic modulus at the water/gas interface to be directly concerned with the KHIs' performance thus offering a new way of assessing KHIs. Nakarit et al. (2013), applied the synergetic effect of active groups and N-vinyl lactam copolymers to inhibit the formation of THF hydrate (sII). To achieve their aim, they prepared 3-alkyl-1-vinylimidazolium bromides, tributylammoniummethacrylate bromide (TBAEABr) monomers, homopolymers and copolymers with N-vinyl lactams. They concluded that the synergetic effect of the functional groups and N-vinyl lactam polymers as kinetic inhibitors are not better than PVCAP polymer. Furthermore, a cationic TBAEABr homopolymer had a good kinetic inhibition effect on both THF and SII gas hydrates. Kang et al. (2014) carried out the experimental and modeling investigation on the inhibition influence of PVP and PVCap (poly N-vinylpyrrolidone, PVP and poly N-vinylcaprolactam, PVCap)

on the induction time of natural gas hydrate formation and they suggested a new model based on the driving force of hydrate formation. Difference between experiment and equilibrium condition fugacities was selected as the driving force and the Freundlich adsorption isotherm was utilized to predict the gas hydrate induction time with PVP or PVCap. They concluded that their proposed new model has a good performance to predict the minimum concentration of inhibitor required to prevent hydrate plugging at different temperatures and pressures. Naeji et al. (2014) applied a series of natural amino acids at concentrations ranging from 0.05 to 1.5 wt% in a batch cell under atmospheric pressure, with and without the presence of acetone, for the inhibition of THF hydrate formation because they are environmentally friendly and biodegradable. They also used the thermodynamic natural path for determining the hydrate formation rates. The results proved that glycine has shown better inhibition performance than L-leucine. They also proposed that the lower hydrophobicity of glycine helps it to be a better kinetic inhibitor in the studied system.

Polyethylene oxide (PEO) is a non-ionic, water-soluble and linear polymer. It has a general chemical formula of $-(\text{CH}_2-\text{CH}_2-\text{O})_n-$. Hydrate formation experiments have shown that the induction time is prolonged in the presence of the PEO by an order of magnitude in some cases compared to cases in which the inhibitor are only applied (Lee and Englezos, 2005; Talaghat, 2010, 2012). PEO is not a kinetic inhibitor by itself. The mechanism of the action of PEO is unknown. The performance of certain KHIs was found to be enhanced by the presence of small molecular weight materials like 2-butoxyethanol (Cohen et al., 1998).

The importance of biodegradability and hazardous associated with toxic ionic surfactants are known. Researches on inhibition chemicals are geared toward synthesis and use of more environmentally friendly materials. The recent programs of hydrate prevention research address global issues such as biodegradability and non-toxicity of the hydrate inhibitor chemicals. Most of commercial and low dosage hydrate inhibitors are cationic surfactants. The fact that nonionic surfactants are less toxic and more environmentally-friendly materials allows the researchers to investigate the effects of non-ionic surfactants on hydrate formation rates. The effect of polyacrylamide on nucleation and growth of crystals in water treatment and brine purification led us to investigate effect of this polymer on hydrate formation.

Due to the importance finding suitable chemicals to prevent hydrate formation both in hydrocarbon transportation pipelines and drilling operations, in this study, the performance of surfactants, polymers and their synergetic effects have been investigated. To carry out this study, polyacrylamide (PAM), the families of nonylphenol ethoxylates (NPE), lauryl alcohol ethoxylates (LAE), polyvinylpyrrolidone (PVP), polyethylene glycol (PEG), ethylene oxide propylene oxide copolymer (EO/PO) have been utilized. In order to recognize the degree of inhibition for each case, a synergetic parameter is also defined. The synergy parameter for each case is discussed and the best one is also determined.

2. Experimental

2.1. Materials

Ethane was purchased from the Technical Gas Services with a purity of 99.5%. The inhibitor solutions were solutions of pure PAM and mixtures of (PAM + non-ionic surfactant). Applied surfactants and polymers belong to the family of Nonylphenol ethoxylates (NPE), Lauryl alcohol ethoxylates (LAE), polyvinylpyrrolidone (PVP), polyethylene glycol (PEG) and Ethylene Oxide/Propylene Oxide copolymer (EO/PO) and castor oil ethoxylates (COE). Also, TBAB a former applied chemical which shows synergetic inhibition effect

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