

Performance of Poly Vinyl Caprolactam as Hydrate Inhibitor in a Prototype Horizontal Subsea Flowline

Toyin Olabisi Odutola, Okomo Felicia*

Department of Petroleum and Gas Engineering, Faculty of Engineering, University of Port Harcourt, Port Harcourt, Nigeria

Email address:

bissy.odutola@gmail.com (T. O. Odutola)

*Corresponding author

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Abstract: Hydrate formation in horizontal subsea flowlines can pose serious issues during petroleum production. In this study, a 12 meters laboratory flowline that closely mimics the conditions in a horizontal flowline is used to analyse Poly Vinyl Caprolactam's performance (PVCap) as a hydrate inhibitor. The 1/2inch diameter 12meter closed laboratory loop is immersed in a 4inch insulated PVC pipe containing cold water, simulating the offshore pipeline surrounded by cold water. Compressed natural gas comprising methane and carbon dioxide is fed into the hydrate loop and some water. The loop was pressurised to 150psia using compressed natural gas temperature, and pressure along the loop was observed using the several temperatures and pressure gauges around the loop. It was observed that a pressure decline in the loop indicated hydrate formation in the constant volume batch experiment conducted for two hours. The effect of 0.01wt%, 0.2wt%, 0.03wt%, 0.04wt%, 0.09wt% and 0.1wt% of PVCap was also studied. A reduction in the loop pressure indicated how much gas was used up in forming hydrates. As the concentration of PVCap increased, the volume of gas used up reduced, implying that hydrate formation reduced with increasing PVCap concentration. The optimum concentration in the study considered is 0.1wt%PVCap. PVCap performed optimally in preventing hydrate formation in the simulated subsea horizontal pipeline.

Keywords: Hydrate Inhibition, Horizontal Flow Loop, Poly Vinyl Caprolactam, Kinetic Hydrate Inhibitor

1. Introduction

The oil and gas industry is constantly exploring cheaper methods for producing oil and gas. To maintain optimal production level, the oil industry must find cheap solutions to harness the relatively small and medium fields already discovered. One of such methods include constructing underwater installations which are coupled with existing platforms and the introduction of subsea multiphase production. This will require knowledge of multiphase flow and affordable inhibitor technology for wax, corrosion, scale, hydrates, etc. The cost of inhibiting hydrate formation is an important factor in deepwater production [1].

Some methods of managing hydrates in subsea production include chemical treatment and the use of pipeline insulation. A innovative method that involves maintaining the produced fluids outside the hydrate region by having an outside jacket around the production line into which hot water is injected from the platform is being developed for a field in the UK

sector of the North Sea [2]. The deepwater environment exposes subsea flowlines to temperatures near 40° F, which can cause hydrate formation and create production problems. These hydrate plugs have been as long as 6.2 mi and have even blocked large pipelines of about 40 inches in diameter. Some of these plugs can take weeks and even months to dissociate. Not only do these plugs cause a loss in production, but they also create severe safety and environmental hazard [3].

Gas hydrates are solid crystalline substances that are formed by the interaction of water and gas molecules under suitable temperature and pressure conditions. Prevention of hydrate formation during deepwater drilling operations is of paramount interest to the drilling engineer because it causes congestions, blockages and flow assurance concerns in the wellbore and the flow components.

Gas hydrates were first obtained by Joseph Priestley in 1778 by bubbling SO₂ through 0°C water at atmospheric pressure and temperature. Priestley discovered Oxygen, hydrogen, SO₂, formed crystals. However, when describing

the crystals he obtained, he did not name them hydrates. Later, in 1811, similar crystals of aqueous chlorine were named hydrates of gas by Davy. Priestley was the first scientist to create gas hydrates in the laboratory but Davy gave the name hydrates to the crystals.

After this discovery, the oil industry ventured into various researches on hydrate related scenarios. It is speculated that hydrates are one of the most promising unconventional resources for supplying future's energy because 1m^3 of hydrate can contain as much as 170Sm^3 of gas [4].

The formation of a hydrate requires the following three conditions [5], as seen in Figure 1:

1. The right combination of temperature and Pressure (Hydrate formation is favoured by low temperature and high pressure).
2. The presence of a hydrate former (such as methane, ethane, and carbon dioxide).
3. Sufficient amount of water.

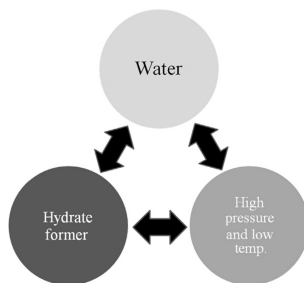


Figure 1. Hydrate cycle.

Gas hydrates can form several structures. It is important to understand the different types of hydrate structures when proposing mitigating measures. The most well-known and researched hydrate structures are called- Type I and Type II. However, recently a third structural configuration of hydrate known as Type H was discovered and has attracted much attention because it contains a large cavity that can hold larger molecules than either Type I or II. Saturated cyclic hydrocarbons such as cyclopentane have been found to contain Type H hydrates. Evidence of Type H was found in a natural gas hydrate collected from the seafloor of the Gulf of Mexico. However, there has barely been any proof to suggest that Type H hydrates form in oil and gas production.

Hydrates cause a lot of flow assurance problems which may lead to huge losses in revenue during production activities, especially in an offshore environment. Hence it is imperative to prevent hydrate formation. Techniques for preventing or inhibiting hydrate formation include lowering the system pressure, increasing the system temperature by heating, and drying the system to get rid of water by dehydration. All of these methods are theoretically possible but not practical and, therefore, are not commonly used. For instance, dehydration is not possible for subsea wells or small platforms with limited space. Heating and insulation can be used independently or jointly; however, it may not be cost-effective for longer flow lines carrying high gas-oil ratio fluids cause its installation is expensive. The chemical

method is the most widely used hydrate prevention method. It involves the use of three kinds of inhibitors namely: thermodynamic inhibitors (THI), kinetic hydrate inhibitors (KHI) and anti-agglomerants (AA).

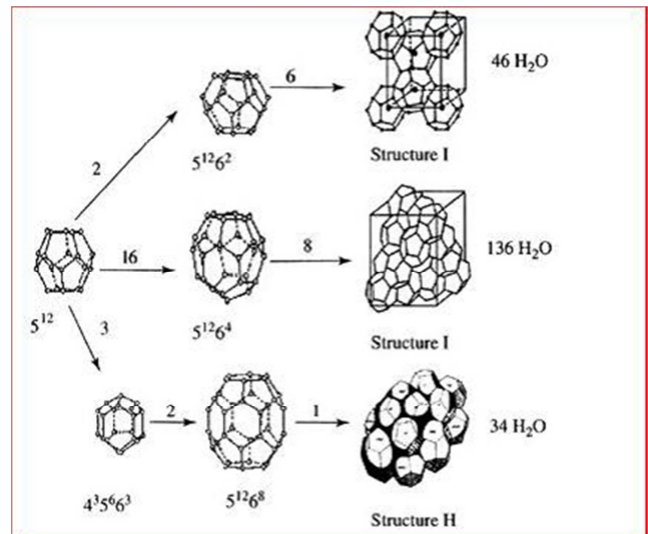


Figure 2. Showing different structures of hydrates [6].

The thermodynamic inhibitors are alcohols, glycols, and ionic salts. They depress the freezing point by shifting the equilibrium to a lower temperature, thus reducing the region where hydrates can exist as well as changing the thermodynamics of the system [7]. This method, although efficient, is not economical due to the high volume of THI required, giving rise to increased production cost, and they also have a negative impact on the environment [8].

The low dosage hydrate inhibitors (LDHI) are in two classes: kinetic inhibitors and anti-agglomerants. They are called low dosage because they can be applied in significantly lower concentrations than the thermodynamic hydrate inhibitors.

Anti-agglomerant (also called anti-coagulant) inhibitors do not prevent hydrate formation but prevent the accumulation of hydrate into a plug (Corrigan et al., 1996). The chemicals prevent agglomeration of the hydrate crystals formed. The crystals stay in a slurry that can still be transported and will not plug the line.

Kinetic inhibitors are polymers, and their effective concentration for preventing hydrate formation is about 10-100 times lower than that of methanol and ethylene glycol. They prevent hydrate nuclei from forming larger crystals and thus delays hydrate formation (Lederhos et al., 1996). Some examples of kinetic hydrate inhibitors (KHI) are PVP (polyvinylpyrrolidone), VC-713 (Ndimethylaminoethylmethacrylate), PVCap (Poly Vinyl Caprolactam), VP/VC (polyvinylpyrrolidone/Nvinylcaprolactam polymers) [11]. The use of Kinetic Hydrate Inhibitors involves the minimal dosage of inhibitor and reduction in production cost based on logistics and chemical purchase.

The equipment used in this study is a horizontal 12-meter

closed loop that models offshore horizontal flow. This equipment has been used in studying the effect of several KHI as recorded, such as 2-(dimethylamino)ethyl methacrylate [12], Poly Vinyl Caprolactam [13], and modified starch [14]. This experimental study is aimed at investigating the effectiveness of Polyvinyl caprolactam (PVCap) on hydrate prevention and selecting the optimum dosage of poly-vinyl Caprolactam for hydrate inhibition in a laboratory hydrate flow loop that closely simulates offshore conditions.

2. Methodology

The experiment was conducted in a 12meter laboratory flow loop that closely simulates offshore flowline conditions. The loop consists of a 1/2inch pipeline that is immersed in a 4inch insulated PVC pipe containing cold water being generated from the refrigerating unit. The half-inch pipe, which represents the subsea flowline, contains methane and sufficient water for hydrate formation. The loop has pressure and temperature monitors at strategic parts in the loop (Figure 3).

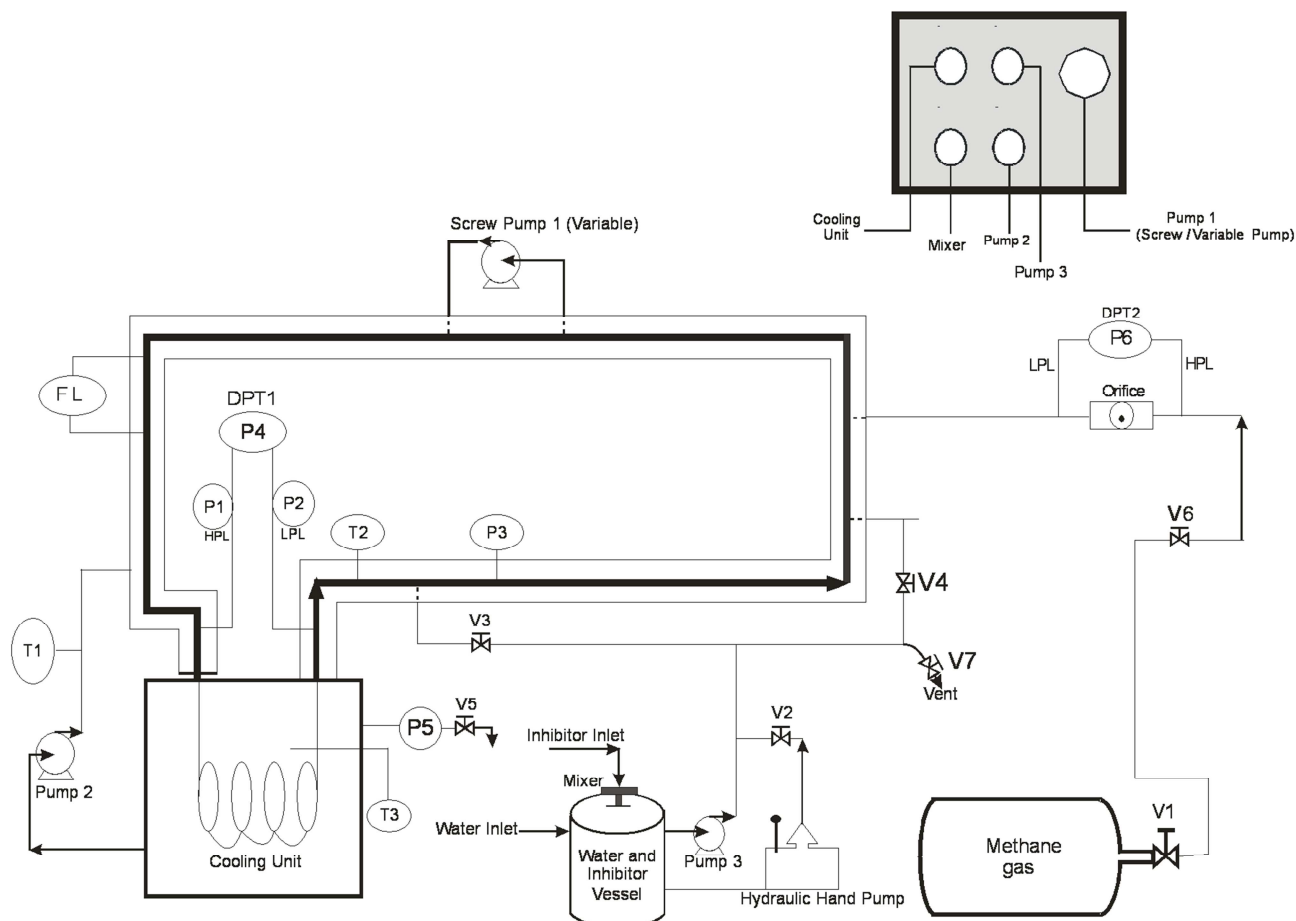


Figure 3. Flow Diagram of the Mini Fluid Flow Loop [15].

The experiment was conducted at a pressure of about 150psi with different concentrations 0.01 wt%, 0.02 wt%, 0.03 wt%, 0.04 wt%, 0.09wt%, 0.1wt% of Polyvinyl Caprolactam (PVCap) to obtain the maximum concentration of PVCap. The batch experiment was run for 2 hours for each PVCap concentration considered. The properties of PVCap used in this study are shown in Table 1, while the composition of the compressed natural gas used in this study is shown in Table 2.

Table 1. Composition of CNG.

	Mole fraction (%)	Molar mass	Mass
Methane	98.44	14	13.78
CO ₂	1.56	44	0.6864
Total			14.47

Table 2. Properties of PVCap.

Properties	
Chemical formula	C ₆ H ₁₁ NO
Molar mass	113.16 g·mol ⁻¹
Appearance	White solid
Density	1.01 g/cm ³
Melting point	69.2°C (156.6°F; 342.3 K)
Boiling point	270.8°C (519.4°F; 544.0 K) at 1013.25 hPa
Solubility in water	866.89 g/L (22°C)
Vapour pressure	0.00000008 mmHg (20°C)

3. Results and Discussion

The experimental apparatus used in this study operates a constant volume batch process. This implies the

reactants (hydrate former and water) were put in the loop, and the loop was conditioned to the hydrate formation conditions (high pressure and low temperature) for two hours. The pressure and temperature were observed in this two-hour period to draw up inferences on whether hydrate formation occurred or not. A reduction in the loop pressure is an indication of hydrate formation. This is

because some volume of gas has been used up in forming hydrates; hence there is a reduction in the loop pressure. Figure 4 is a plot of pressure against time in the uninhibited experiment. Notice that the pressure drops rapidly from 150psia to about 70psia during the two hours experiment.

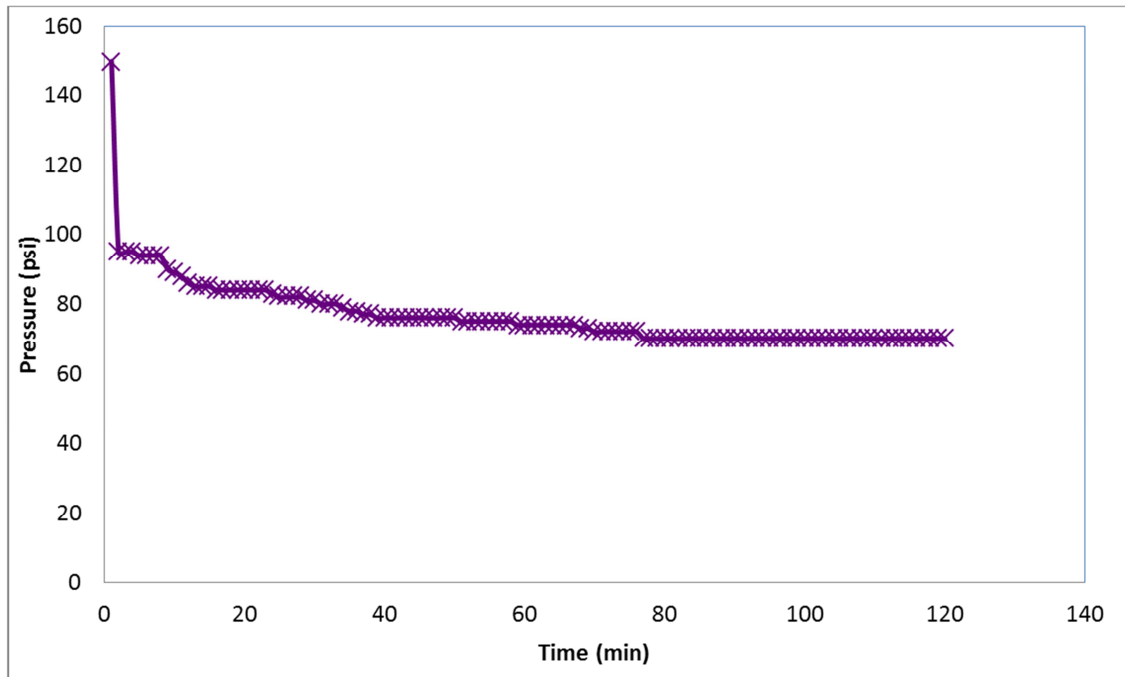


Figure 4. Plot of Pressure against time for the uninhibited system.

Figure 5-10 shows the plot of pressure against time in the experiments conducted with 0.1wt% PVCap, 0.2wt% PVCap, 0.03wt%PVCap, 0.04wt%PVCap, 0.09wt% PVCap and 0.1wt%PVCap. Notice that the final pressure at the end of the experiment was about 120psi for the experiments conducted with 0.01 to 0.04wt% PVCap. However, the pressure at the end of the experiment in the higher concentrations of 0.09wt% and 0.1wt% are 145psia and 125psia, respectively.

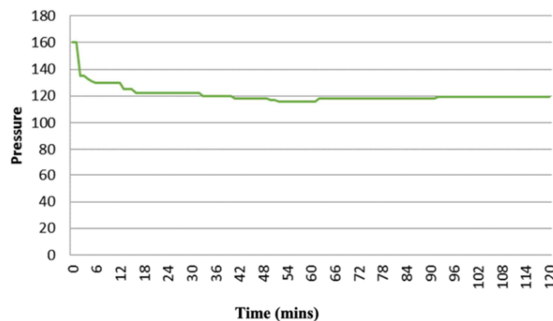


Figure 5. Plot of Pressure against time for the system with 0.01 wt% PVCap.

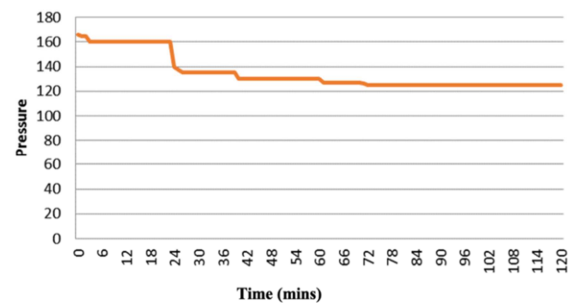


Figure 6. Plot of Pressure against time for the system with 0.02 wt% PVCap.

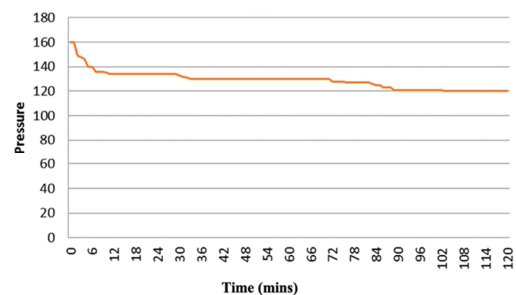


Figure 7. Plot of Pressure against time for the system with 0.03 wt% PVCap.

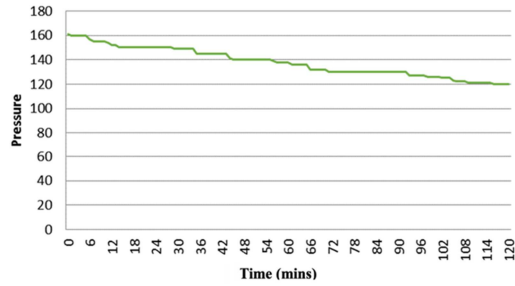


Figure 8. Plot of Pressure against time for the system with 0.04 wt% PVCap.

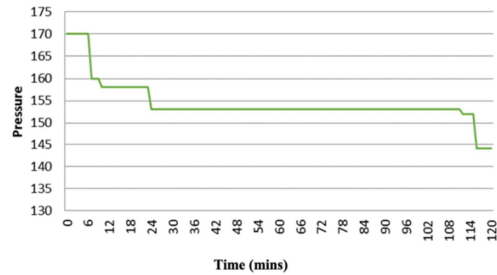


Figure 9. Plot of Pressure against time for the system with 0.09 wt% PVCap.

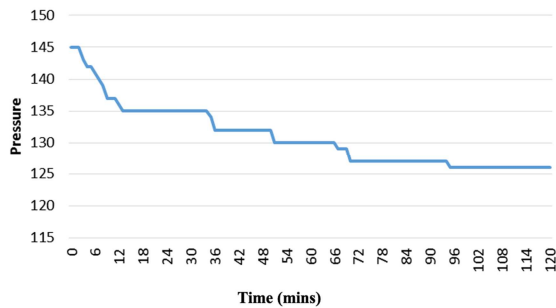


Figure 10. Plot of Pressure against time for the system with 0.1 wt% PVCap.

Table 3 shows the pressure changes measured in the loop when different concentrations of PVCap were used as hydrate inhibitors. Noted that as the concentration of gas increased, there was a decrease in pressure change; this shows the effectiveness of the inhibitors as the inhibitor concentration was increased.

Table 3. Change in Pressure caused by the addition of different concentration of PVCap.

Concentration of PVCap (wt%)	Change in pressure (psia)	Used Volume (cm ³)
0	85	0.002417
0.01	41	0.000481
0.02	41	0.000439
0.03	40	0.000451
0.04	41	0.000456
0.09	36	0.00023
0.1	20	0.000205

The loop change in pressure is an indication of the amount of gas used up during the experiment. The higher the change in loop pressure, the less effective the hydrate inhibitor was. The cumulative volume of gas consumed in each experiment was computed using equation 1

$$V_2 = \frac{P_1 V_1 T_1}{T_1 P_2} \quad (1)$$

Where:

P_1 =Initial Pressure of the gas dominated system from gauge P1 (psia)

V_1 =Initial Volume of the gas (cm³)

T_1 =Initial Surrounding Temperature from gauge T1 (°C)

T_2 =Final Surrounding Temperature from gauge T1 (°C)

P_2 =Final Pressure of the gas dominated system from gauge P1 (psia)

The computed volume of gas shows the amount of gas used up in the system in forming hydrates and can also be used as an indicator for inhibitor effectiveness. This is because as the volume of gas consumed decreases, it implies that less hydrate was formed, and the inhibitor is effective. Figure 11 is a plot of the volume of gas consumed versus percentage concentration of Poly Vinyl Caprolactam. Notice that the uninhibited system consumed a gas volume of 0.002417cm³ while the system inhibited with 0.1wt% PVCap consumed a volume of gas of about 0.000205cm³, indicating that less hydrate was formed in the system with 0.1wt% PVCap and the inhibitor was efficient.

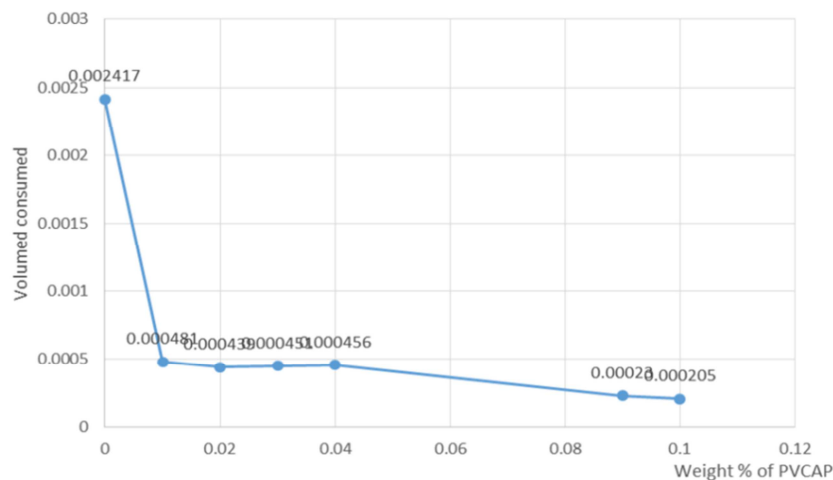


Figure 11. Plot of the volume of gas consumed versus concentration of PVCap.

4. Conclusion

This study investigated the use of Polyvinyl Caprolactam as a hydrate inhibitor in a 12-meter laboratory flow loop. It was discovered that PVCap efficiently reduced hydrate formation. Increasing the concentration of PVCap applied in the loop reduced the volume of gas used up in the loop. Hence, the increase in PVCap concentration reduced the hydrate formation in the hydrate loop. Also, increasing the concentration of PVCap decreased the change in loop pressure, indicating less hydrate formation. The optimum concentration of PVCap in this study is 0.1wt%. PVCap is strongly recommended as a viable hydrate inhibitor.

Further studies should be conducted with higher concentration of PVCap. The performance of PVCap should be compared to other thermodynamic hydrate inhibitors. Also, the experiment should be designed to be a constant pressure continuous flow experiment and results compared to the batch experiments conducted.

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