Journal of Petroleum
Science and Technology

Synergistic Effect of Glycol Ethers with a Kinetic Inhibitor (Poly(VP-VCap)) for Sweet Natural Gas Hydrate Formation: (Concentration Effect of Glycol Ethers)

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ABSTRACT

Formation of natural gas hydrate is a serious problem in the gas and oil industry because it can plug pipelines and destroy the equipment. This study aimes to evaluate the concentration effect of glycol ethers on their synergism with a commercial kinetic hydrate inhibitor (Luvicap 55W) in sweet natural gas-water systems at a constant temperature of 4 °C and pressure of 95 bar. Hydrate formation experiments have been designed and conducted in a static, stirred autoclave. Finally, the results indicated that concentration changes dosen't affect the inhibition time greatly, while the growth rate of hydrate crystals decreases considerably with the increase in the concentration of glycol ethers.

Keywords: Hydrate, Natural Gas, Synergistic Effect, Kinetic Inhibitor, Glycol Ethers.

INTRODUCTION

During the production of oil and gas, water is often a co-product resulting in a multi-phase system containing oil, water and gas. Moreover, gas hydrates, which are ice-like crystalline compounds, are easily formed during the transportation of oil and gas containing certain amounts of water and under conditions of low temperature and high pressure [1]. The formation of gas hydrates may block pipelines and production facilities in the oil and gas industry, which can lead to the destruction of equipment and loss of life [2]. There is a variety of methods for preventing the formation of gas hydrates. The injection of chemical additives, referred to as hydrate inhibitors, is in principle a simple method for controlling hydrate formation. Thermodynamic hydrate inhibitors (THIs) such as alcohols and ethylene glycol are the most widely used chemical compounds for inhibition of hydrate formation [3,4]. These compounds shift the thermodynamic equilibrium of hydrates towards lower temperatures and higher pressures, which can effectively prevent gas hydrate formation. However, a large quantity of these compounds (10-60 wt.%) is required for effective inhibition, which is expensive and raises environmental and logistical concerns [5]. Therefore, attempts are being made to replace these compounds with low dosage hydrate inhibitors (LDHIs). In addition, LDHIs are subdivided into anti-agglomerants (AA) and kinetic hydrate inhibitors

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Article history
Received: May 30, 2018
Received in revised form: August 06, 2018
Accepted: September 18, 2018
Available online: May 21, 2019
DOI: 10.22078/jpst.2018.3339.1531

(KHI). Anti-agglomerants modify the hydrate growth resulting in smaller hydrate particles and formation of a transportable slurry [6-7]. Moreover, kinetic inhibitors such as polyvinylcaprolactam (PVCap) and polyvinylpyrrolidone (PVP) are usually water soluble polymers with surfactant properties, which delay hydrate nucleation and/or crystal growth for a period of time (induction time) [8-11]. These compounds can be effective at low dosages (<1 wt.%) and are therefore preferable for both economic and environmental reasons. Also, it is generally suggested that polymeric kinetic inhibitors hinder hydrate formation by adsorbing to the surface of hydrate crystals and sterically blocking the guest molecules from entering and completing hydrate cavities [12]. However, given the poor performance of kinetic hydrate inhibitors especially at higher pressures and large degrees of super cooling, combinations of kinetic and thermodynamic hydrate inhibitors have been used [13,14]. Furthermore, it has been reported that the inclusion of some compounds such as polyethylene oxide and glycine into a kinetic inhibitor solution enhances the performance of the inhibitor [15,16]. Recently, the synergistic effect of glycol ethers on the performance of kinetic inhibitors has been studied. The results indicate that the addition of diethylene glycol monobutyl ether to the solution containing PVP considerably increases the inhibition capability of this kinetic hydrate inhibitor [17]. In addition, the presence of glycol ethers such as ethylene glycol monobutyl ether and ethylene glycol ethyl ether alongside PVCap prolongs the induction time and delays the growth rate of hydrate crystals for natural gas hydrate formation [18]. Moreover, the synergistic effect of PVCap with glycol ethers has also been observed in hydrate dissociation. On the other hand, hydrates formed in the presence of (PVCap) and glycol ether have shown slightly increased dissociation temperature in comparison with those formed with PVCap alone [19]. However, the effect of concentration of glycol ethers, which is economically and environmentally important, on their synergism with the inhibitor has not yet been studied. Also, the low cloud point of PVCap solution in water (30 to 35 ^{o}C) is a disadvantage of the gas hydrate inhibitor application since the polymer can precipitate in the gas/oil/water phase. Moreover, cloud point is the temperature at which the mixture starts to split into two phases, resulting in a cloudy solution. On this basis, the application of copolymers including poly(vinylpyrrolidone (VP)-vinylcaprolactam (VCap)), which have higher cloud points, seems more appropriate [20]. In this work, the concentration effect of glycol ethers on the performance of a commercial kinetic hydrate inhibitor known as Luvicap 55W, whose main ingredient is poly(VP-VCap), has been investigated.

EXPERIMENTAL PROCEDURE

The tests were conducted in a 750 ml stainless steel, high pressure reactor equipped with a magnetic drive stirrer. A cooling jacket connected to a temperature control bath, which maintained the temperature throughout the experiment, surrounded the reactor. A thermocouple with an accuracy of ± 0.1 ^{o}C and a pressure transducer with an accuracy of ± 0.1 bar were connected to the high pressure reactor to measure the temperature and pressure respectively. The thermocouple and pressure transducer were connected to a data acquisition system and a personal computer to record the temperature and pressure as functions of time. A pressure relief valve was set to relieve

the pressure at 140 bar and prevent the pressure overload inside the reactor. Moreover, a schematic diagram of the experimental apparatus used in this work is shown in Figure 1. In hydrate formation experiments in the presence of additives, the additives are added to the aqueous solution of the inhibitor to form 300 cm^3 of the kinetic inhibitor and glycol ether solution. In all the experiments, the inhibitor concentration is 0.5 wt. % while the concentration of glycol ethers ranges from 0.2 to 1.5 wt. % depending on the experimental conditions. Each test was performed at the temperature of 4 °C and pressure of 95 bar. A stirring rate of 250 rpm was chosen to ensure stable gas uptake rate and temperature, following the nucleation.

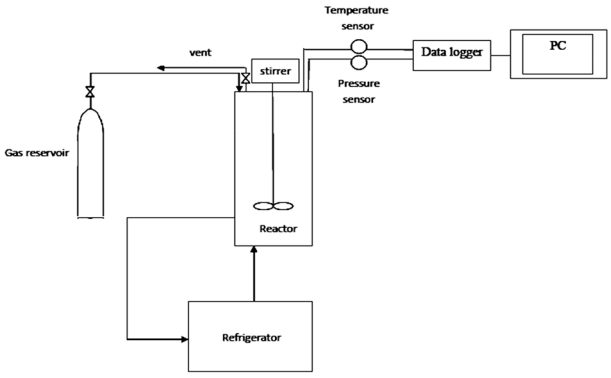

Figure 1: Schematic representation of the experimental apparatus.

After reaching equilibrium under initial pressure and temperature conditions, the system was cooled down to the hydrate formation temperature. The induction time was recorded by observation of both a sudden pressure decrease and a temperature increase. The start of the growth period is considered as the point where a spike in the pressure differential and liquid reactor temperature is observed. Sweet natural gas has been used as the hydrate former, and its composition is shown in Table 1.

Luvicap 55W commercial inhibitor, containing poly(VP-VCap) as the active polymer and water as the solvent, were obtained from BASF Chemical Co. The used glycol ethers, were purchased from Merck Chemical Co., included ethylene glycol monomethyl ether (EGME), ethylene glycol monopropyl ether (EGPE) and ethylene glycol monobutyl ether (EGBE). The purity of all the glycol ethers was 99%. Molecular structures of (VP-VCap) copolymer and glycol ethers are shown in Figure 2.

Table 1: The composition of the sweet natural gas used.

Component	Mol%
O_2	0.1
N_2	3.9
C_1	88.8
CO_2	2.2
C_2	3.4
C_3	0.9
i-C_4	0.2
n-C_4	0.27
i-C_5	0.11
n-C_5	0.07
C_6	0.03
C_7	0.02

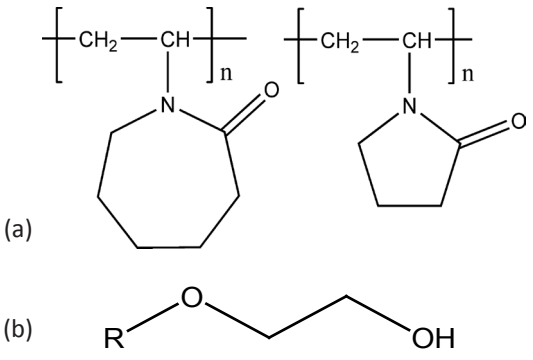

Figure 2: Molecular structure of: (a) poly(VP-VCap) and (b) glycol ethers.

RESULTS AND DISCUSSION

Natural gas hydrate nucleation and formation experiments were carried out in a static, stirred autoclave under isochoric and isothermal conditions at temperature and pressure of 4 °C and

95 bar respectively. The performance of the kinetic inhibitor is usually evaluated in terms of induction time and hydrate crystal growth. Induction time is defined as the time between the beginning of stirring and observation of hydrate formation, which indicates the growth initiation. A sudden increase in the temperature is observed in addition to pressure reduction at this point. This is expected since gas hydrate formation is an exothermic process. Figure 3 shows the time dependence of natural gas hydrate formation at a temperature of 4°C and pressure of 95 bar for the blank sample and a system containing the kinetic inhibitor. As observed, in the presence of 0.5 wt. % of the kinetic hydrate inhibitor, the induction time increases from 60 (corresponding to the blank sample) to 150 min. Furthermore, after nucleation, gas hydrate formation causes considerable pressure drop to about 70 bar in 9 h in the blank sample (Figure 3, sample a) while during the formation period, hydrates are continuously formed in the presence of the kinetic inhibitor (Figure 3, sample b) at lower rates in comparison with the blank sample. From a microscopic point of view, the molecules of kinetic inhibitor adsorbed on hydrate crystal by hydrogen bonds between the oxygen atoms of poly(VP-VCap) and the cavity surfaces cause a delay in gas hydrate nucleation [21].

It is believed that there are three steps in the quantitative hydrate formation: gas dissolution, hydrate nucleation and hydrate crystal growth respectively. Hydrate crystal growth starts after nucleation, which is indicated by a noticeable pressure decrease [12]. In other words, the rate of pressure drop is an indication of the growth rate of hydrate crystals.

Table 2 shows the hydrate inhibition times and rates of pressure drop corresponding to the water-natural gas mixtures in the presence of the kinetic inhibitor and different concentrations of glycol ethers. Repeatability, expressed as relative standard deviation, ranged between 1.9% and 4.3%. The results indicate that the addition of glycol ethers to the water phase containing the kinetic inhibitor considerably increases the induction time from 150 to 180-250 min. Therefore, a synergistic effect is observed between glycol ethers and the kinetic inhibitor in delaying hydrate crystal nucleation in the natural gas-water system.

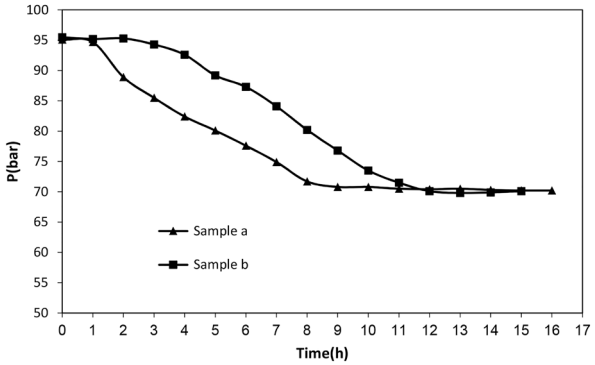

Figure 3: The time dependence of natural gas hydrate formation for: (a) blank sample, (b) in the presence of Luvicap 55W kinetic hydrate inhibitor (0.5 wt. %).

Glycol ethers are common solvents in the chemical industry. These compounds have hydroxyl groups and can form hydrogen bonds with water. It seems that glycol ethers alter the inhibition characteristic of kinetic inhibitor by enhancing the adsorptivity of polymer molecules on the nucleation sites. The main factors in the inhibition by poly(VP-VCap) are the bulky spaces formed by the five and seven membered rings and occupation of hydrate cavities. The synergistic effect of glycol ethers may be a result of the stronger hydrogen bond between water and glycol ether molecules compared with that between water and the inhibitor molecules. Moreover, the density of the electron cloud on the single bonded oxygen of glycol ethers is higher than that of doubly bonded oxygen in poly(VP-VCap) and thus the former yields stronger hydrogen bonds [17].

However, the variations in glycol ether concentration have little effect on induction times. For example, increasing the concentrations of EGME and EGPE from 0.5% to 1% did not affect the inhibition time. The strong bonding of water molecules to glycol ether as well as the solubility of polymeric hydrate inhibitor in glycol ether has caused the performance of glycol ether as a surfactant in this system. Consequently, a small amount of glycol ether is enough for more effective distribution of the polymeric inhibitor and occupation of hydrate formation cavities.

The rate of gas hydrate formation is directly proportional to gas consumption. The measurement of gas consumption is simpler than that of hydrate formation. Hence, the gas consumption rate well represents the hydrate formation rate. The gas consumption rate measured directly from experimental pressure drop was considered equivalent to the hydrate growth rate in this work.

Figure 4 shows the time dependence of the experimental pressure drop during natural gas hydrate formation at a constant temperature of 4 °C and pressure of 95 bar in an isochoric system in the presence of mixtures of the inhibitor and 0.5 wt.% of different glycol ethers. As shown in Figure 4, the addition of glycol ethers to a system containing the kinetic inhibitor remarkably delays hydrate crystal growth so that in the presence of ethylene glycol monobutyl ether, for example, after 32 h, hydrate crystal growth is finished, and the system pressure stabilizes while the system containing the kinetic inhibitor alone reaches this point after 12 h (Figure 3 sample b). In other words, the average pressure drop for the mixture of ethylene glycol monobutyl ether (0.5 wt.%) and kinetic inhibitor is 0.72 bar/h while the corresponding value for the system containing the kinetic inhibitor alone is 2.6 bar/h. Therefore, similar to the inhibition time, glycol ether has also had a synergism with the inhibitor with regards to delaying the hydrate crystal growth rate. The effect of glycol ether concentration on average pressure drop is shown in Table 2. Interestingly, unlike induction period, the rate of crystal growth of natural gas hydrate is greatly influenced by the concentration of glycol ethers so that increasing the concentration of EGBE, for example, from 0.2 to 1.5 wt.% reduces the average pressure drop rate from 0.9 to 0.52 bar/h. The effect of kinetic hydrate inhibitors on hydrate crystal growth has been previously studied [21]. It is believed that the growth inhibition is a result of polymer adsorption on the crystal surface, with the adsorbed molecules acting as barriers to further growth. In other words, hydrate crystals will not be able to grow between the polymer strands.

Table 2: Synergistic effect of the kinetic inhibitor with different concentrations of glycol ethers in natural gas hydrate formation.

System	Induction time (min)	Average pressure drop (bar/h)
Blank	60	2.78
Inhibitor	150	2.6
Inhibitor + EGME (0.2 wt.%)	180	2.38
Inhibitor + EGME (0.5 wt.%)	195	2.13
Inhibitor + EGME (1 wt.%)	195	1.7
Inhibitor + EGME (1.5 wt.%)	210	1.5
Inhibitor + EGPE (0.2 wt.%)	200	1.5
Inhibitor + EGPE (0.5 wt.%)	200	1.16
Inhibitor + EGPE (1 wt.%)	200	0.97
Inhibitor + EGPE (1.5 wt.%)	220	0.84
Inhibitor + EGBE (0.2 wt.%)	210	0.9
Inhibitor + EGBE (0.5 wt.%)	210	0.72
Inhibitor + EGBE (1 wt.%)	230	0.63
Inhibitor + EGBE (1.5 wt.%)	250	0.52

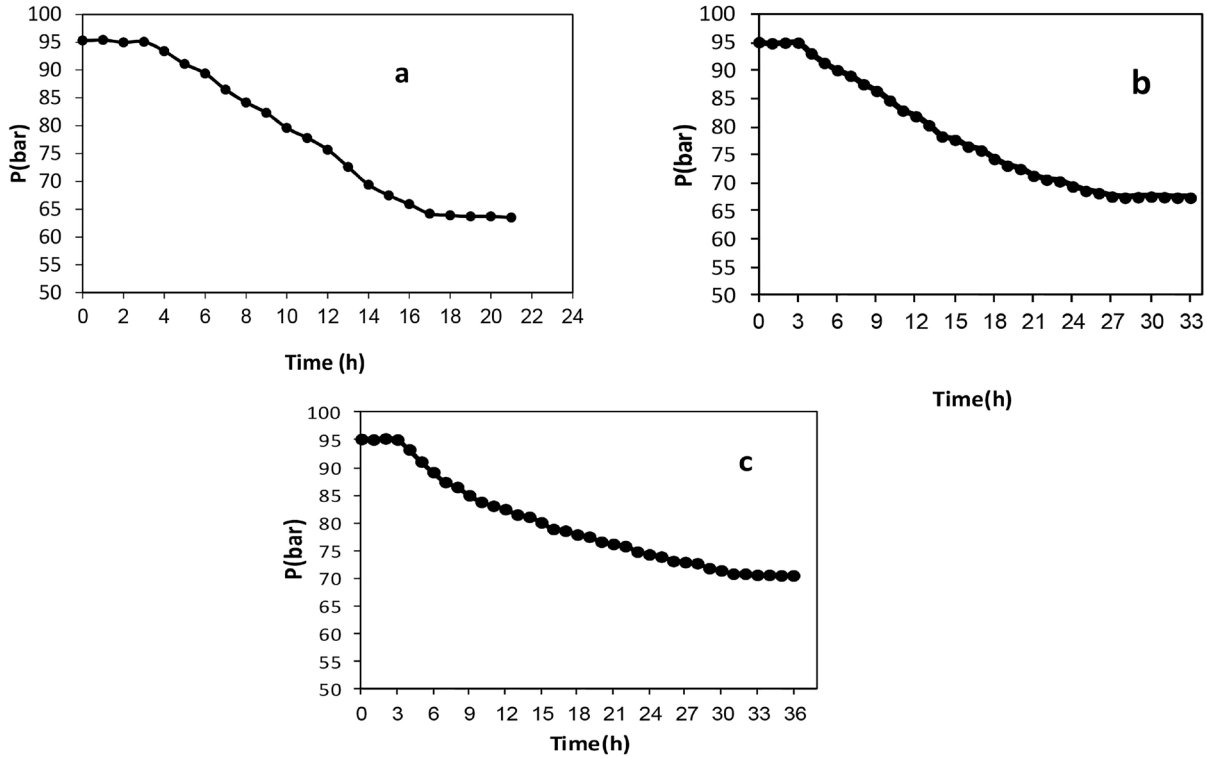

Figure 4: The change of pressure with time for natural gas hydrate formation: (a) in the presence of the kinetic inhibitor (0.5 wt.%) + EGME (0.5 wt.%), (b) in the presence of the kinetic inhibitor (0.5 wt.%) + EGMP (0.5 wt.%), (c) in the presence of the kinetic inhibitor (0.5 wt.%) + EGMB (0.5 wt.%).

It seems that in the crystal growth step, glycol ether molecules help the interaction of poly(VP-VCap) with crystal growth sites and prevent the natural gas hydrates from fast growth as they do in the nucleation step. The results in Table 2 show a better adsorption of the polymeric inhibitor on hydrate growth site at higher concentrations of glycol ethers. However, more comprehensive research on chemical characteristic of glycol ethers in conjunction with KHI is required to deduce the real effect of concentration in this media.

Among the glycol ethers shown in Table 2, ethylene glycol monobutyl ether has the strongest synergism with the kinetic inhibitors at all concentrations compared with its smaller homologs. The presence of this compound alongside the kinetic inhibitor has delayed hydrate crystal growth for the longest period of time. The high synergistic effect of ethylene glycol monobutyl ether may be attributed to its hydrophobicity. Glycol ether may allow the expansion of polymer conformation in the solution if the hydrophobicity of the hydrocarbon chain is associated with the dissolved polymer. This may happen if the weak bond between the polymeric segments pulling the coils together and tightening the conformation is broken by the surfactants. In addition, more length of an extended polymer is probably accessible for the interaction with a crystal surface. This may the reason for the improved performance of the hydrate inhibitor. Therefore, it can also be stated that glycol ethers cause a distribution of inhibitor molecules in the solution and thus provide more effective contact with the growth sites, especially at higher concentrations.

CONCLUSIONS

According to the results, glycol ethers cause a wide distribution of inhibitor molecules in the solution and show a remarkable synergistic effect on the performance of kinetic hydrate inhibitors in sweet natural gas-water systems at constant temperature and pressure. However, the concentration of glycol ethers considerably affects only the growth rate of hydrate crystals while showing a weak effect on the inhibition time such that increasing ethylene glycol monopropyl ether concentration from 0.2 to 1.5 wt.%, for example, it reduces the average pressure drop by 36%. The same increase in the concentration increases the inhibition time by only 10%. Therefore, it can also be stated that inhibitor molecules contact with the growth sites more effectively in higher concentrations of glycol ethers.

Ultimately, among the glycol ethers studied, ethylene glycol monobutyl ether has the greatest synergism with the inhibitor, especially in a hydrate crystal growth delay. In fact, the higher length of this molecule, in comparison with its smaller homologs, causes more dispersion of poly (VP-VCap) molecules in the solution, which increases its interaction with nucleation and growth sites.

NOMENCLATURES

AA	: Anti-agglomerants
EGME	: Ethylene Glycol Monomethyl Ether
KHI	: Kinetic hydrate inhibitors
PVCap	: Polyvinylcaprolactam
PVP	: Polyvinylpyrrolidone
THIs	: Thermodynamic hydrate inhibitors

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