Predicting Methane and Ethane Hydrate Formation Pressure in the Presence of Thermodynamic and Ionic Hydrate Inhibitors

Odutola Toyin O. and Aliyu Hajarat Nenne

Abstract— Hydrate deposition is a significant flow assurance problem. Managing hydrates involves adequately predicting the right hydrate formation conditions and the right concentration of inhibitor required for efficient hydrate inhibition. In this study, the experimental equilibrium hydrate formation pressure for single gases (methane and ethane) in the presence and absence of thermodynamic hydrate inhibitors (THI) was predicted using HYDOFF software and compared to over 114 published experimental data points. There was a close match between the predicted and experimental data with a coefficient of determination of 0.97 for methane system and 0.90 for ethane system. It was discovered that Sodium chloride has a higher inhibitive effect than Methanol at the same concentration. However, due to scaling issues sodium chloride may not be used in large quantity. HYDOFF was used in predicting the performance of hybrid THI comprising of Sodium Chloride and Methanol. In each Sodium Chloride -methanol hybrid, the inhibitor with a higher concentration of sodium chloride was more effective. This study will greatly reduce the occurrence of hydrate plugs in production systems as the hydrate formation conditions can be accurately determined, and the appropriate concentration of inhibitors can be predicted using HYDOFF.

Index Terms— Methane Hydrate, Ethane Hydrate, Thermodynamic Hydrate Inhibitor, Ionic Hydrate Inhibitor, HYDOFF, Hydrate prediction, Hydrate prevention

1 Introduction

NATURAL gas hydrate is a naturally occurring ice-like solid, which is made of water molecules as the cage forming host and other molecules (mostly methane) as the guest. The guest molecules, like methane or carbon dioxide, are of an appropriate size such that they fit within cavities formed by the host material [1].

Gas clathrate hydrates are crystalline inclusion compounds composed of a lattice of hydrogen-bonded water cages which can encage small guest molecules, such as methane, carbon dioxide, and hydrogen [2].

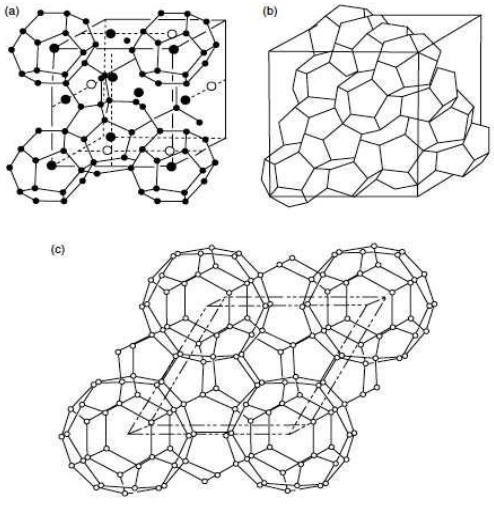

Figure 1: Hydrate crystals (a) sI type, (b) sII type, (c) sH type [3].

There are three structures of gas hydrates, namely Structure I and Structure II and Structure H (Figure 1). It is imperative to know the structure of the hydrate when designing a hydrate management plan. The most researched hydrate structures are Structure I and Structure II Structure I is a body-centred cubic structure which forms with natural gases containing molecules smaller than propane; consequently sI hydrates are formed in situ in deep oceans with biogenic gases containing mostly methane, carbon dioxide, and hydrogen sulphide. Structure I is formed with guest molecules having diameters between 4.2 and 6 Å, such as methane, ethane, carbon dioxide, and hydrogen sulfide [4].

Structure II is a diamond lattice within a cubic framework which forms when natural gases or oils contain molecules larger than ethane but smaller than pentane; sII represents hydrates from thermogenic gases [3].

Studies have shown three conditions promote hydrate formation in gas pipelines and in petrochemical processes: Coexistence of water, natural gas components (ranging from C1 to C4 and including CO2, N2 and H2S) and low temperatures and high pressures. Other factors that favour hydrate formation can be listed as high fluid velocities, agitation, pressure, pulsations (or any source of fluid turbulence. The water needed for hydrate formation can come from free water produced from the reservoir or from water vapour condensed by cooling the hydrocarbon fluid [5].

Natural gas hydrates are easily formed during the transportation of oil and gas when it contains a certain amount of water and is operated at high pressure and low-temperature conditions [6]. Hydrates are solid metastable compounds, and their properties and stability depend upon temperature and pressure. Natural gas hydrates can be hazardous during production

operations when it forms in platforms, pipelines and other engineering structure [5].

Gas hydrate formation is very problematic in offshore operations. Hydrates can form in the wellbore as the fluids undergo temperature and pressure phase changes near the mud line. Hydrates also form in the flow line from subsea completion to the surface facility. Finding an effective method for hydrate control in a system at hydrate conditions is difficult in offshore environments where one has no control over stream composition, bottom hole temperature and pressure [7].
There are different methods used for managing hydrate formation in hydrocarbon transfer lines and process facilities. These include:

i. At fixed pressure, operating at temperatures above the hydrate formation temperature. This can be achieved by insulation or heating of the equipment [8].
ii. At fixed temperatures, operating at pressures below hydrate formation pressure [9].
iii. Dehydration, that is, reducing water content below the required for hydrate formation [10].
iv. Changing the feed composition by reducing the hydrate forming compounds or adding non-hydrate forming compounds [11].
v. Inhibition of the hydrate formation conditions by using chemicals such as Methanol and salts. The most common inhibitors are thermodynamic inhibitors such as Methanol and glycols; however, produced water that contains electrolytes also has inhibiting effects. Thermodynamic hydrate inhibitors can be polar consisting of alcohols and glycols or ionic; consisting of salts [12].
vi. Preventing, or delaying hydrate formation by adding kinetic inhibitors [13].

Most oil and gas companies across the globe today are concerned with maximizing cost of production. Combating hydrate problems using chemicals may be time-consuming and capital intensive. Several software have been developed to predict hydrate formation conditions and evaluate hydrate inhibition using specific inhibitors. This can eliminate the cost of experimentation before selecting the most effective hydrate inhibitor.
This research uses HYDOFF software to predict hydrate equilibrium conditions in the presence of inhibitors. HYDOFF is a gas hydrate and thermodynamic prediction software designed to provide phase equilibria of hydrates in a manner consistent with available experimental data [3]. The HYDOFF software was developed since 1998 by Professor E. Dendy Sloan Jr. and coworkers at The Centre for Hydrate Research at the Colorado School of Mines.

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2 RESARCE METHODOLOGY

2.1 Data Collection

The data points for Methane/Methanol, Methane/NaCl and Ethane/Methanol system were obtained from Ahmed and Ali [14] while that for pure methane and Ethane/NaCl system were obtained from Katz chart [15] and a plot in Fahd [16] respectively. The data points for the hydrate formation conditions of Ethane gas in the presence of sodium chloride salt were gotten through the use of a GetData graph digitizer. For uniformity sake, all Pressure readings were converted to KPa and Temperature readings to K.

2.2 Data Analysis

About 34 data points were obtained for Ethane/NaCl system having inhibition weight fraction ranging from 10 wt% to 15 wt%, a temperature range of 273.687 - 277.100 K and Pressure ranging from 880 – 2151 KPa. Also, for a system of pure uninhibited methane, 39 data points were obtained from Katz chart having pressure ranging from 366.272 psia to 4241.472 psia and temperature ranging from 32.112 ^{o}F to 70.238 ^{o}F. Finally, for Methane/Methanol and Methane/NaCl system, 41 data points with temperature ranging from 233.1K to 284.3 K and pressure ranging from 1470 KPa to 18800 KPa were obtained.

The concentrations of Methanol considered in this study are 5wt%, 10wt%, 35wt%, and 50wt% while the concentration of sodium chloride considered are 10 wt% and 35wt%. Data points for prediction with hybrid inhibitors comprising of a mixture of Methanol and NaCl were generated using HYDOFF. The concentration of solutions used were 5wt% methanol/10wt% NaCl, 10wt% methanol/5wt% NaCl, 15wt% methanol/10wt% NaCl, 10wt% methanol/15wt% NaCl, 20wt% methanol/10wt% NaCl, 10wt% methanol/20wt% NaCl.

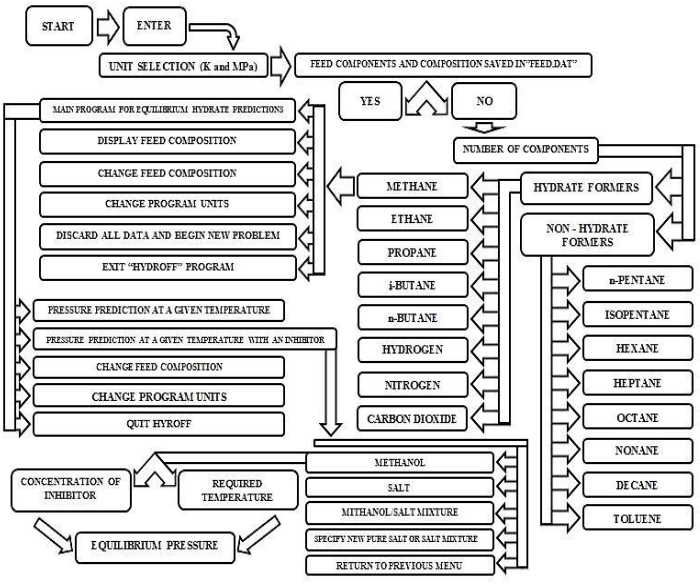

Figure 2: Hydrate Formation Pressure Prediction flow chart

3.0 RESULT AND DISCUSSION

HYDOFF predicts the thermodynamics of stable hydrate structures at a given pressure, temperature and composition conditions. At the lowest pressures, HYDOFF is a very good fit. However, as the pressures increase, the deviation becomes larger. Once the pressure reaches 10 MPa, HYDOFF predicts hydrate temperatures that are about 1°C too high.
During the course of this research, HYDOFF couldn't predict Pressures for Ethane/Methanol system at temperatures ranging from 242 to 262.2 K with inhibitor concentration ranging from 35wt% to 50 wt%.
HYDOFF was used in predicting hydrate formation pressure using the experimental conditions (temperature and inhibitor concentration) from experiments conducted by Ahmed and Ali [14] and Fahd [16] respectively. The HYDOFF predicted pressure was used in generating a hydrate formation curve and compared with the experimentally generated hydrate formation curve (Figure 3).

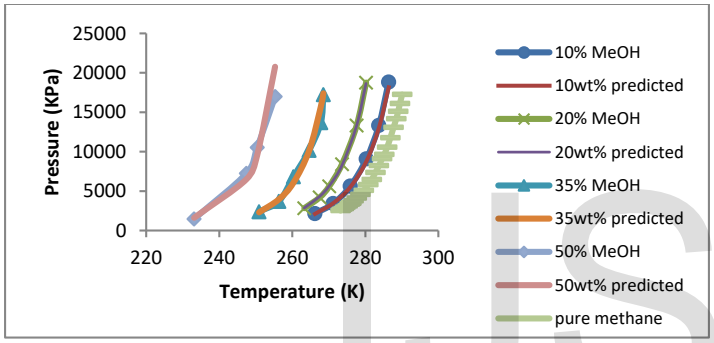

Figure 3: Methane hydrate formation curve with varying methanol concentration

Notice that the HYDOFF closely predicted the experimental results as the predicted and experimental curves are closely matched. Notice that the methane hydrate formation curve shifted leftwards with increasing concentration of Methanol. This implies that increasing the concentration of the inhibitor enables will enable operation take place without fear of hydrate formation. Also, observe that hydrate formation pressure increases with increasing concentration of inhibitors at a particular temperature. For instance, when 10wt% of Methanol was used at a temperature of 270K the pressure observed was 3476.624KPa, and when 20wt% of Methanol was used as inhibitor, the pressure at temperature 270K increased to 5648.316KPa.

A similar trend, as observed in Methane hydrate inhibition with Methanol was observed in the methane hydrate inhibition with sodium chloride salt (NaCl). However, HYDOFF prediction of methane hydrate- sodium chloride system was not as closely matches as the HYDOFF prediction of methane hydrate-methanol system very closely matched as (Figure 4). This implies that HYDOFF predicted methanol methane gas hydrate systems better than its prediction of sodium chloride methane hydrate systems.

In the prediction of methane hydrate formation pressure with varying concentration of sodium chloride inhibitors and 10wt% to 24.2wt% respectively (Figure 5) it was observed that pressure also increases with increasing inhibitor concentration in the presence of sodium chloride. Notice that the pressure obtained when 10wt% of sodium chloride at a temperature of 270K was used is 3949.15KPa, when the concentration was increased to 20wt%, a pressure of 6180KPa was observed.

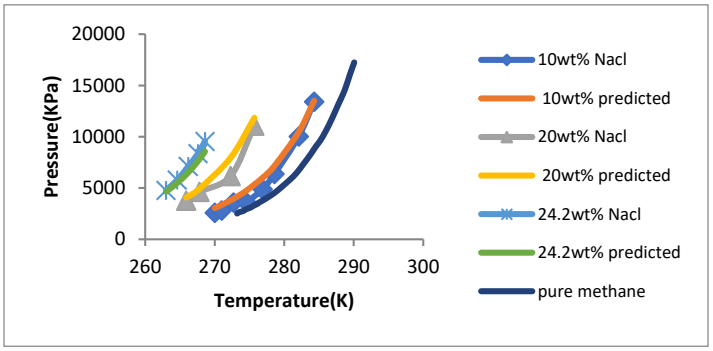

Figure 4: Methane hydrate formation curve with varying salt concentration

However, notice that NaCl performed better than Methanol because higher pressure was observed when NaC1 was used as inhibitor than when Methanol was used as inhibitor. (20wt% NaCl gave 6180KPa while 20wt%MeOH gave 5648.316KPa at 270K). Since it is not practical to use a high concentration of salt as hydrate inhibitor as it may cause problems during crude refining and may also cause scaling, it is imperative to combine the excellent inhibitive property of the salt with Methanol.

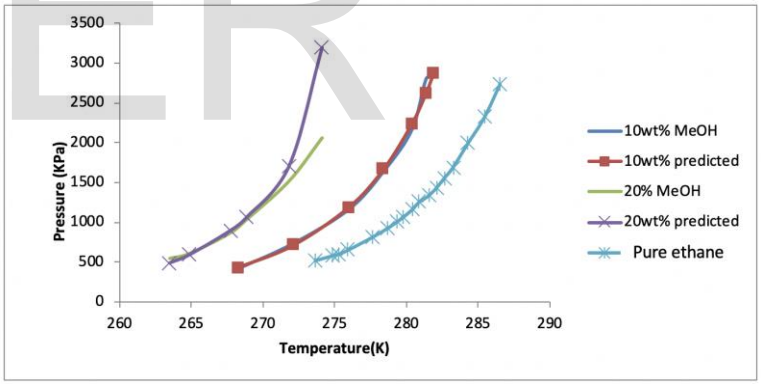

Figure 5: Ethane hydrate formation curve with varying methanol concentration

A comparison was done between experimentally obtained ethane hydrate formation curve (from Ahmed and Ali [14] and Fahd [16]), and HYDOFF predicted hydrate formation curve. Notice that the hydrate formation curves shifts leftwards with increasing concentration of Methanol (Figure 5). This implies that increasing the concentration of ethanol increases the hydrate safe region. Note that increasing the concentration of ethanol also increased the hydrate formation pressure. A pressure of 709.172KPa was observed when 10wt% of Methanol was used at a temperature of 270K. When ethanol concentration is increased to 20wt% at the same temperature of 270K, the pressure increased to 1520KPa.

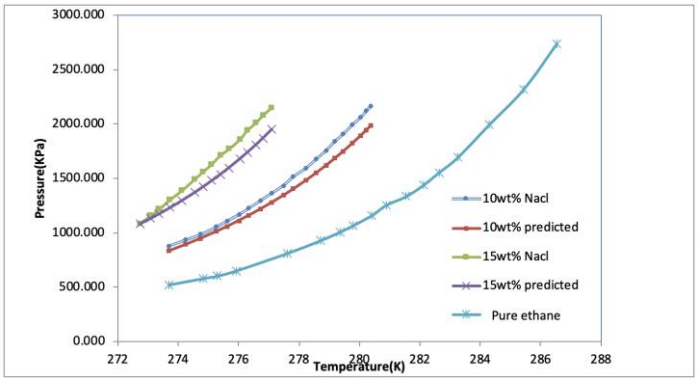

Figure 6: Ethane hydrate formation curve with varying NaCl salt concentration

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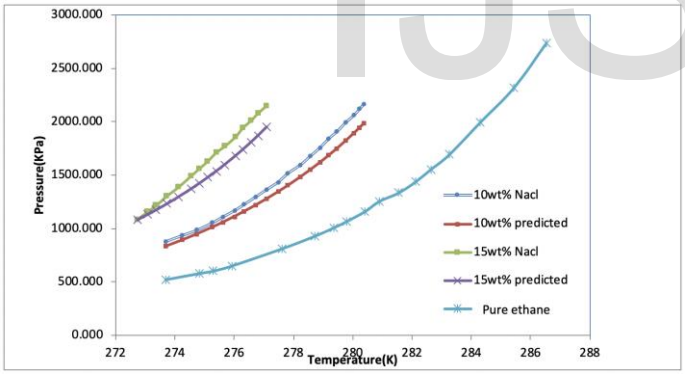

Figure 6: Ethane hydrate formation curve with varying NaCl salt concentration

Experimental data by Ahmed and Ali [14] and Fahd [16] for Sodium Chloride (NaCl)- ethane hydrate system was plotted alongside with HYDOFF predicted the NaCl- ethane hydrate formation curve (Figure 6). Notice that the increasing concentration of NaCl shifted the hydrate formation curve leftwards, thereby increasing the hydrate safe zone. At about 270K with 10wt% NaCl as an inhibitor, the hydrate formation pressure is 850Kpa.

A cross plot between the experimental data and HYDOFF predicted data for methane hydrate systems (Figure 7) and ethane hydrate system (Figure 8) were obtained.

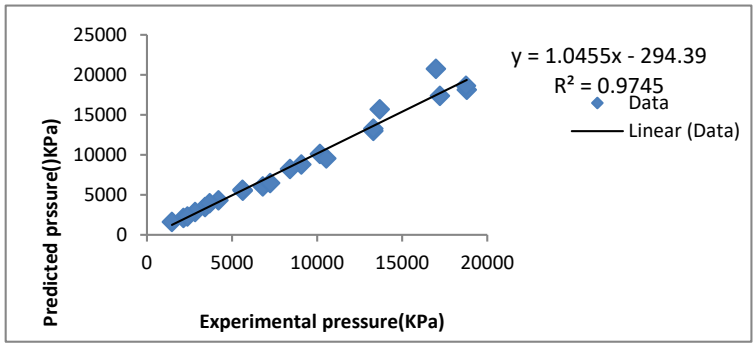

Figure 7: Correlation between experimental and predicted data for inhibited methane hydrate

A mean absolute deviation of less than 1% was obtained when HYDOFF predicted gas hydrate formation pressure at the same experimental conditions temperature. This shows a good agreement between the predicted and experimental data as shown in R2 value of 0.9745 for the methane hydrate system (Figure 7) and 0.9001 for the ethane hydrate system (Figure 8) obtained for inhibited methane and ethane hydrate system.

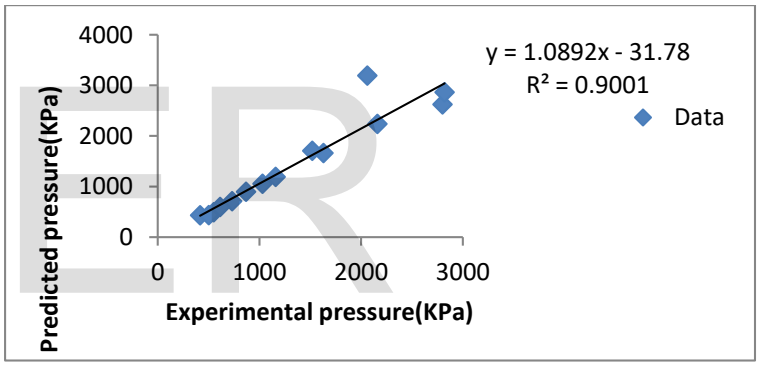

Figure 8: Correlation between experimental and predicted data for ethane hydrate

3.1 HYBRID INHIBITORS

Having established that HYDOFF closely predicts experimentally generated hydrate formation conditions, the effect of hybrid hydrate inhibitors comprising of a mixture of Methanol and salt on methane and ethane hydrate formation can be predicted using HYDOFF.

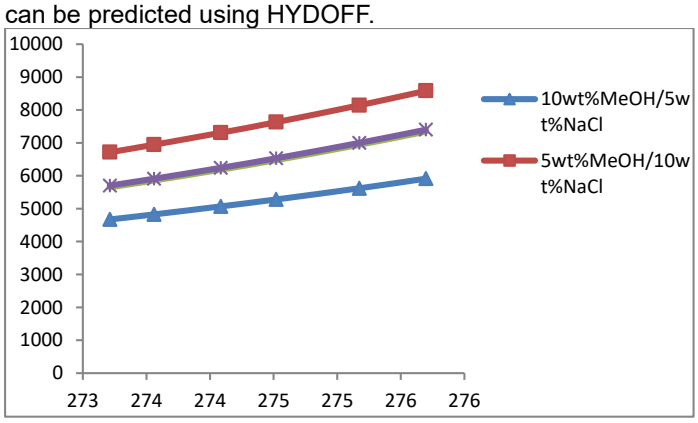

Figure 9: Effect of Hybrid inhibitors (MeOH +NaCl) in methane hydrate system

Figure 9 shows the performance of 15wt% methanol, 15 wt% NaCl and a hybrid inhibitor comprising of 10wt%MeOH+5wt%NaCl and 5wt%MEOH+10wt%NaCl. Notice that the hybrid inhibitor comprising of 5wt%MeOH+10wt%NaCl performed best as it will enable hydrate free operations at higher pressures than other inhibitors considered in Figure 9. The performance of 15wt% NaCl closely matches the performance of 15wt% MeOH. The least performing inhibitor in Figure 9 is the hybrid of 5wt% MeOH +10wt% NaCl.

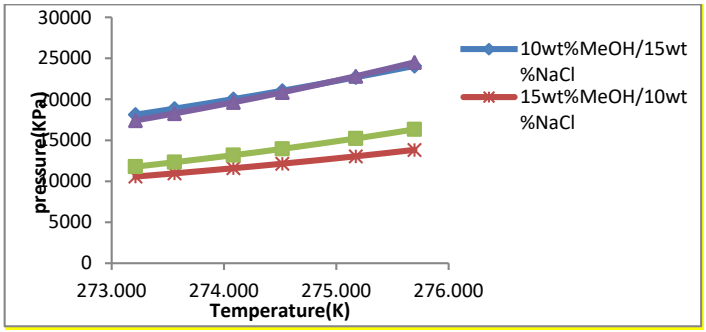

Figure 10: Comparison of varying concentrations of hybrid inhibitors with 25wt% of MeOH and NaCl

Figure 10 shows the performance of 24wt% methanol, 25wt% NaCl, and a hybrid inhibitor comprising of 10wt% MeOH+ 15wt%NaCl and 15wt% MeOH+ 10wt%NaCl. Notice that 10% MeOH + 15wt%NaCl has an almost corresponding inhibitive effect as 25wt% NaCl (Figure 10). It may not be practicable to use a very high concentration of NaCl for hydrate inhibition due to scaling issues and catalyst poisoning from high salt content in the crude.

Also, the hybrid of 10wt% MeOH +15wt%NaCl performed far better than 25wt% MeOH. Using Methanol as a hydrate inhibitor can be quite expensive as due to the large doses usually required for effective inhibition. Also, a large concentration of Methanol could pose potential problems in the field due to its high flammability.

Therefore, it imperative to explore combining the inhibitive effect of both Methanol and NaCl to provide less expensive hydrate free operations.

4.0 CONCLUSION

Natural gas hydrate is a major nuisance to the oil and gas industry when they plug oil and gas pipelines. The best way to determine the hydrate-formation temperature and pressure is to measure these conditions experimentally for every gas system. Since this is not practical in terms of time and money, predictions are the other alternative tool. In this study, the equilibrium hydrate formation pressure for single gases with inhibitors was predicted at a given temperature using HYDOFF software. These predictions are based on over 114 published data points of gas-hydrate formation temperatures and pressures with and without inhibitors. The data samples include pure-hydrate formers such as methane and ethane. From the results and discussion, the following can be concluded:

1. HYDOFF was able to predict hydrate formation pressure for inhibited methane and ethane system with R2 value of 0.97 and 0.90 for methane and ethane systems respectively. This shows a good agreement between the predicted and experimental data.
2. The software was also able to generate hydrate formation pressure data for various concentrations of mixed or hybrid inhibitors.
3. Sodium chloride has a higher inhibition effect than Methanol at the same concentration, which is very obvious at higher pressures.
4. In the presence of hybrid inhibitors, i.e. MeOH-NaCl, the inhibitor with a higher concentration of sodium chloride is more effective than the one with a higher concentration of Methanol.

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