

Evaluating the Performance of Deep Eutectic Solvent using Synergetic Compounds in Gas Hydrate Inhibition

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Abstract

This work focuses on inhibiting hydrate formation by investigating and improving the performance of choline chloride-based deep eutectic solvent (DES) inhibition using a synergetic compound such as MEG, DES and (DES+MEG) as hydrate inhibitors at varying percentage of 1wt%, 3wt%, and 5wt% and then evaluates the effect on a mini flow loop. It was observed that the synergetic compounds improved the inhibition effect of DES and the inhibition performance in ascending order of DES, MEG and DES+MEG. It was observed that 5wt% of (DES+MEG) gave the best performance with an efficiency of 80% as calculated. However, 3wt% was the optimum weight with efficiency of 73.75% while 1wt % of (DES+MEG) also performed better than all the weight percentages of DES and MEG when used alone. A model for computing the percentage efficiency of the inhibitor has been developed to forecast the efficiency of other inhibitors to be developed in the future. Based on the results gotten (DES+MEG) could be recommended for field trial.

Keywords: Gas hydrate; Ethylene glycol; Choline chloride; Deep eutectic solvent; Flow loop.

1. Introduction

Natural gas operation has its own problems in exploration and processing stage. One of the most challenging problems in natural gas is loss in revenue because of hydrate formation in processing and distribution facilities [1]. Gas hydrate forms at a very low temperature and high pressure in the presence of adequate amount of free water in the facility, e.g. flow line. Gas hydrates are attributed to quantifiable health and safety risk and loss in production due to flow blockage as a result of its formation leading to economic loss. Hydrate production problem can occur in pipelines, valves, and orifice plates due to Joule-Thompson effect (water condensation because of low temperature leading to gas expansion [2]).

Hydrate build-up can cause reduction in internal diameter of the tubular, increased surface roughness on the pipe wall, burst pipe, wear and tear of tubular and damage to valves thereby making it difficult, hence forcing shutdown of the operation or production facility [3]. In gas hydrate, lattice structure and water molecules are linked together by strong hydrogen bond and as such, the water molecules can be put in different configurations with its ability to accommodate more guest molecule of different sizes and one cavity holding up to a single molecule but in extreme condition especially in the presence of hydrogen clathrate, 2 to 4 are observed in each cavity [4]. While many hydrates forming gases of different sizes have been identified, we have only three (3) main hydrates structure and they are: structure I, structure II and structure H.

Hydrate formation involves four basic steps which are: diffusion of gas into water, nucleation, crystal growth and agglomeration. In order to prevent production problem relating to hydrate formation, the gas hydrate flow assurance relies on modifying or removing one or

more of the elements required for formation of hydrate i.e., removing the amount of water available for hydrate formation by dehydration and also by keeping the operating pressure and temperature off the hydrate formation region during normal production. This is achieved either by adding chemical compounds such as thermodynamic inhibitors e.g., methanol and/or monoethylene glycol (MEG) or heating/insulating the flow line to increase the temperature, operating the pressure outside the hydrate stability zone using a method called depressurization. New method used in gas hydrate flow assurance is the use of low dosage hydrate inhibitors. It includes anti-agglomerate which prevent hydrate agglomeration by the control of solid hydrate particles or kinetic hydrate inhibitor (KHI) which delays crystal growth [1]. Thermodynamic method is the most used technique in preventing gas hydrate blockage. The amount needed is measured in the laboratory or predicted using thermodynamic model for the specific fluid composition, worst operating condition and water cut. It specifically shifts the hydrate phase equilibrium curve out of the hydrate free zone [5]. However, kinetic hydrates inhibitors being water soluble polymers with additional organic molecules delay nucleation and the crystal growth of gas hydrate [4]. There are several industrial accepted methods deployed on our production facilities to prevent hydrate formation, they are: Insulation, continuous heating, use of chemical and periodic remediation. The cost of each of the methods varies as new technology evolves. Chemical inhibition such as methanol, ethylene glycol or low dosage hydrate inhibitor (LDHI) can be used for short time operation such as planned shut down or delay in well start.

Deep eutectic solvent (DES) has low vapor pressure and therefore non-flammable with high viscosity, biodegradable and are considered a unique family of ionic liquid and its non-toxic nature holds potential as green solvent for chemical reaction. They contain large non-symmetric ions with low lattice energy and melting points. They are mostly obtained by the complexation of quaternary ammonium salt with a metal salt or hydrogen bond donor (HBD) [6]. The term DES and ionic liquid have been used interchangeably in the literature. However, they are two different types of solvents. DES are formed from the eutectic mixture of Lewis or Bronsted acids and bases and can contain varieties of anionic and/or cationic species. The structures of choline chloride and urea is shown in Figure 1.

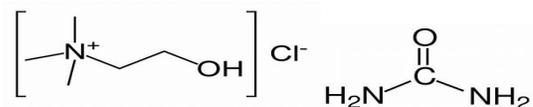


Figure 1. Choline chloride and urea structure respectively

Ionic liquids (ILs) on the other hand are formed from a system composed primary of one type of discrete anion and cation.

Deep eutectic solvents are generally classified as organic solvents with special quality, they are made up of one or more compounds in a mixture form to give a eutectic melting point much lower than either of the individual component. A good eutectic mixture is choline chloride and urea in the ratio of 1:2 molar ratio. The resulting mixture has a melting point of 12°C which is lesser than the melting point of urea 133°C and choline chloride 302°C and as such becomes liquid at room temperature. There are 4 types of eutectic solvents, and these are: Type I (quaternary ammonium salt + metal chloride); Type II (quaternary ammonium salt + metal chloride hydrate); Type III (quaternary ammonium salt + hydrogen bond donor), and Type IV (metal chloride hydrate + hydrogen bond donor).

Ethylene glycol is an inorganic compound widely used in the industry to inhibit hydrate formation especially in offshore hydrate control operations. Conventional thermodynamic hydrate inhibitors (THIs) methanol and monoethylene glycol have been mostly used because of their low cost and good performance. However, it poses issues in pipelines due to their corrosive, flammable and toxic nature. Hence for this reason, several research are currently being carried out on the development of eco-friendly ionic liquids from naturally derived substances e.g. urea. The mixture of choline chloride and urea to form a deep eutectic solvent which exist

in liquid state at room temperature has an advantage of being used as THIs in terms of handling, transport, and injection [7]. Generally, this form hydrogen bonds with water molecules, Ionic liquids and some naturally derived substance also exhibit distinct properties and functional groups required to act as effective hydrate inhibitors and hence demonstrate significant hydrate inhibition effect and biodegradability.

Tariq *et al.* [8] investigated hydrate formation in a Qatari gas sample and nitrogen gas in the ratio of 1:1, two experimental set up was used (a gas hydrate autoclave and a bench top reactor) which gave similar result. An inhibitor with a thermodynamic property (choline chloride) was used and from his result, he found that mixing Qatari gas sample with nitrogen gas inhibited and reduced hydrate formation and its mixture with choline chloride at 1% and 5% pushed hydrate equilibrium towards lower temperature and higher pressure. Sapir *et al.* [9] investigated the inexpensive deep eutectic solvent (DES) which he prepared by mixing choline chloride and urea in 1:2 molar ratio and heating to 60°C. The resulting deep eutectic solvent which is liquid at room temperature was shown to possess a unique solvating environment compared to water when polyvinylpyrrolidone was used as solute in the resulting solution, and at higher concentration, there was expanded conformation and good interaction among the component that made up the mixture compared to water as solvent in a solution with PVP. He found that the osmotic pressure of PVP solution in DES was like that of water and reinstated the fact that DES is a promising class of good solvent. In his work, he failed to compare the properties of PVP in DES during gas hydrate inhibition. Odutola *et al.* [10] designed and fabricated a 12-meter-long laboratory flow loop used for predicting hydrate formation and nucleation growth effectively and for screening and selecting hydrate inhibitors due to its ability to mimic the flowline. Roda *et al.* [11] discussed the green and versatile behavioral properties of deep eutectic solvent in the development of green and sustainable technologies. He further emphasized more on the application of DES in polymer synthesis and summarized his work by explaining that DES application is versatile and can be used as active component for polymer-based formulation. Sivabalam *et al.* [12] presented a mini review and discussion on the application of DES as the solvent of the future. He examined the advantages it possesses where it has been used e.g., Enhanced oil recovery (EOR), flow assurance issues and impurities removal and encouraged researchers to investigate greener alternatives as the awareness towards environmental issues increases and more work to enhance the viability of DES in oil and gas application especially in flow assurance. Lee *et al.* [6] investigated the thermodynamic inhibition effect of choline chloride and urea in a deep eutectic mixture on methane hydrate using a hydrate liquid vapour equilibrium (HL-VE) in the presence of choline chloride (1wt%, 3wt% and 5wt%), urea (1wt%, 3wt% and 5wt%) and DES (3%wt). The result illustrated that choline chloride, urea and DES were able to shift the hydrate equilibrium temperature to a stable inhibition region at constant pressure and can therefore function as a good thermodynamic inhibitor. It was shown that choline chloride had the most inhibition effect and the inhibition performance of DES was slightly higher than that of urea. However, its availability and non-toxic nature makes it a considerable option for future flow assurance problems. Hussain *et al.* [13] evaluated and reviewed low dosage quaternary ammonium salts and ionic liquids which can function as the thermodynamic and kinetic hydrate inhibitors. His work covers the latest quaternary ammonium salt used and its inhibition mechanism, hydrate suppression temperature, hydrate dissociation enthalpies and electrical conductivities. His work gave an insight to future understanding of quaternary ammonium salts.

This study enhances hydrate inhibition performance of deep eutectic solvents using ethylene glycol as a synergetic compounds to improve the inhibition performance of DES (mixture of choline chloride and urea) on methane hydrate. It was achieved by preparing a deep eutectic solvent from choline chloride and urea in 1:2 molar ratio, the behavioral properties of deep eutectic solvent was ascertained on a mini flow loop so as to determine the most effective concentration within a specified range of inhibitor that could inhibit gas hydrate formation in the presence of synergetic compounds and finally, design a hydrate inhibitor for shut in and start up by adding synergetic compounds to improve the nucleation.

2. Methodology

2.1. Hydrate formation equipment and materials

The flow loop comprises a refrigerator, a manual pump, three circulation electric pumps, inhibitor vessel, control panel, gas cylinder with compressed natural gas (CNG), 0.5-inch stainless steel pipe, differential pressure meter, pressure gauges and temperature gauges [10]. Figure 2 is the modified schematic diagram of the loop while the detailed information about the pumps used during the experiment are shown in Table 1.

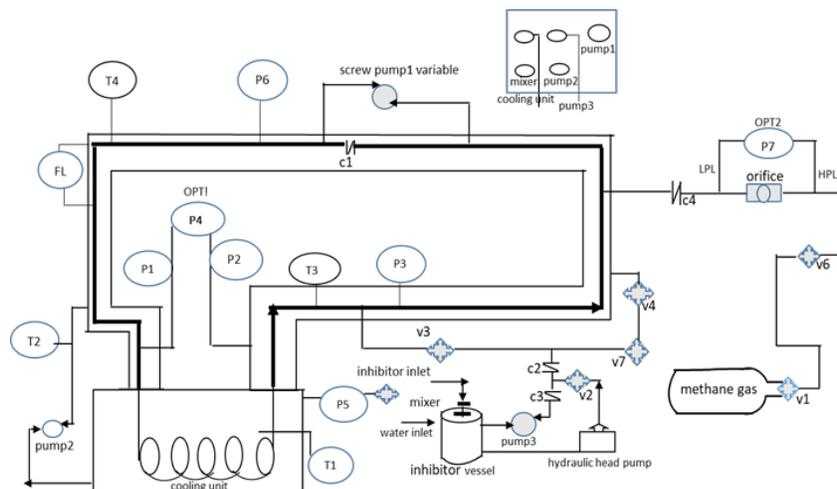


Figure 2. Process flow loop schematic diagram

Table 1. Detailed information of pumps used

Operating condition	Pump 1 (INGCO QB60 type)	Pump 2 (INGCO Q860 type)	Pump 3 (ATLAS 125 ATP 1.25 type)
Power, W	372.8	372.8	745.7
Rated capacity	220volt, 2.5 amperes	220volt, 2.5 amperes	220volt, 4.8 amperes
Speed	2850 rev/min.	2850 rev/min.	2850 rev/min.
Frequency	50hertz	50 hertz	50 hertz
Max. liq. tempt.	50°C	50°C	50°C
Maximum suction	8 meters	8 meters	8 meters
Maximum head	35 m	35m	60m
Uses	It moves fluid along the loop	It pulls cooling water from cooling unit circulate it between inner surface of PVC pipe and outer surface of 0.5-inch stainless steel pipe.	It moves the mixture of inhibitor and water into 0.5inch ID stainless steel pipe

2.2. Experimental materials

Detailed information on the chemicals used in the work are displayed in Table 2.

Table 2. Information of chemicals used

Materials	Chemical formula	Producers	Purity (%)	Molecular weight (g/mol.)
Choline chloride	C ₅ H ₁₄ NO.Cl	Lobachemie PVT Ltd, India	98	139.62
Urea	CH ₄ N ₂ O	Lobachemie PVT Ltd, India	99	60.06
MEG	C ₂ H ₆ O ₂	Lobachemie PVT Ltd, India	99	62.07

The ice block and water were present inside refrigerator. The water has no specific volume but was maintained at a considerable amount while ice block was added depending on the temperature of the cooling water gauge reading needed.

This comprises of 98.44% of methane gas and 1.56% of carbon dioxide. Composition of compressed natural gas is shown in Table 3. The specific gravity of compressed natural gas (CNG) is calculated as follows $S.G = \frac{\text{mass of CNG}}{\text{mass of air}} = \frac{15.78+0.6864}{29} = 0.5$.

2.3. Inhibitors

The inhibitors consist of monoethylene glycol (MEG), DES (which is a mixture of choline chloride and urea mixed thoroughly at 1:2 molar ratio and heated to about 60°C and the resultant eutectic mixture is liquid at room temperature), tetramethylammonium chloride (TMACL). The inhibitors used were classified as:

- i. Sample A: monoethylene glycol (MEG) with percentage of 1%, 3% and 5%
- ii. Sample B: Deep eutectic solvent with percentage of 1%, 3% and 5%
- iii. Sample C: A mixture of Deep eutectic solvent and monoethylene glycol in the ratio of 1:1 volume percentage and the resultant mixture kept at 1%, 3% and 5%
- iv. Sample D: A mixture of deep eutectic solvent and tetramethylammonium chloride in the volume ratio of 4:1 and the resultant mixture was mixed with monoethylene glycol at 1:1 volume percentage and kept at 1%, 3% and 5%.

2.4. Inhibitors preparation

Deep eutectic solvent (sample B was prepared by mixing choline chloride and urea in 1:2 molar ratio and placing it in a water bath at 70°C for 30 minutes and stirring for eutectic mixture, the new product changed to liquid at room temperature. Before starting the experiment with the inhibitors, the volume of inhibitors to that of water with respect to the different weight percentages are displayed in Table 4.

2.5. Experimental runs and procedures

A total of thirteen experiments were conducted for a time of two hours each as follows:
First experiment runs with only water:

Steps:

- i. Power source and control panel were switched on.
- ii. The system was flushed with water to ensure it was free from debris and particles that would have interfered with experimental results.
- iii. 2660ml of water was poured into the inhibitor vessel.
- iv. Valve 4 and pump 3 were turned on to build the pressure up to 25psi.
- v. Compressed natural gas (CNG) was injected into the system to build up pressure to 150psi.
- vi. Pump 2 was turned on to fill the jacket with cold water from the cooling unit and was kept running as ice blocks were added to the unit to obtain the desired temperature.
- vii. At every two minutes time interval, pressure and temperature readings were taken and recorded.
- viii. The volume of water used in the absence of inhibitor was 2660mL.

Further experiment run using 1%, 3% and 5% of each of the samples A, B, C and D.

This was carried out by measuring and mixing 26.6mL, 79.8mL and 133mL of the inhibitor/samples with 2633.4mL, 2580.2mL and 2527mL of water respectively.

Steps:

- i. Power source and control panel was switched on.
- ii. The system was flushed with ordinary water to ensure it was free from debris and particles that might affect experimental results.
- iii. The inhibitor sample and water mixture were poured into the inhibitive vessel.
- iv. Valve 4 and pump 3 were turned up to build up the pressure to 25psi.

- v. Compressed natural gas was injected into the system to build it up the pressure to 150psi.
- vi. Pump2 was turned on to fill the jacket with cold water and kept running at desired temperature.
- vii. At time interval of two minutes, pressure and temperature readings were taken and recorded.

2.6. Inhibitor efficiency

In this work, the inhibitor efficiency is calculated using equation 1

$$E = \left(\frac{P_f - P_w}{P_w} + C \right) \times 100 \quad (1)$$

where E = Efficiency; P_i = initial pressure = 150psi; P_f = final pressure; P_w = final pressure uninhibited.

Constant,

$$C = 1 - \left(\frac{P_i - P_w}{P_w} \right) \quad (2)$$

If C is negative, then

$$C = 1 - \left(\frac{P_i - P_w}{P_i} \right) \quad (3)$$

3. Results and discussion

3.1. Suppression performance plots

The DES, MEG, and DES+MEG was evaluated using the laboratory flow loop which depicts the pressure and temperature variation with respect to time. The effect of various weight of the composition was comprehended.

3.1.1. Pressure versus time plot

The performance of the inhibited and uninhibited system is shown in Figures 3, 4 and 5. The first experiment was run without inhibitor, 950mL of cloudy effluent and gas hydrate particles were observed and obtained from the sample point opening at the end of the experiment. There was a sharp pressure drop to 110psi at the first 24 minutes of the experiment. After 60 minutes, the pressure decreased to 101psi. In 90 minutes, the pressure of 94psi was observed which dropped drastically to 82psi at 92nd minute and finally to 80 psi at the end of 120 minutes. As hydrate started forming in the inner line, more gas was used up which caused the drastic decrease in the loop pressure [14].

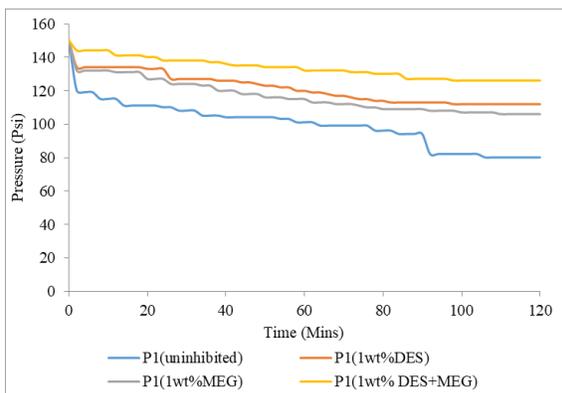


Figure 3. Graph of pressure against time for 1wt.% of inhibitors

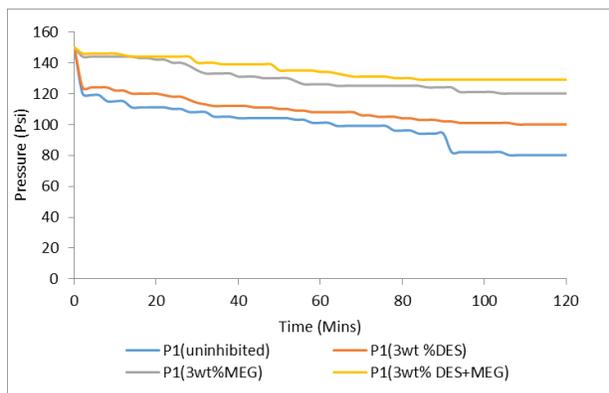


Figure 4. Graph of pressure against time for 3wt.% of inhibitors

The influence of MEG on DES is also in the Figures 3, 4 and 5. The strong attraction between hydrophobic group and the gas molecule inhibited the mass transfer of gas molecule from the gas phase to the aqueous phase decreasing the growth rate [15]. The various weight percentage of the mixture were all able to regulate the pressure drop except for the uninhibited

experiment with a value of 80psi at the end of the experiment, this is due to the gas being encapsulated by water to form clathrate leading to an increase in hydrate composition and decrease in overall potential energy which favours hydrate growth rate sustenance.

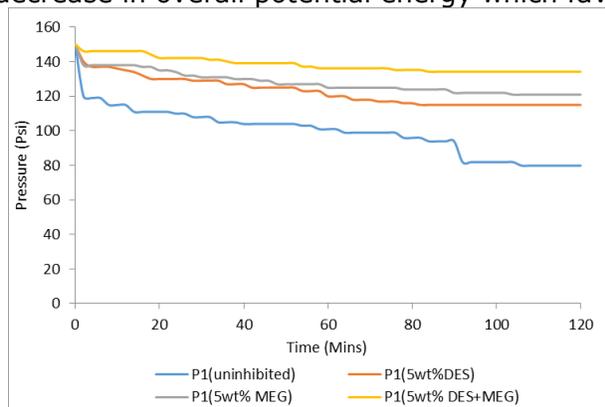


Figure 5. Graph of pressure against time for 5wt.% of inhibitors

The flow loop had pressure delayed or decreased drastically as an indication of hydrate inhibition or formation respectively. A rapid pressure decrease from the base pressure during the experiments indicate gas hydrate formation and as such water molecules encapsulates the gas in the system containing the hydrate formers to form cages but if the inhibitor is active, the inhibitor aligns in a pattern that water forms around them and not the cages.

During the uninhibited phase, the gas mixed exponentially with water leading to rapid agglomeration and growth in hydrate crystal which is considered the first phase of gas hydrate formation [16].

From the experiment, the addition of MEG as a synergetic substance to DES increases the inhibitive performance, this may not only be attributed to increase in hydroxide ion (OH^- group), DES contains bioactive compounds like quaternary ammonium salt from Choline chloride and Amides from urea which contributed to faster interaction with water to disrupt hydrate formation.

DES+MEG had the least change in pressure values in all wt.% at 126psi, 129psi and 134psi at the end of the experiment corresponding to 1wt.%, 3wt.% and 5wt.% respectively, performing better than all the wt.% of DES and MEG when considered independently. It prevented hydrate by adsorption to the hydrate crystal due to the presence of the functional groups contained in them (amides, ammonium salts and hydroxide ion). The presence of the amide group and more hydroxide ions added to the inhibition capacity of the DES+MEG.

3.1.2. Temperature versus time plot

Figure 6 shows temperature versus time plot for uninhibited, DES, MEG and DES+MEG for 1wt.%, 3wt.% and 5wt.% respectively. At the end of the 120 minutes, the temperature in the system was regulated by the wt.% of all the mixture better than the uninhibited where temperature tends to decline from 30°C to 18°C in 40minutes and to 13°C in 74 minutes after which there was a spike resulting to increase in temperature to 20°C at the end of the 120 minutes. The temperature increase was because of dissolution of methane gas in the cooling water causing reduction in induction time thereby inducing the agglomeration and precipitation of crystals particles signaling the onset of crystallization as saturation was reached. The onset of crystallization was seen as a spike in temperature due to the enthalpy of fusion caused by latent heat released and given out as experiment progressed. These findings concur with the findings of [17-20].

3.2. Initial pressure (P_i), final pressure (P_f), change in pressure and inhibition efficiency

The quantity of gas left in the system and the inhibition efficiency denotes the inhibitive capacity to suppress gas hydrate formation. The effectiveness of the DES+MEG shows that

the molecule did not only adsorb to the water/gas surface but were more hydrophilic in suppressing hydrate growth crystals. Figures 7, 8 and 9 show the pressure drop for each wt.% of the inhibitors studied and Figure 10 shows its inhibition efficiency.

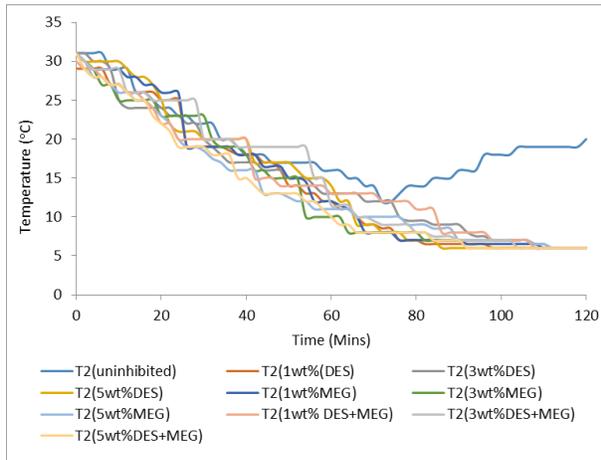


Figure 6. Temperature versus time plot for uninhibited, DES, MEG and DES+MEG

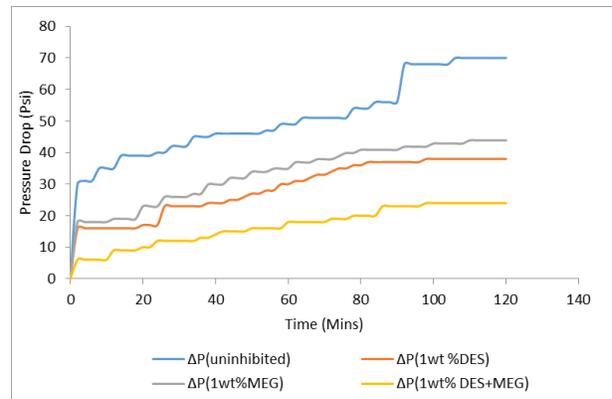


Figure 7. Pressure drop against time for 1wt.%

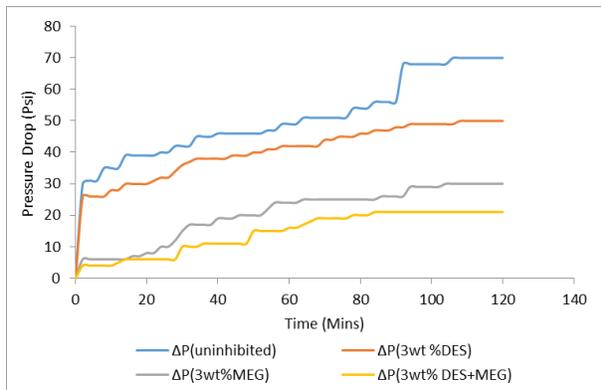


Figure 8. Pressure drop against time for 3wt.%

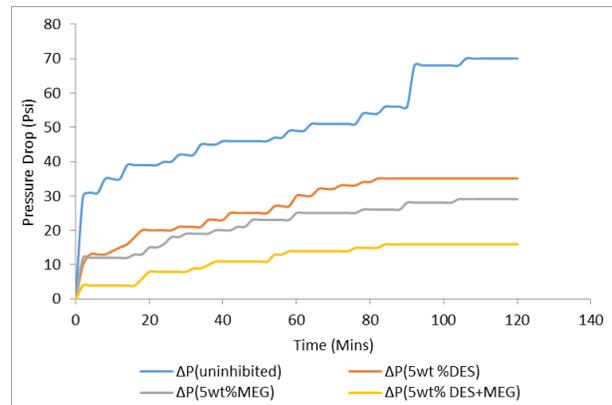


Figure 9. Pressure drop against time for 5wt.%

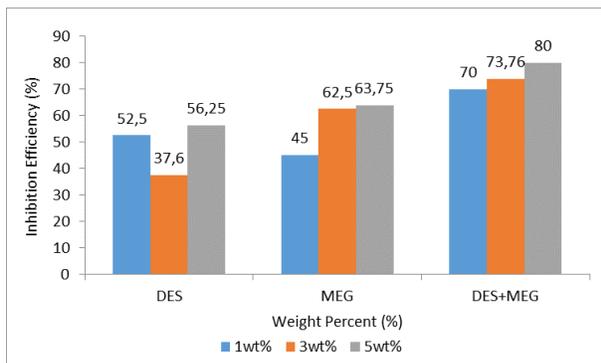


Figure 10. Graph of inhibition efficiency against weight percent of inhibitors

For the uninhibited, the efficiency was 12.5% and there was pressure drop of 70psi denoting that almost all the gas was used up forming gas hydrate as gas molecules kept dissolving thereby moving towards the hydrate crystal nucleation zone with new formed cages resulting to decrease in quantity of molecules of gas in the gas phase [17]. There was a pressure drop of 38psi, 50psi and 35psi with inhibition efficiency of 52.5%, 37.5% and 56.25% at the end of the experiment corresponding to 1wt%, 3wt.% and 5wt% respectively for DES and 44psi,

30psi, and 29psi with inhibition efficiency of 45%, 62.5% and 63.75% corresponding to 1wt.%, 3wt.% and 5wt.% respectively for MEG. The DES+MEG performed much better with a pressure drop of 24psi, 21psi and 16psi with efficiency of 70%, 73.75% and 80% corresponding to 1wt.%, 3wt.% and 5wt.%. 1wt.% of the synergist (DES+MEG) performed better than

the studied weight percentages of DES and MEG when used alone. This was due to the presence of amide; additional hydroxide ion and ammonium salt all adsorbing to the water/gas interface and disrupting hydrate formation.

4. Conclusion

In this work, the effect of monoethylene glycol, a conventional inhibitor was used to improve the performance of DES, a promising class of green (non-toxic and biodegradable) inhibitor. The presence of (DES+MEG) increased the induction time as observed, the interaction of the OH⁻ with water molecules and the subsequent disruption of hydrogen bonding of host water framework as the chloride and ammonium ions retarded the hydrate growth phase. The effectiveness of the DES+MEG shows that the molecule did not only adsorb to the water/gas surface but were more hydrophilic in suppressing hydrate growth crystals.

Based on the plots of pressure versus time for both the DES+MEG, MEG and DES inhibited systems, gas hydrate was inhibited but the DES+MEG performed better than the conventional MEG and DES in all the weight percentages considered. This is because at the end of 120 minutes, the pressure was more controlled and had a greater value than that of MEG and DES. The efficiency of (DES+MEG) at 1%wt (70%), 3%wt (73.75%) and 5%wt (80%) respectively yielded better result than when the 1%wt, 3%wt and 5%wt of DES and MEG were used separately whereas increasing the concentration of the (DES+MEG) lead to increase in the hydrate inhibition performance.

5wt% of (DES+MEG) yielded the best result and as such is the best synergy for choline chloride based deep eutectic solvent but the optimum wt.% for the DES+MEG inhibitor is 3%, this is because the performance at this stage exceeds that of DES and MEG when used alone and the inhibitors molecules were more aligned and had accurate adsorption on the hydrate crystal surface thereby reducing the hydrate cluster/nucleus contact with water and gas molecule to prevent growth and stabilization of the cages in all weight percentages considered except in 5wt% with the value of 6.25% above that of 3wt% but is in line with a study where higher concentration of ionic liquid do not offer a lot of advantages [21]. Hence, since (DES+MEG) in 1:1 volume ratio was observed to have a good inhibition effect and also reduces the toxicity of MEG, it should be developed and tested for field trial while other volume ratio of the synergy should also be considered, and its kinetic performance should also be evaluated at lower weight percentages for future work.

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