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Experimental investigation on the impact of Vinisil, Rubber Latex and Methacrylate Ester with Dimethylaminoethyl for dehydration in natural gas pipeline

Godloves NT*, Alerechi UP, Onwuchekwa OV

ABSTRACT

Hydrate formation is a major issue with flow assurance in the oil and gas business. Hydrates compounds are crystalline and non-stoichiometric substances that form when gas and water are combined at high pressure and low temperature. Hydrates accumulating along flow line could cause restrictions to flow. In order to conduct a constant volume experiment in this work, three kinetic hydrate inhibitors—Vinisil, Rubber Latex, and Methacrylate Ester with Dimethyl aminoethyl—are utilized in a laboratory flow loop at 150 psi for two hours. The laboratory flow loop of 12 meters is built from 316 stainless lengths of steel with an internal diameter of 0.5 inches. Coolant is contained in a 4-inch Polyvinyl Chloride (PVC) conduit that encircles the steel pipe. The loop's goal is to look at how hydrate production and inhibition work. Three indicators to indicate that hydrate formation is taking place in the loop are a rise in the loop temperature, a rise in the differential pressure, and a decline in the loop pressure. It was discovered that 0.05 weight percent Rubber Latex and 0.05 weight percent Vinisil effectively inhibited hydrate formation in the loop. In terms of inhibiting hydrate formation, 0.05 weight percent Methacrylate Ester with Dimethyl aminoethyl performed poorly, as shown by the laboratory flow loop. This research succeeded in deriving mathematical models that reflected the behaviors of these inhibitors within the laboratory flow loop. The experiment reported in this article can be used to screen hydration inhibitors prior to field application.

Keywords: Characterization, Hydrate, Rubber Latex, Vinisil, Methacrylate Ester, Gas Pipeline

1. INTRODUCTION

Gas hydrates are non-stoichiometric crystalline structures because of hydrogen bonding between water molecules, which form holes that can store gas or volatile liquid molecules (Chatti et al., 2005). Low temperature and high pressure promote hydrate formation, which also needs the presence of a hydrate former and a sufficient volume of water (Bazvand et al., 2021). At temperature at which hydrates develop, hydrogen bonds in water cause molecules to align in a regular orientation, forming cages. When particular substances, referred to as guests or formers, stabilize the water lattice, hydrate is produced. The latter establishes the exact pressure and temperature at which hydrate formation takes place.

Based on their crystal structure; hydrates fall into three major categories: Structure I, Structure II, and Structure H hydrates. Hydrates of Structure I are produced by hydrogen sulfide, methane, carbon dioxide, and ethane; Structure II hydrates are produced by nitrogen, propane, and iso-butane. These compounds are commonly found in the petroleum industry (Gajanan et al., 2024). All common hydrate formations, according to Ibrahim, (2023) include about 15 mol% hydrocarbons as guests and 85 mol% of water as the host. In addition to well control lines during drilling Liu et al., (2021), permafrost during enhanced oil recovery using carbon dioxide gas Sousa et al., (2019), and other systems where the conditions required for hydrate formation are met hydrate can form in pipes used in petroleum production, according to.

The initial discovery was made by Zhang et al., (2024) of gas hydrate while studying gas transmission lines. Given the right conditions, hydrates can form in a variety of gas systems, including compressed natural gas Nikolaou, (2010) and liquefied petroleum gas (Zhu et al., 2023). The management of hydrates during gas expansion was covered by (Sarker et al., 2012). Production losses, irreparable damage, dangerous circumstances, and production shutdowns could result from the presence of gas hydrates. Pressure control, pigging Gao et al., (2018), thermal insulation Bell et al., (2021), electrical heating Urdahl et al., (2004), heat removal of hydrate formers, or fluid separation, and the most effective and practical method the chemical method have all been used to control hydrates (Cha et al., 2019). Earlier on following hydrate discovery Zhang et al., (2024), hydrate blockage in pipes was avoided by using thermodynamic hydrate inhibitors (THI) like methanol and glycol.

Still, THI's exorbitant price Okereke et al., (2019), THI's incompatibility with manufacturing chemicals like asphaltene inhibitors and chemical wax and THI's toxicity and inefficiency Lesor and Alozie, (2023) have forced the manufacturing industry go in search for an inhibitor substitute. The introduction of HYDRAFLOW, a cold flow technique for hydrate management Tohidi, (2014), avoided the need for expensive thermal/chemical inhibitors. The cold flow concept that has been proposed is based on allowing gas hydrate formation in the presence of excess water and employing low dose anti-agglomerates when needed to prevent hydrate agglomeration in order to remove the gas phase by converting it into hydrates through reactivity with generated or added water (Ground water from the ocean). Although it hasn't gained much traction, this approach is still in its infancy.

According to Lesor and Alozie, (2023) testing, cationic starch can be used to remove formed hydrates or inhibit hydrate formation by acting as an anti-agglomerate and kinetic inhibitor alongside little concentrations of polyethylene oxide (PEO). Using reactive compounds like epoxypropyltrimethylammonium chloride on a slurry of partially swollen starch granules (from wheat, potatoes, tapioca, and amylocorn) and cationization reagents from ammonium group, sulphonium group, amino group, or quaternary ammonium group, is how cationic starch is produced in this method. It takes a lengthy and intricate process to produce the cationic starch, and edible starch is needed. The first successful deployment of KHI chemistry in a wet gas pipeline that connected the Hyde-West Sole gas field to the onshore Easting gas terminal located in the UK region of the southern North Sea was reported by (Bazvand et al., 2021).

KHI chemistry replaced both methanol and glycol. Offshore logistics were greatly reduced because KHI deployment only required a storage tank and metering pumps, and the required concentration of KHI for hydrate inhibition was approximately 5500 ppm. The use of vinylmethylacetamide (VIMA) and vinylcaprolactam copolymer (VCAP) was discussed by Liu et al., (2021) as a kinetic hydrate inhibitor. This KHI's effectiveness was verified by flow loop testing prior to its successful implementation in three offshore and one inland area. The effective dosage range for this KHI was 550–3000 parts per million. The KHI was used to regulate hydrates in production flow lines and gas lift lines.

In addition, compared to earlier methanol programs, it reduced the chemical cost for hydrate inhibition by 16 to 55 percent and was environmentally benign and compatible with other manufacturing chemicals. The addition of THI at high concentrations (10–60 weight

percent) alters the chemical potential of the aqueous or hydrate phase (Heidaryan et al., 2010). On the other hand, by changing the hydrate structure, KHI slows down hydrate production and raises the energy needed to produce hydrates (Kannan et al., 2024). Furthermore, KHI can inhibit gas diffusion into the hydrate phase, which forces hydrate crystals to develop between and around polymer strands, so slowing down the growth of hydrates (Huang et al., 2024).

KHI functions better with fluctuating water cuts and lower emulsions. Additionally, they honor the environment (Kannan et al., 2024). However, because of their limited sub cooling they are vulnerable to brine salinity Kamal et al., (2016) and offer quicker shut-in times (Taheri et al., 2024). KHI creates a cleaner condensate/oil phase with minimal to no methanol, which refineries like. It also overcomes logistics (supply and delivery) issues. It was discovered by Kannan et al., (2024) that employing a KHI rather than methanol in a deepwater pipeline would save approximately \$125000 to \$140000 per month.

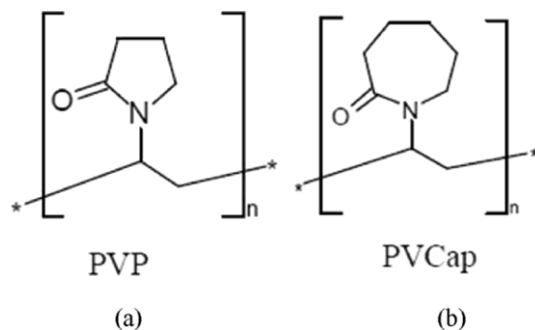


Figure 1 The Molecular configurations of (a) Vinisil and (b) Rubber Latex.

Initially, KHI was produced using Poly Vinylpyrrolidone and Poly-Vinylcaprolactam as shown in Figure 1 was identified early in the 1990s by Colorado School of Mines (Okereke et al., 2019). In order to enhance these polymers' functionality, synergists have been added since then. The vinylcaprolactam/polyvinylpyrrolidone/dimethylaminomethacrylate terpolymer was employed by Bloys and Lacey, (1995) in their field experiment. Each terpolymer component—Methacrylate Ester with Dimethyl aminoethyl, Rubber Latex—is evaluated for its inhibitive quality in this study as seen in Figure 2 as well as Vinisil (First, with a flow loop in a laboratory). Some KHI patents employ these polymers as fundamental elements, particularly PVP and PVCap (Bazvand et al., 2021; Pomicpic et al., 2023).

The conventional methodology for collecting data in a laboratory flow loop involves observation, which involves indirectly monitoring the hydrate phase by indications such as a concomitant rise in temperature or drop in fluid phase pressure. Hydrate production is seen in a constant volume apparatus in the event of a sudden reduction in pressure or rise in temperature. Temperature rises Wang et al., (2023), Lan et al., (2024) as a result of the exothermic process of hydrate production and the drop in pressure caused by the concentration of the gas confined in hydrate crystals.

2. EXPERIMENTAL SETTING

For this work, a closed 12-meter laboratory flow loop (Figure 3) made of 0.5-inch-diameter 316 stainless steel tubing and 4-inch insulated polyvinyl chloride (PVC) pipe was used. The skid-mounted loop was equipped with multiple components, including three valves, a gas mixing vessel, an inhibitor mixing vessel, five temperature gauges, eight pressure gauges, a manual pump, three electric pumps, and a compressed natural gas (CNG) compressor. The materials for the experiment are water, ice for cooling, methane-containing natural gas (CNG; Table 1), and potassium hydroxide (KHI) (Rubber Latex, Vinisil, and Methacrylate Ester with Dimethyl aminoethyl for hydrate inhibition.

$$\text{Specific Gravity (SG)} = \frac{\text{mass of gas}}{29} \quad (1)$$

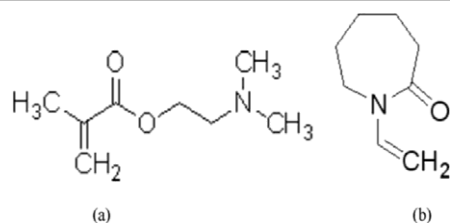


Figure 2 Molecular configurations of (a) 2-(dimethylamino)ethylmethacrylate and (b) N-Vinyl caprolactam.

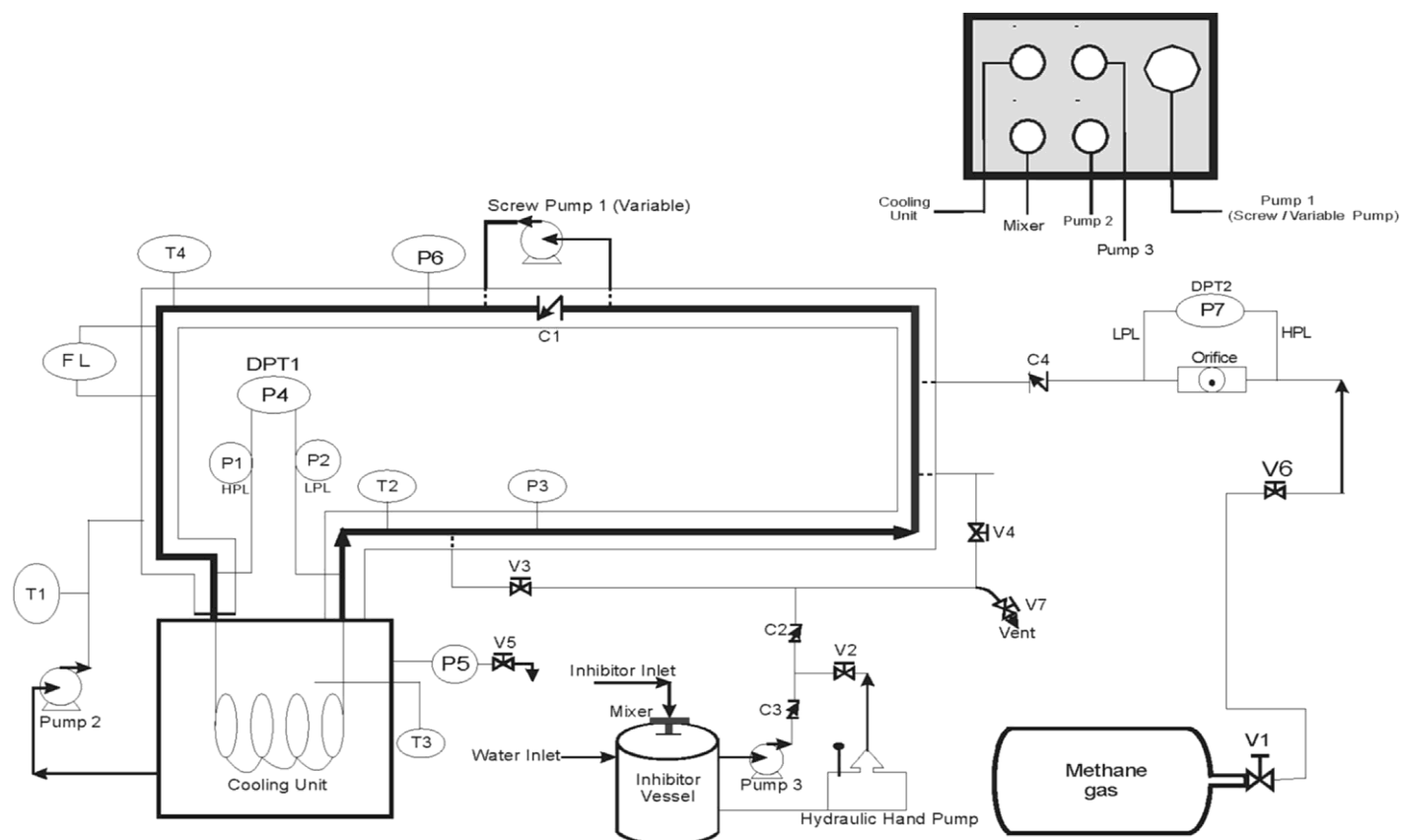


Figure 3 Process diagram of laboratory flow loop.

$$SG = \frac{(13.78 + 0.69)}{29} = 0.5$$

The CNG composition utilized in this investigation is displayed in (Table 1). Equation (1) was also utilized to compute the gas's specific gravity. During each experimental run, the loop pressure was increased to 25 psi by feeding it around 435 ml of water (or a mixture of water and inhibitor). After the loop achieves a pressure of 150 psi, the aperture is used to feed CNG into it. As the variable screw pump is turned on, 250 feet per hour flow rate is chosen. To speed up cooling, Pump 2 fills the refrigerator with ice. To remove the cold water from the refrigerator, it is turned on.

Temperature and pressure readings are taken every two minutes during the two hours of the experiment. The production of hydrate was indicated by decreased loop pressure (due to gas being used up in the constant volume experiment), a rise in differential pressure (because of hydrate crystal buildup), and an increase in loop temperature (due to the exothermic nature of hydrate formation). Comparable studies were conducted to assess the effectiveness of the various KHI replacing the water supplied into the loop in the uninhibited trial with a solution containing water and the required amount of inhibitor.

3. RESULTS AND DISCUSSION

To assess how well the KHI inhibited hydrates in the lab flow loop (Figure 3), the Differential Pressure was plotted against Time. The inhibitors used have the following concentrations:

Table 1 Composition of CNG.

	Mole fraction (%)	Molar mass (g/mol)	Mass (g)
Methane	98.44	16	13.78
CO2	1.56	44	0.6864
Total			14.47

0.05 wt% Methacrylate Ester with Dimethyl aminoethyl, 0.05 wt% Rubber Latex and 0.05 wt% Vinisil were also used. Temperature dropped from 310C to roughly 90C in 32 minutes during the inhibitor-free experimental run. After that, the temperature rises quickly from 90 to 1150 degrees Celsius. The exothermic reaction leading to hydrate formation is signaled by the temperature increase. Within 90 minutes, the temperature dropped sharply to 62.5 °C due to the cooling fluid circulating around the pipe's exterior walls.

However, a further temperature rise was then noted, indicating a more exothermic reaction involving the formation and growth of hydrates. The temperature increased steadily until the experiment ended at 8C after 120 minutes. Differential pressure increased progressively as temperature decreased in the differential pressure versus time plot. The differential charts were noisy due to the screw pump creating agitation in the loop. A spike in the pressure differential as seen in Figure 4 represents the obstruction brought on by hydrate crystals that have deposited along the loop's walls.

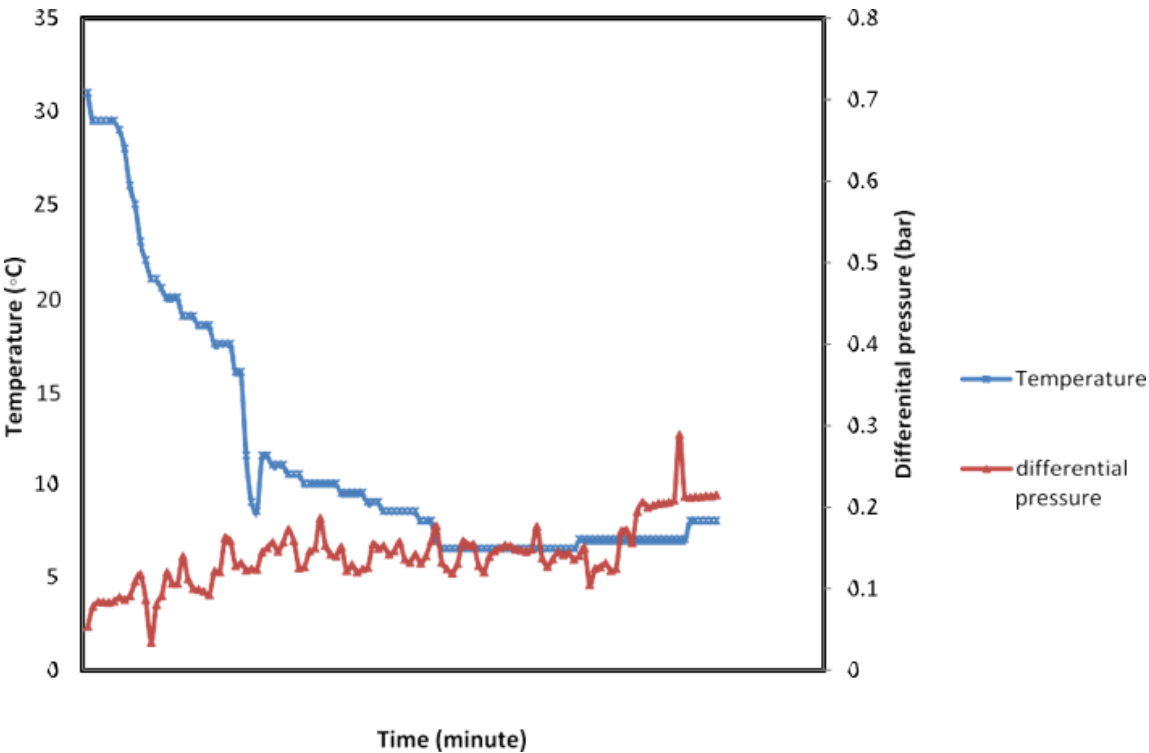


Figure 4 Differential Pressure and Temperature against time for uninhibited experiment.

As a result, the constant volume experiment validates hydrate formation by using compressed natural gas with the composition listed in Table 1 for two hours at 150 psi in a laboratory flow loop. To determine the impact of the inhibitors, a rerun of the experiment was carried out with 0.05% weight of Rubber Latex, Vinisil, and Methacrylate Ester with Dimethyl aminoethyl. Using 500 parts per million by weight (ppmw) of Rubber Latex as an inhibitor in the laboratory flow loop at 150 psi shown in Figure 5 resulted in a negligible change in differential pressure during the course of the experiment. It dropped in temperature from 31.05C to 6.05C. A rise in

temperature was not noticed. As a result, there was not a discernible rise in the differential pressure of the loop as a result of hydrate development or buildup around the pipe walls. This shows that there was not an exothermic event that created hydrate during the experiment.

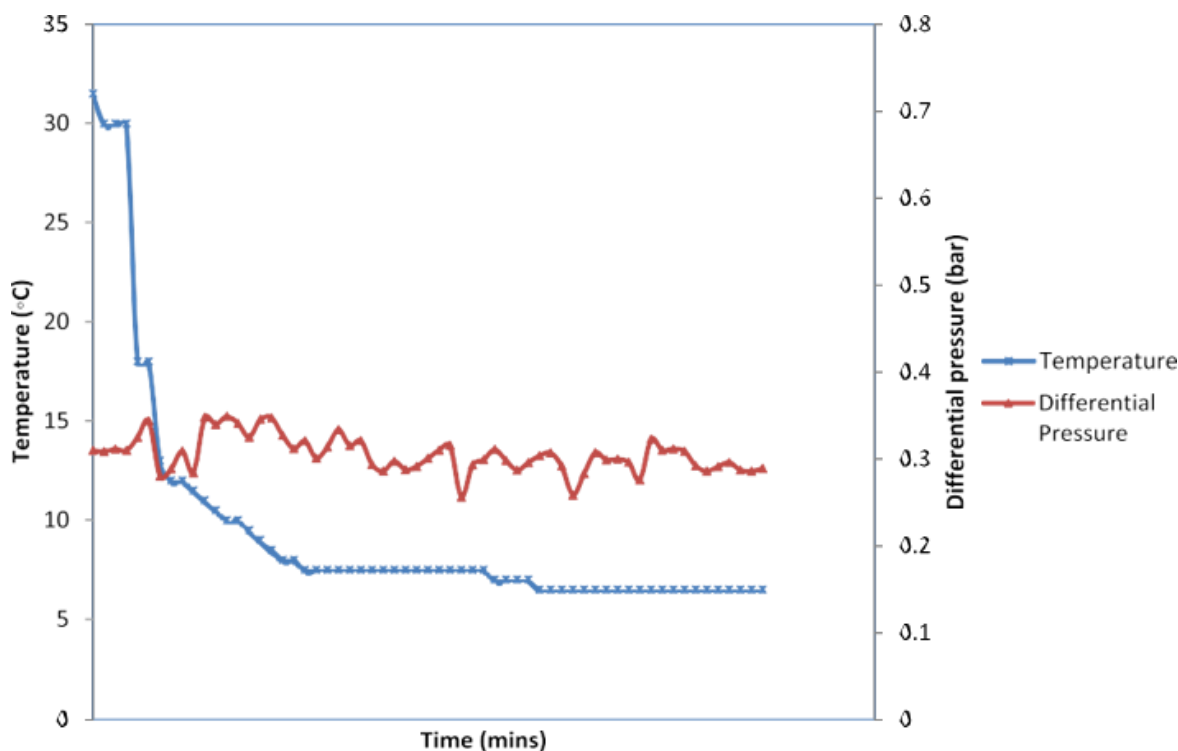


Figure 5 Differential Pressure and Temperature against time for system inhibited with 0.05 wt% Rubber Latex

In the experimental run using 500 ppmw or 0.05 weight percent of Vinisil, the differential pressure started at 0.68 bar for 20 minutes and then dropped to 0.5 bar as shown in (Figure 6). The differential pressure increased gradually after 50 minutes. The difference pressure dropped sharply once more after sixty-six minutes, this time from 0.55 bar to 0.42 bar. The differential pressure in the loop remained constant at 0.42 bar until the completion of the experiment. This implies that the differential pressure could not have rapidly increased if there had been a discernible buildup of hydrate crystals. Furthermore, in 34 minutes, the temperature plummeted from 27.5-27.5 oC to 8 oC, where it remained for 16 minutes before falling again to 7oC and remaining stable for 26 minutes in Figure 6 the temperature eventually dropped to 7oC at 76 minutes, and it remained there until the experiment was completed.

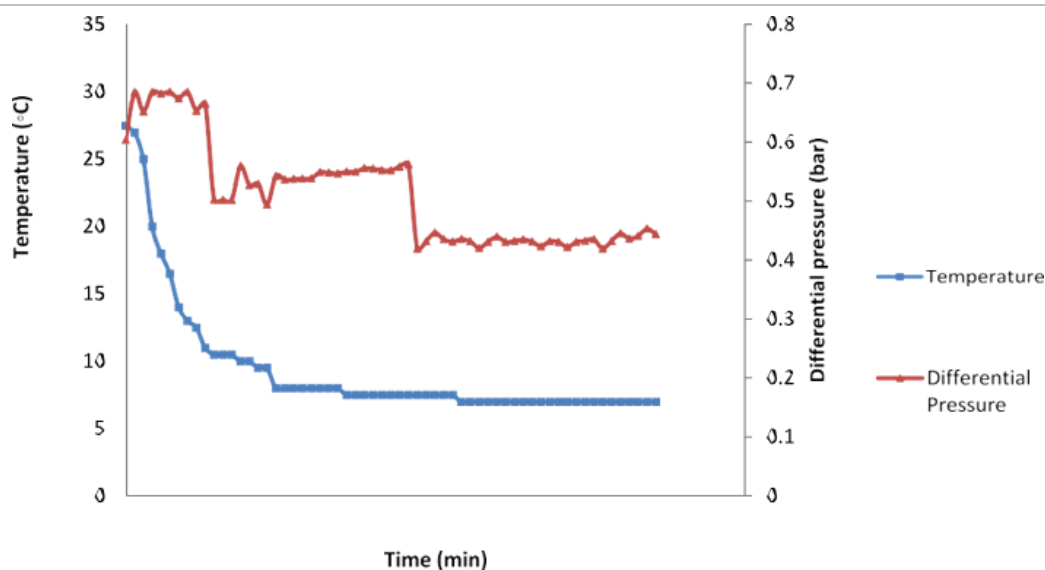


Figure 6 Differential Pressure and Temperature against time for system inhibited with 0.05 wt% Vinisil.

When 0.05% weight percent (500ppmw) Methacrylate Ester with Dimethyl aminoethyl was used as an inhibitor, the differential pressure dropped from 0.36 bar to 0.28 bar in about 40 minutes as seen in Figure 7; at 44 minutes, the differential pressure then somewhat increased to approximately 0.37 bar. After decreasing progressively to 0.33 bar for about 32 minutes, the differential pressure dropped quickly to 0.13 bar depicted in (Figure 7). Approximately 0.13 bar was the difference pressure at the conclusion of the experiment. The increase in differential pressure indicates that the hydrates particles may have produced partial constriction around the pipe walls. Eventually the differential pressure dropped because the hydrate crystals were unfortunately carried away by the loop pressure.

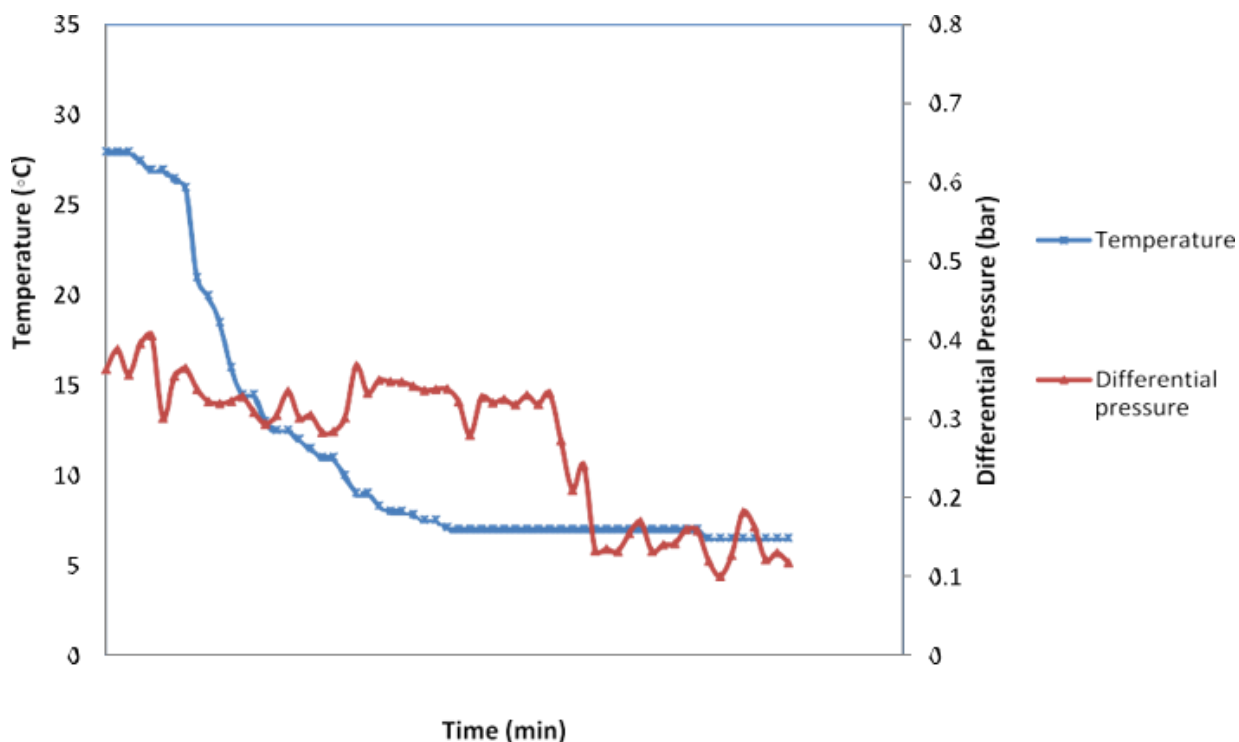


Figure 7 Differential Pressure and Temperature against time for system inhibited with 0.05 wt% Methacrylate Ester with Dimethyl aminoethyl

The loop temperature dropped from 28°C to 7°C in 58 minutes when Methacrylate Ester with Dimethyl aminoethyl was present, and it stayed at 7°C for around 38 minutes as seen in (Figure 7). The loop's temperature then fell to 6.5 °C, where it remained until the experiment was completed. The differential pressure plot suggests the potential for hydrate formation when Methacrylate Ester with Dimethyl aminoethyl was used as an inhibitor at 0.05 weight percent, but no temperature increase was seen. The extremely minor temperature rise in this Methacrylate Ester with Dimethyl aminoethyl experiment those results from hydrate formation was probably missed by the experimental loop due to equipment constraints because data was manually gathered every two minutes.

Plotting the loop pressure against time for both the experimental runs with and without inhibitors allowed researchers to compare the effectiveness of the inhibitors utilized in this work shown in (Figure 8). An indicator of a KHI's effectiveness is its ability to delay the formation of hydrates in a given system for a set period of time, or "hold time". The pressure reduction gave an indirect indicator of the amount of gas used in hydrate formation and, thus, the inhibitor's effectiveness. Each trial run began with a visible and brief reduction in pressure during the first five minutes due to the mixing of the gas and water phases and the gas being absorbed by the water phase. The uninhibited system was originally subjected to pressures of 95 psi, Methacrylate Ester with Dimethyl aminoethyl, 110 psi, 123 psi, and Rubber Latex, 130 psi, respectively depicted in (Figure 8).

In the inhibitor-free experimental run, the initial rapid reduction from 150 psi to 95 psi was followed by a progressive drop in loop pressure from 95 psi to 70 psi in about two hours. The loop pressure remained constant at 70 psi after the experiment was concluded. Also, in the trial conducted with 0.05 weight percent Rubber latex, an alternative pattern was seen. After the initial, abrupt reduction in pressure from 150 psi to 120 psi at 8 minutes, the pressure steadily decreased to 110 psi at 36 minutes, where it remained for around 26 minutes. After that, it dropped to 108 psi at 72 minutes and finally to 105 psi from 112 minutes until the end of the experiment. There was only a 45-psi total pressure reduction from the start of the experiment to the finish, as opposed to 80 psi in the uninhibited experiment.

This indicates a decrease in the amount of gas used up in the hydrate formation process within the loop and a slowdown of the process caused by the addition of 0.05 weight percent of Rubber Latex. The loop pressure declined from 150 psi to 123 psi in 6 minutes during the 0.05 weight percent Vinisil trial run. It then gradually reduced to 110 psi in 28 minutes and remained there until the 22nd minute. The loop pressure steadily dropped from 110 psi to 105 psi at minute 92, and it remained there until the end of the experiment shown in (Figure 8). Compared to the 80 psi pressure decline in the inhibitor-free experimental run, less pressure was lost during the 45 psi pressure decline in the Vinisil experimental run. This implies that 0.05 % weight Vinisil was successful in inhibiting the laboratory loop at 150 pressures.

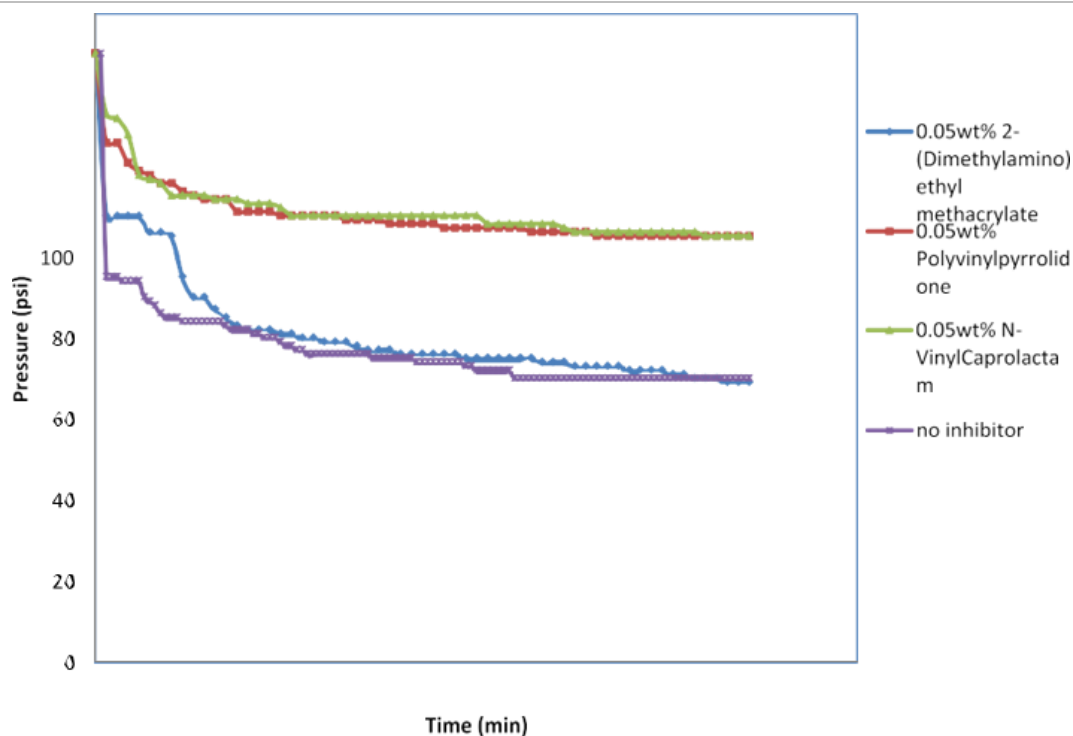


Figure 8 Plot of pressure against time for the commercial KHI.

Noteworthy, Rubber Latex demonstrated a better ability to prevent hydrate formation in the laboratory flow loop early in the experiment than Vinisil because its initial pressure decline of 20 psi (from 150 psi to 130 psi) was smaller than the 27 psi (from 150 psi to 123 psi) observed in the Vinisil experimental run. In the early 14 minutes of the experiment, Methacrylate Ester with Dimethyl aminoethyl showed good inhibitory activity, blocking the formation of hydrates during the 0 point05 weight percent Methacrylate Ester with Dimethyl aminoethyl period 8. However, when the residence period exceeded 14 minutes, 0.05 weight percent Methacrylate Ester with Dimethyl aminoethyl could no longer prevent the development of hydrate crystals. By the time the experiment ended, the loop pressure had dropped to 70 psi.

Hydrates were formed through the extraction of gas molecules from the constant volume experiment. This indicates that the experiment's overall pressure reduction was 80 psi, the same as the uninhibited trial's total pressure decline. Based on the experimental data, mathematical models were developed to describe the hydrate formation in the laboratory flow loop during the constant volume experiment, as well as the effects of Rubber Latex, Vinisil, and Methacrylate Ester with Dimethyl aminoethyl on hydrate inhibition shown in (Figure 9 to Figure 12). The mathematical models can be used to calculate the loop pressure for any of the several tests discussed above at any given time.

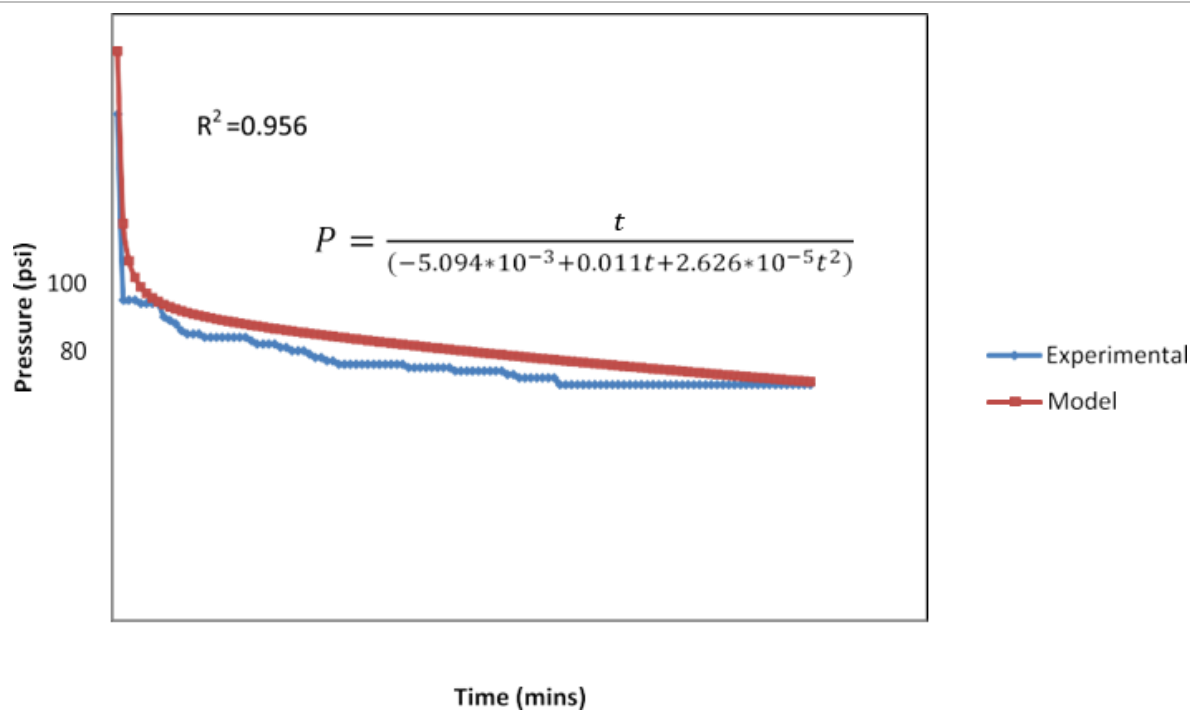


Figure 9 Mathematical model of hydrate formation in uninhibited laboratory flow loop.

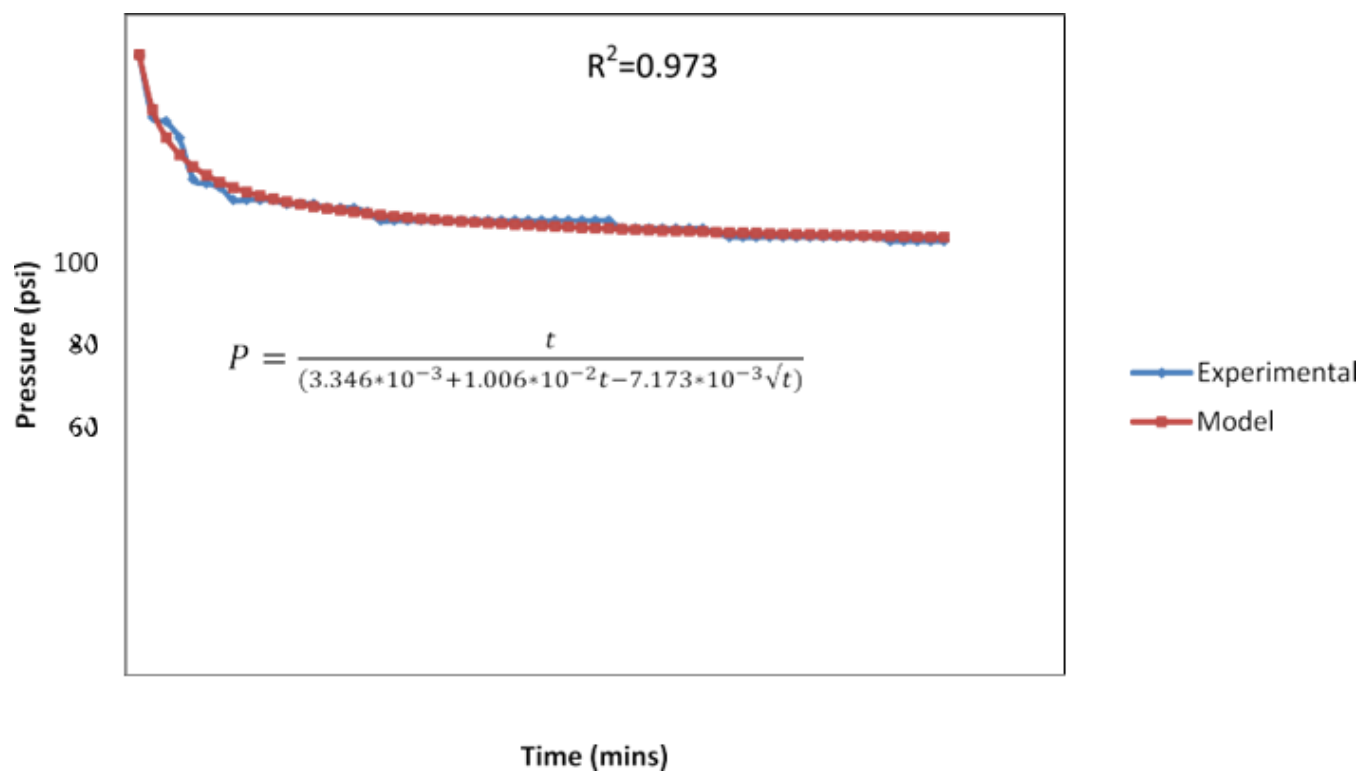


Figure 10 Mathematical model of Hydrate Inhibition in Laboratory flow loop using Rubber Latex.

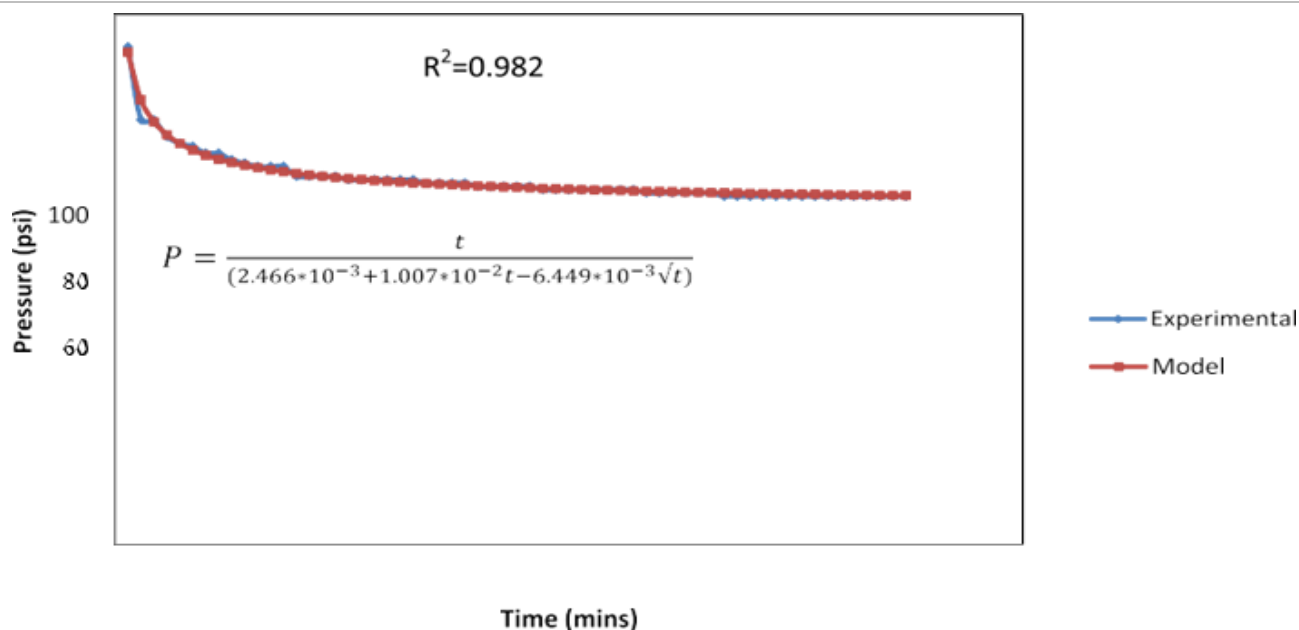


Figure 11 Mathematical model of Hydrate Inhibition in Laboratory flow loop using Vinisil.

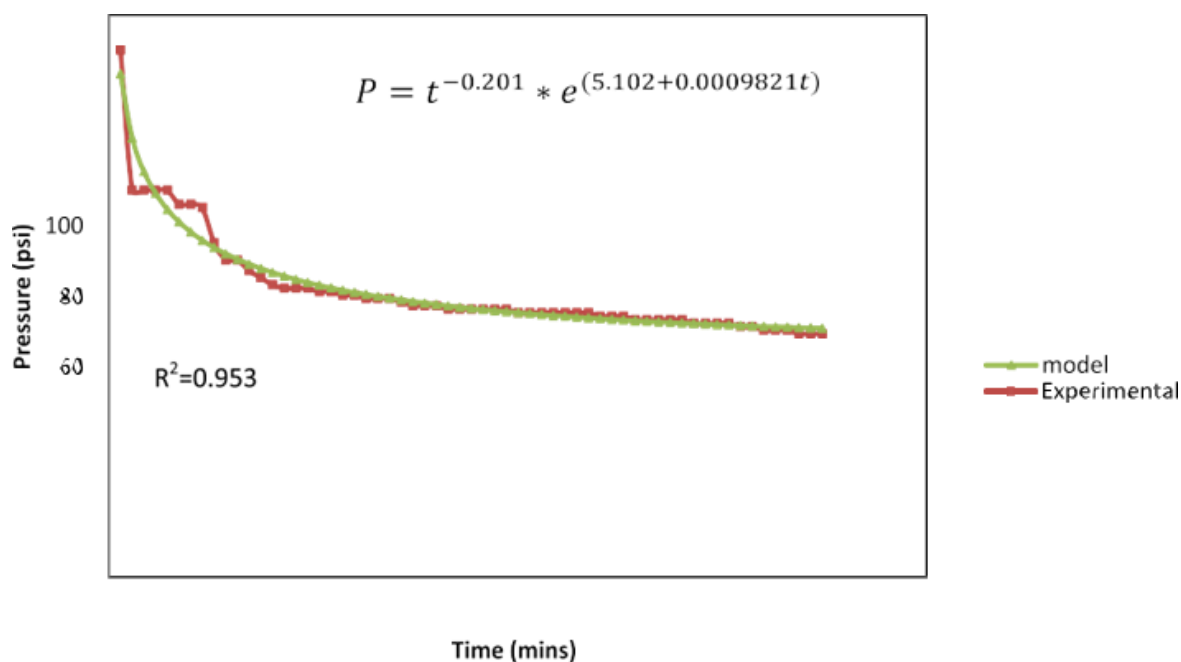


Figure 12 Mathematical model of Hydrate Inhibition in Laboratory flow loop using Methacrylate Ester with Dimethylaminoethyl

4. CONCLUSION

This work studied hydrate production and inhibition over a two-hour period at 150 psi using compressed natural gas of SG 0.5 in a constant volume experiment in a laboratory flow loop. In a comparative investigation, three KHIs—Methacrylate Ester with Dimethyl aminoethyl, Rubber Latex, and Vinisil—at similar doses were utilized to look at hydration inhibition. In the initial part of the experiment, Rubber Latex and Vinisil both pre-vented hydrate formation in the loop, with Rubber Latex slightly outperforming Vinisil. Conversely, 0.05 weight percent Methacrylate Ester with Dimethyl aminoethyl failed to effectively prevent loop hydration. A mathematical description of these inhibitors' efficacy in the loop was provided.

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Author Contributions

Contributions to the study were made by the authors.

Ethical Approval

Not applicable

Informed consent

Not applicable.

Conflicts of interests

The authors declare that there are no conflicts of interests.

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Data and materials availability

All data associated with this study are present in the paper.

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