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Synergistic Hydrate Inhibition of Mono ethylene Glycol (MEG) With Poly Vinyl Pyrrolidone (PVP) In Thermodynamically Underinhibited System

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Abstract

Thermodynamic hydrate inhibitors, although effective, are expensive because they are used in high dosages. They are also unsafe as some THI is lost to the hydrocarbon phase. On the other hand, Kinetic hydrate inhibitors are efficient and required in very low dosages, but they do not prevent hydrate formation; they only control the retard the growth. This work studies the synergy between a THI (monoethylene glycol) and a KHI (polyvinyl pyrrolidone) in preventing hydrate formation in a horizontal flow loop. The constant volume experiment was conducted using compressed natural gas as the hydrate former. The inhibitor blend studied was 2wt% monoethylene glycol MEG blended with 0.01wt%, to 0.1wt% PVP, respectively. A constant volume experiment was conducted in the loop, and a reduction in pressure was an indication that gas was used up in forming hydrates. An effective hydrate inhibitor will cause less pressure decline in the loop. The best blend in this study was the blend of 2wt% MEG blended with 0.04wt%PVP as it gave the least loop pressure decline. This research work is applicable in the Oil and Gas Industry for minimizing cost and preventing non-productive time (NPT).

***Keywords**: Under-inhibited hydrate system; Mono ethylene glycol; Poly vinyl pyrrolidone; Hybrid hydrate inhibitor.*

1. Introduction

Naturally occurring gas hydrates in the permafrost have been highlighted as a potential source for methane gas. However, hydrates in offshore flow lines have been a serious concern in the oil and gas industry. Their formation can cause blockage leading to costly production stoppage and complex remediation work. Hydrate plugs form rapidly and without warning due to low temperatures and relatively high pressures in the marine environment.

Gas hydrate formation can cause many problems in the oil and gas industry. During normal operating conditions, natural gas pipelines are known to operate at extremely high pressures. If an outdoor ambient condition (OAC) such as temperature drops below a specific value, the formation of gas hydrates may become unfavourable. If this occurs, hydrates will begin to form in the gas pipeline causing a hydrate plug and inevitably ceasing gas flow. To date, hydrate plugs are of grave concern to the oil and gas industry. It has been estimated that approximately one hundred million dollars are spent annually to prevent gas hydrates for the overall industrial processes [1].

To avoid hydrate formation in offshore flow lines transporting hydrocarbons, thermodynamic hydrate inhibitors (THIs). THIs interfere with the hydrate formation process by first interacting with the free water molecules available for hydrate formation, disrupting their ability to form a lattice [2]. They also destabilize the hydrate lattice by acting as an ineffective "guest" molecule. To date, the most readily available thermodynamic inhibitors are methanol, glycols and electrolytic solutions. Methanol and mono ethylene glycol (MEG) are commonly injected to shift the hydrate equilibrium curve outside the flow line operating conditions. However, this conventional method faces difficulties associated with larger injection volume, such as space limitations on floating structures and bulk logistics, as the energy industry moves to deeper and colder regions of the subsea to produce hydrocarbons.

The injection rate of THI is usually overestimated when calculated because some THI will be lost to the water phase and gas phase [3], causing further pollution of these phases. Methanol is a very effective inhibitor; however, it is not an environmentally friendly chemical as it can cause a high death rate in aquatic life [4]. Glycols can also be used as a hydrate inhibitor, but they are not as efficient as methanol due to their larger chemical structure. Sloan *et al.* [5] reported that as the inhibitor molecular size increases, the inhibitor efficiency decreases. Of all glycols, MEG is the most widely used due to its low viscosity, low solubility in liquid hydrocarbons and low cost compared with others [6]. Electrolytes, the third inhibitor from the list above, also inhibit water from forming a hydrate lattice. Electrolyte solutions can ionize and form dipole-dipole bonds with the available free water and inhibit hydrate formation. The downside of such inhibition is the possible increase in corrosion on sensitive equipment; therefore, consideration should be made if electrolytes are to be used.

Although the addition of a thermodynamic inhibitor may seem like a perfect solution to the prevention of gas hydrates, in some situations, the process or locations of the process may not make it feasible. For example, thermodynamic inhibitors are not very practical in offshore or remote production facilities due to the high potential costs associated with such processes. Furthermore, at nominal conditions, a high concentration of inhibitors (10-50 wt%) is required to stop hydrate formation [7]. If conditions are beyond nominal, inhibitor concentration can be extremely high (up to 60%), making such uses economically unfeasible [8].

Recent approaches for avoiding hydrate risks in offshore flowlines have been moving from complete avoidance toward risk management, which involves allowing hydrate formation in flowlines but delaying nucleation or preventing agglomeration of hydrate particles using kinetic hydrate inhibitors (KHIs) or anti-agglomerants (AA), commonly called as low-dosage hydrate inhibitors (LDHI). AAs prevent agglomeration of hydrate crystals, while KHIs effectively delay hydrate nucleation and reduce hydrate crystal growth. LDHI are less expensive and can be used in volumes as small as 0.01wt% to 1wt%. The costs associated with using kinetic and anti-agglomerant inhibition can be significantly reduced due to the low concentrations required to prevent hydrate formation effectively. Compared to methanol, the cost may be reduced by up to 50% [9]. Lastly, these inhibitors have a low chemical injection requirement compared to thermodynamic inhibitors [10].

Molecular dynamics simulation studies suggest two roles of KHIs: (i) disrupting the organization of the forming clathrate by strong interactions with liquid water phase and (ii) binding to the surface of hydrate crystal and retarding further growth once nucleation occurs [11]. KHIs are believed to increase the activation energy barrier for the formation of hydrate nuclei by raising the surface energy of pre-nucleating aggregates [7]. The most common types of kinetic inhibitors are usually polymers and co-polymers, such as anti-freeze proteins (AFP) and anti-freeze glycoproteins which are both derived from fish; polyvinylpyrrolidone [12], polyvinylcaprolactam [13], poly (N-vinylpyrrolidone-co-N-vinyl caprolactam) [14], N-vinylpyrrolidone/ N-vinyl caprolactam/ N, N-dimethyl amino ethyl methacrylate (VC-713) [15], polyaspartamides [16] and modified starch [17].

Although KHIs would reduce the growth rate of hydrate crystals by binding to growth sites, the small-sized crystals may eventually deposit and block the hydrocarbon flow before the fluid arrives at the platform. KHIs may have limitations such as difficulty preventing structure I hydrate and ineffectiveness at sub-cooling conditions higher than 14°C [18], especially during the extended shut-in of flowlines. Therefore, the industry still relies on proven THIs for hydrate inhibition in the offshore oil and gas fields.

There have been attempts to develop synergist materials that improve the performance of KHIs. It has been found that polyethylene oxide or glycol ether compounds noticeably prolong the nucleation time and significantly extend the delay of catastrophic growth; however, its effects are limited on delaying the hydrate onset [19]. Therefore, the limitation of using KHI remains.

The industry is making substantial operating and capital expenditures for hydrate prevention via methanol or MEG injection; thus, even a slight reduction of the THI injection rate can result in significant savings. Here, we present the potential of synergistic hydrate inhibition in a thermodynamically under-inhibited system by mixing MEG with PVP. From the available literature, the hydrate inhibition performance when PVP is added to MEG solution has not been investigated thoroughly and could offer quantitative estimation for reducing the amount of thermodynamic hydrate inhibitors. The experiment constant volume experiment in this work was carried out in a mini flow loop [20].

2. Materials and methodology

The constant volume batch experiments to evaluate the synergy between MEG and PVP were conducted using a Hydrate Mini Flow Loop. The loop is a closed loop of 12meters, fabricated using 0.5inch 316 stainless steel pipe enclosed in an insulated 4inch Polyvinylchloride (PVC) pipe. The skid-mounted loop was fitted with pumps, temperature gauges, pressure gauges, differential pressure transmitters, a gas mixing vessel, an inhibitor mixing vessel, a compressed natural gas cylinder and other components, and their functions are listed below.

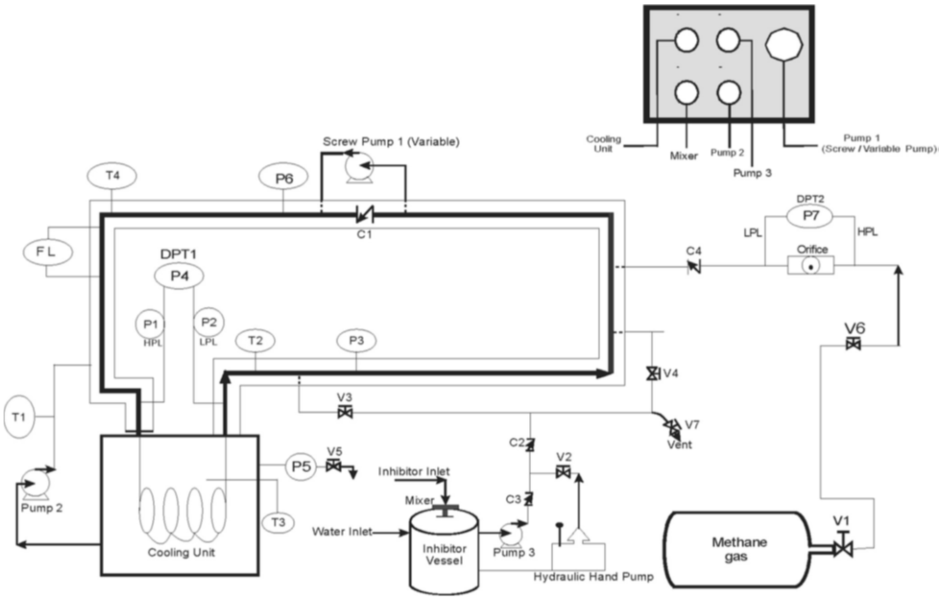

Figure 1. Process flow diagram of hydrate mini loop [20]

Materials used in this research include water, compressed natural gas (CNG), mono ethylene glycol (MEG), methanol (MeOH), and polyvinylpyrrolidone (PVP), and ice for cooling. Procedure for conduction the constant volume experiment in the loop is discussed in [17]. The inhibitors were tested in the loop at a concentration of 2wt%. The experiment conducted is a constant volume batch experiment where the reactants (CNG, water and inhibitor) were fed into the loop, and the loop was shut in and conditioned to hydrate formation conditions. A rapid reduction in loop pressure at the end of the 2-hour experiment is an indication that the reactants formed hydrates, and the inhibitor used was not efficient.

3. Results and discussion

The pressure against time for the experiments performed with the thermodynamic hydrate inhibitors (MeOH and MEG) was plotted (Figure 2). The chart shows a significant decrease in temperature in the experiment conducted with MEG compared to the experiment conducted with MeOH. This suggests that 2wt%MEG was not efficient and preventing hydrate formation in the two-hour experiment conducted in the loop. Also, at the end of the experiment, valve v5 (Figure 1), which is attached to the coldest pipe in the loop was clogged by hydrate crystals. Valve v5 was not plugged-in experiments conducted with 2wt% MeOH. This implies that at

2wt%, methanol was sufficient at preventing hydrate formation; however, MEG was not. Although methanol gave favourable results, it poses a lot of health and safety concerns.

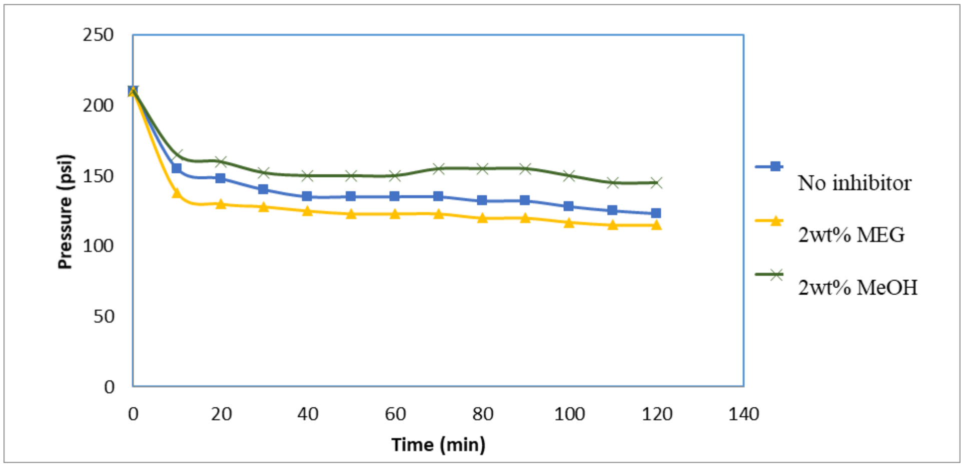

Figure 2. Plot of Pressure versus time for 2wt% methanol, 2wt% mono ethylene glycol and the uninhibited system

Although MEG performed poorly at inhibiting hydrate formation in the loop, it is a better inhibitor because it has fewer health and safety concerns. It can also be regenerated, which can help with conserving the cost of purchasing new inhibitors. Hence to improve the performance of MEG, this research studies the synergy from adding KHI to MEG. Although THIs are effective at retarding hydrate growth and slowing down hydrate formation, they may be inefficient at preventing hydrate formation in shut down and restart conditions. It is desirable to have the combined advantage of THI depressing hydrate formation conditions and KHI retarding hydrate growth.

Figure 3 shows the plot of loop pressure against time in the experiment conducted without inhibitor. The loop pressure steadily declines from 150psi to 100psia at the end of the 2-hour experiment. To make the MEG/PVP blend, 2wt% MEG was combined with 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09 and 0.1wt% of Polyvinyl Pyrrolidone (PVP) respectively to evaluate the best blend that can synergistically inhibit gas hydrate formation across mini flow loop. Figure 4 show the plot of pressures against time for the various blends used in the constant volume experiment. The extent to which the loop pressure changes from start to end of the experiment indicates the inhibitor's effectiveness. If the loop pressure declines slightly, the inhibitor is efficient at reducing hydrate formation. However, if there is a rapid pressure decline, the inhibitor was inefficient, and gas was used up in forming hydrate.

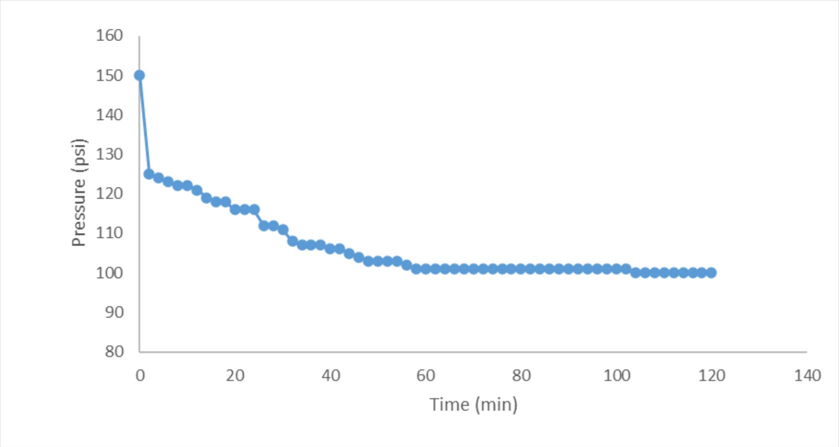

Figure 3. Plot of pressure against time with no inhibitor

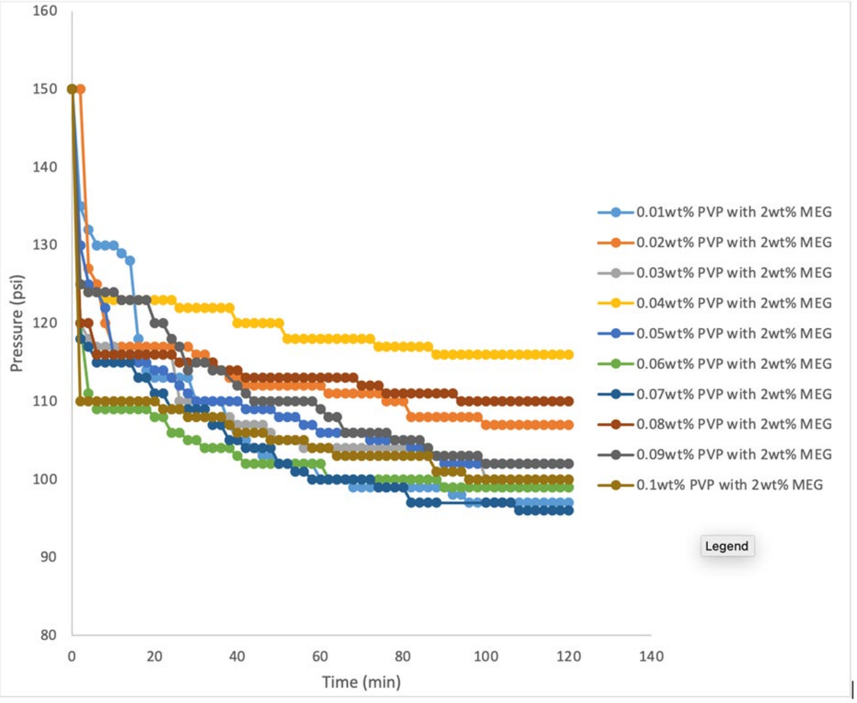

Figure 4. Plot of pressure against time for experiments conducted with the various blends of PVP and MEG

The pressure decline in each experiment is summarized in the bar chart (Figure 5). When 2wt% is blended with 0.01wt%, the total pressure decline in the loop was 53psi. 0.02wt%PVP blended with 2wt%MEG performed better as the experiment conducted with this blend recorded a 35psi pressure decline, showing that the blend was more effective and less gas was used up in forming hydrates. However, increasing the concentration of the PVP to 0.03wt%PVP blended with 2wt% MEG resulted in a reversal trend as the total pressure decline of the loop was 51psia. This trend is observed as the inhibitor concentration increases, the pressure drop of the loop decreases and subsequently rises with increasing PVP concentration.

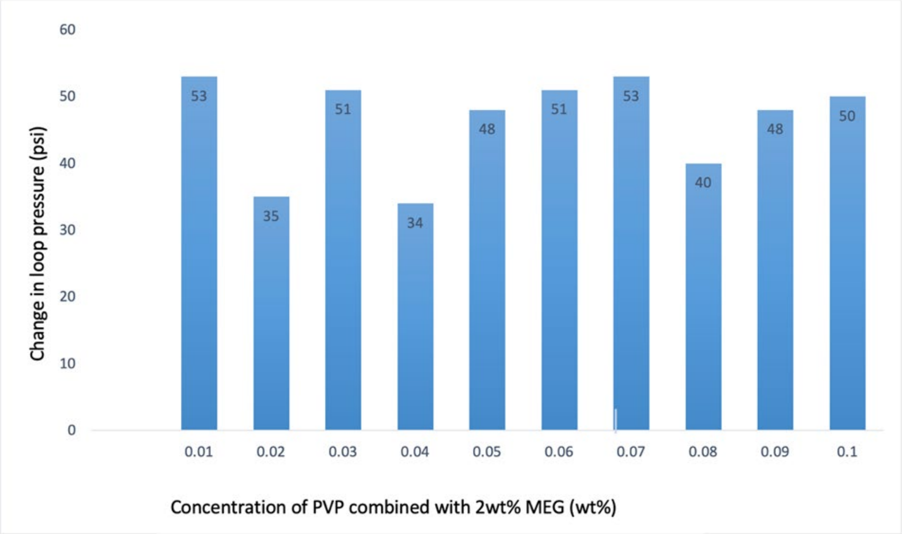

Figure 5. Plot of change in loop pressure against inhibitor concentration

From all the MEG PVP blends considered, the best blend is 2wt%MEG mixed with 0.04wt%PVP. It gave the minor pressure decline. Although in terms of cost, it will be preferable to use 0.02wt% PVP blended with 2wt%MEG, which showed a pressure decline of 35psia.

4. Conclusion

Experiments were conducted to study the synergistic effect of PVP and MEG in inhibiting hydrates in a horizontal skid-mounted laboratory flow loop. This was done to enhance the performance of MEG, which erstwhile could not prevent hydrate formation at the concentration studied (2wt%). It was desired that the new blend of PVP and MEG will delay hydrate formation and retard hydrate growth. The best blend of PVP and MEG was the blend of 2wt%MEG and 0.04wt%PVP because it gave the lowest pressure drop in the flow loop, indicating less hydrate formation in the loop. Knowledge from this research is helpful in maintaining the operating condition and preventing hydrate plugs formation during the residence time of the fluids in the flow line.

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