A Simulation Study of CO_2 Hydrate Inhibition in CO_2+CH_4 Seawater Mixture

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ABSTRACT

In the oil and gas industry, wax deposition, scaling, corrosion, and hydrates are the main challenges in pipeline flow. Among these, gas hydrate formation is one of the most critical issues, costing the industry millions of dollars annually in mitigation efforts. Various techniques have been employed to prevent hydrate formation, with chemical inhibition being one of the most widely used methods. Several chemical inhibitors have been utilized, but methanol, ethanol, and Mono-Ethylene Glycol (MEG) hold significant commercial importance. These chemical inhibitors were used to inhibit CO_2 hydrate formation in 70 mol% CO_2 and 30 mol% CH_4 synthetic seawater with a salinity of 3.5 mol% NaCl using PVTSim software. The PVTSim software, coupled with the Peng-Robinson (PR) Peneloux equation of state, provided accurate results for flow assurance analysis in the oil and gas industry. The software predictions for pure CO_2 and CH_4 hydrates were validated against experimental data available in the literature. Furthermore, the PVTSim software with the PR Peneloux fluid package was applied to salty water systems containing 5, 7,

and 10 mol% concentrations of methanol, ethanol, and MEG inhibitors. Hydrate-Liquid-Vapor Equilibrium (HLVE) curves, average temperature depression, and enthalpy of dissociation were estimated. It was concluded that methanol at a concentration of 7 mol% is the most effective commercial inhibitor.

Keywords-hydrate inhibition; HLVE; average depression temperature; enthalpy of dissociation

I. INTRODUCTION

Ensuring flow assurance in subsea pipelines is critical, as various issues, such as gas hydrate formation, corrosion, scaling, and wax deposition, can pose significant operational challenges [1]. Among these, gas hydrate formation is particularly problematic, leading to annual mitigation costs of millions of dollars [2].

Gas hydrates are solid crystalline compounds formed when gas molecules become encased within a lattice of water molecules through hydrogen bonding, where the gas acts as a guest and water serves as the host [3, 4]. These hydrates typically form under low-temperature and high-pressure conditions and involve gases such as methane, ethane, propane, and hydrogen sulfide [5, 6].

The natural gas fields in Malaysia are known to contain more than 70% carbon dioxide (CO_2) [7]. This elevated CO_2 concentration not only raises the likelihood of gas hydrate formation but also poses challenges in its separation from natural gas. Gas hydrates can develop within oil and gas midstream pipelines under favorable pressure and temperature conditions, potentially disrupting the flow [8].

Although gas hydrates show promising potential as a source of hydrocarbon energy and as a medium for natural gas storage and transport, they also pose significant operational risks. One of the major concerns is the potential for hydrate formation to cause blockages or ruptures in subsea pipelines, which can lead to the leakage of hazardous materials with serious environmental consequences [9]. Pipeline failure not only poses safety risks but also involves high repair and maintenance costs. Mechanical methods, such as heating and thermal insulation, are sometimes employed to prevent hydrate-related issues. However, these approaches may be impractical or ineffective under certain field conditions. As a result, chemical inhibitors are often used to control hydrate formation. These inhibitors fall into two main categories: Low-Dosage Hydrate Inhibitors (LDHIs) and Thermodynamic Hydrate Inhibitors (THIs). LDHIs are further categorized into two types: Kinetic Hydrate Inhibitors (KHIs) and Anti-Agglomerates (AAs). KHIs function by delaying the onset of hydrate formation, effectively increasing the induction time, which is the period before hydrates begin to form [10]. On the other hand, THIs work by shifting the HLVE toward lower temperatures and higher pressures, thereby expanding the hydrate-free region [11]. Green inhibitors, such as ionic liquids and amino acids, have been used as THIs and KHIs, but they have not been commercialized yet [12]. Accurate prediction of hydrate phase behavior is crucial for developing effective mitigation strategies in industrial applications. Typically, four methods are employed to predict hydrate phase equilibrium in natural gas systems: (1) manual calculations, which are generally limited to single-component systems and have restricted use; (2) empirical correlations that can handle gas mixtures but also have limited applicability; (3) experimental approaches, which, although reliable, are often costly and time-intensive; and (4) simulation techniques using specialized software such as HYSYS [13], HydraFLASH, Multiflash, CSMGem, CSMHyd [14], and Pressure Volume Temperature Simulation (PVTSim). Among these, simulation-based methods are preferred due to their efficiency, cost-effectiveness, and broader applicability.

The commercially available software PVTSim has been used for the prediction of HLVE. For instance, the HLVE of H_2S was predicted through PVTSim and validated experimentally [15]. PVTSim was also used to determine the equilibrium conditions of natural gas hydrates in MEG aqueous solutions. It was reported that PVTSim provided accurate results with less than 1% error [16].

Most hydrate inhibition studies on pure CO_2 [17-19], pure CH_4 [20-23], or their mixtures [24] have focused on distilled water. However, real offshore environments involve seawater, which contains various salts that influence hydrate behavior. However, limited research is available on hydrate inhibition in CO_2-CH_4 mixtures with seawater. Therefore, this study investigates hydrate inhibition for a CO_2-CH_4 mixture in synthetic seawater with a salinity of 3.5 mol% NaCl using PVTSim simulation. The PR Phenolux EOS was used with 5, 7, and 10 mol% inhibitor concentrations to observe the effect of inhibitors on shifting the equilibrium. The inhibitors considered in this context were methanol, ethanol and MEG. Furthermore, the average depression temperature was calculated to determine the effectiveness of the inhibitors. In addition, the average enthalpy of dissociation was calculated to the difference in crystalline structure.

II. METHODOLOGY

The composition of CO_2-CH_4 mixture was taken with high CO_2 content, as shown in Table I, because Malaysian natural gas contains high CO_2 content. The PVTSim software was used to draw the HLVE curve of the CO_2-CH_4 mixture. In addition, 3.5 mol% NaCl was added to the water in the PVTSim software, because seawater contains about 35 g/kg of salts [25]. The CO_2 hydrate formation conditions were set in the software, with pressures ranging from 1.5 MPa to 3.5 MPa. The temperature range used for validation reflects the typical conditions found on the seabed.

PVTSim, developed by Calsep, is a fluid modeling software designed to simulate fluid properties using various Equations of State (EoS). It serves a wide range of industrial applications, including advanced flash regression analysis, reservoir fluid characterization, and automated fluid regression, reducing the need for manual adjustments. The software offers multiple utilities and modules that cover unit operations, flash calculations, and predictions of wax and hydrate formation.

TABLE I. COMPOSITION OF SAMPLES USED FOR THE HYDRATE INHIBITION STUDIES

Sample	CH_4	CO_2	Water	NaCl	Methanol	Ethanol	MEG
	mol%						
Synthetic seawater	30	70	96.5	3.5	0	0	0
5 mol% methanol	30	70	96.5	3.5	5	0	0
5 mol% ethanol	30	70	96.5	3.5	0	5	0
5 mol% MEG	30	70	96.5	3.5	0	0	5
7 mol% methanol	30	70	96.5	3.5	7	0	0
7 mol% ethanol	30	70	96.5	3.5	0	7	0
7 mol% MEG	30	70	96.5	3.5	0	0	7
10 mol% methanol	30	70	96.5	3.5	10	0	0
10 mol% ethanol	30	70	96.5	3.5	0	10	0
10 mol% MEG	30	70	96.5	3.5	0	0	10

A. HLVE Curve

In this study, the hydrate structure utility within PVTSim was used to simulate the HLVE phase behavior. This specific module was chosen because it enables accurate prediction of hydrate formation conditions and phase equilibria, both in the presence and absence of chemical inhibitors. The inhibitors used were methanol, ethanol, and MEG. They were utilized in mole percentages of 5, 7, and 10. The PR Peneloux fluid package was selected for the prediction of HLVE. The simulation results were compared with published experimental results.

B. Average Depression Temperature

In this simulation study, the average suppression temperature (ΔT) was calculated to determine the inhibition performance of the selected hydrate inhibitors at different concentrations (5, 7, and 10 mol%) in the temperature and pressure ranges of 264–276 K and 1.5–3.5 MPa, respectively [26]:

$$T = \frac{\sum \Delta T}{n} = \frac{\sum_{i=1}^{n}(T_{0,pi} - T_{1,pi})}{n} \quad (1)$$

where $T_{0,pi}$ and $T_{1,pi}$ denote the equilibrium temperatures of the CO_2 hydrate in saline water and the CO_2 hydrate in the selected inhibitors, respectively, and n indicates the number of pressure points assessed.

C. Enthalpy of Dissociation

The enthalpy of dissociation is the amount of energy required to break the bonds between the water cages in 1 mol of gas hydrate. The enthalpy of dissociation (ΔH_{dis}) of the CO_2 hydrate was calculated using the Clausius–Clapeyron equation by differentiating the HLVE data [27]:

$$\frac{\partial \ ln\, P}{\partial \frac{1}{T}} = -\frac{\Delta H_{dis}}{zR} \quad (2)$$

where P and T are the equilibrium pressure (Pa) and temperature (K), R is the universal gas constant (R=8.314 J/mol·K), z serves as the compressibility factor of CO_2, and ΔH_{dis} is the dissociation enthalpy of CO_2 hydrates.

By rearranging (2), we obtain:

$$\partial\, ln\, P = -\frac{\Delta H_{dis}}{zR}\partial\left(\frac{1}{T}\right) \quad (3)$$

Integrating on both sides:

$$\int \partial\, ln\, P = -\frac{\Delta H_{dis}}{zR}\int \partial\left(\frac{1}{T}\right) \quad (4)$$

$$ln\, P = -\frac{\Delta H_{dis}}{zR}\frac{1}{T} + C \quad (5)$$

where C is an integration constant.

Let us consider two points with pressures P_1 and P_2, and the temperatures T_1 and T_2:

$$ln\, P_1 = -\frac{\Delta H_{dis}}{zR}\frac{1}{T_1} + C \quad (5a)$$

$$ln\, P_2 = -\frac{\Delta H_{dis}}{zR}\frac{1}{T_2} + C \quad (5b)$$

By solving simultaneously, we obtain:

$$ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta H_{dis}}{zR}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad (6)$$

Here, P_1 and P_2 are the equilibrium pressures at temperatures T_1 and T_2, respectively.

III. RESULTS AND DISCUSSION

A. Software Validation

The HLVE data for CO_2 and CH_4 in synthetic seawater were sourced from the existing literature and evaluated against the simulation results produced by the PVTSim software using the PR-Peneloux EoS, as depicted in Figure 1.

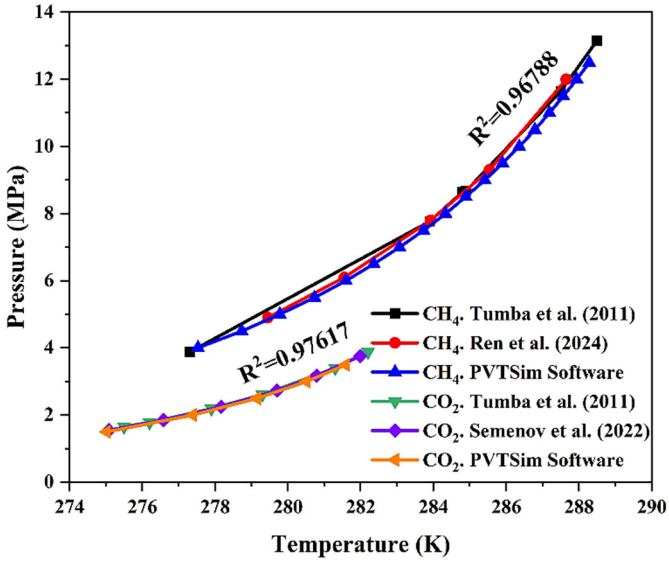

Fig. 1. Comparison of experimental and PVTSim-simulated HLVE data for CO_2 - CH_4 in seawater. The experimental data were extracted from [28-30].

Figure 1 shows that there is an excellent similarity between the PVTSim simulation results and the literature data. The coefficient of determination (R^2) for the PVTSim data was found to be 0.97617 for CO_2 and 0.96788 for CH_4, which is an indication that PVTSim using the PR-Peneloux EoS is suitable for studying natural gas mixtures. Furthermore, according to [31], PR-Peneloux EoS is proposed for simulating hydrate formation in natural gas mixtures.

B. HLVE Curve

The simulated HLVE for CO_2 and CH_4 in seawater with 5 mol% THIs (methanol, ethanol, and MEG) are illustrated in Figure 2. The results show that methanol exhibits the strongest inhibitory effect in seawater, outperforming the other compounds. This conclusion is consistent with previous studies, where methanol was reported to be the most effective THI [1]. The superior inhibition performance of methanol is primarily attributed to its shorter alkyl chain, as compounds with shorter chains tend to offer better hydrate suppression [32]. Additionally, the polar nature of methanol facilitates the formation of hydrogen bonds with water molecules, enhancing its inhibition capability [33]. Methanol exhibits higher hydrate inhibition efficiency than ethanol because of its lower molecular weight, higher water solubility, and stronger hydrogen bonding capabilities [11]. Ethanol also demonstrated a similarly high inhibitory effect, supporting its widespread use as a commercial inhibitor [17]. In contrast, MEG exhibited relatively weaker inhibition than ethanol and methanol. The coefficient of determination was calculated, showing a strong correlation with an R^2 value of 0.99 for all samples.

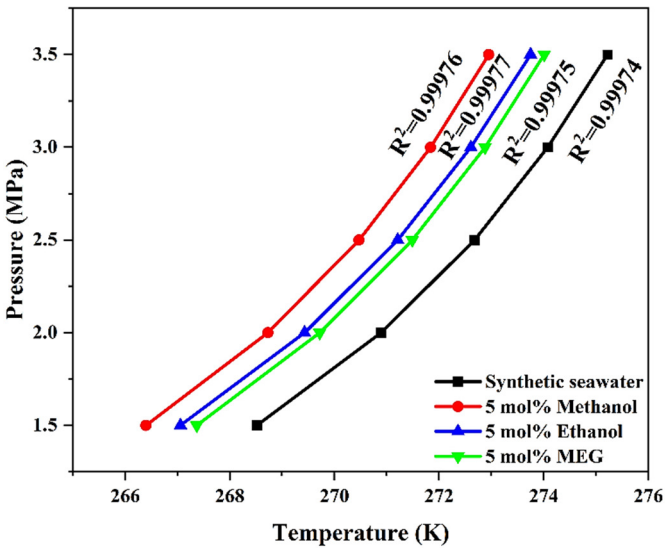

Fig. 2. Simulated HLVE of CO_2 - CH_4 in salty water containing 5 mol% methanol, ethanol, or MEG.

The simulation results for the CO_2-CH_4 mixture in seawater with 7 mol% inhibitors are displayed in Figure 3. The data indicate that methanol provides superior inhibition performance compared to the other inhibitors. The effectiveness of hydrate inhibition is directly influenced by the inhibitor concentration, with better mitigation observed at 7 mol% than at 5 mol%. These findings are consistent with the findings in [34]. Furthermore, the R^2 values calculated were greater than 0.99, indicating a high accuracy of the simulated data.

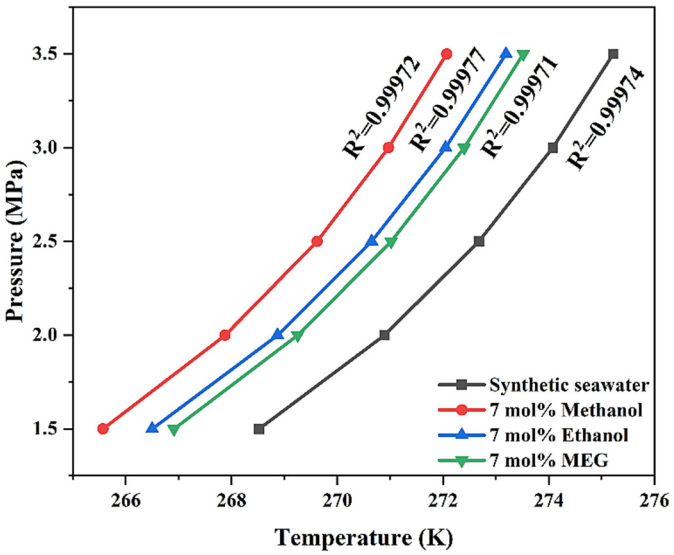

Fig. 3. Simulated HLVE of CO_2 - CH_4 in salty water containing 7 mol% methanol, ethanol, or MEG.

The results for the CO_2-CH_4 mixture using 10 mol% concentration of inhibitors are shown in Figure 4. The findings confirm that methanol continues to demonstrate the most effective inhibition performance among the tested compounds. The hydrate suppression performance increases as the inhibitor concentration increases, with the 10 mol% concentration showing the best performance. These results are consistent with those of [34]. On top of that, the R^2 values, which were above 0.99, highlight the strong accuracy of the simulated data.

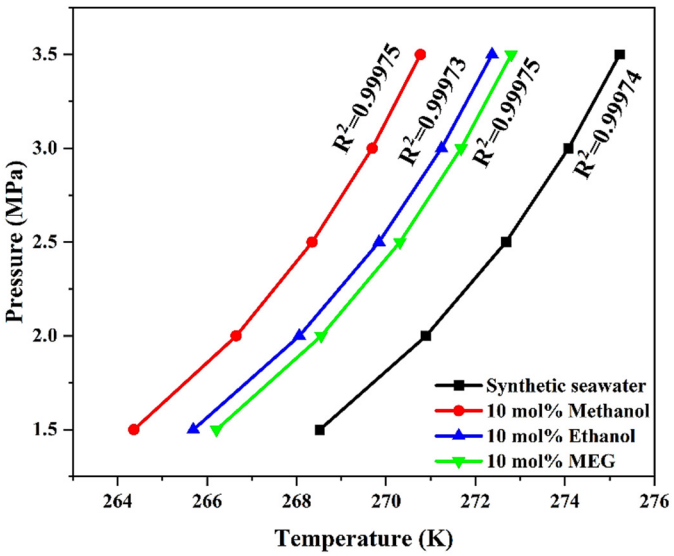

Fig. 4. Simulated HLVE of CO_2 - CH_4 in salty water containing 10 mol% methanol, ethanol, or MEG.

C. Average Depression Temperature

The average depression temperatures of the selected hydrate inhibitors were calculated using (1) and are presented in Table II in ascending order. Among all selected hydrate inhibitors, methanol demonstrated the highest effectiveness. The thermodynamic inhibition effectiveness follows the order methanol > MEG > ethanol. The selected inhibitors exhibited superior performance in the CO_2-CH_4 mixture compared to traditional inhibitors such as methanol (T=6.05K) [35], (T = 4.55 K) [36], and MEG (T=2.6 K) [37] in pure CO_2.

TABLE II. DEPRESSION TEMPERATURES OF HYDRATE INHIBITORS FOR CO_2-CH_4 SYNTHETIC SEAWATER

Pressure (MPa)	Methanol	Ethanol	MEG
5 mol%			
1.5	2.12	1.46	1.15
2	2.16	1.46	1.17
2.5	2.21	1.47	1.19
3	2.24	1.47	1.2
3.5	2.27	1.47	1.21
Average	2.2	1.466	1.184
7 mol%			
1.5	2.95	2.02	1.61
2	3.01	2.02	1.64
2.5	3.06	2.03	1.66
3	3.11	2.03	1.68
3.5	3.15	2.03	1.7
Average	3.056	2.026	1.658
10 mol%			
1.5	4.16	2.83	2.31
2	4.24	2.83	2.34
2.5	4.33	2.84	2.37
3	4.39	2.84	2.4
3.5	4.45	2.85	2.42
Average	4.314	2.838	2.368

D. Enthalpy of Dissociation

The influence of the selected hydrate inhibitors on the structure and occupancy of the CO_2 hydrate formation cage in CO_2-CH_4 saltwater mixture was measured by calculating the enthalpy of dissociation. The Clausius–Clapeyron equation was used to calculate the enthalpy of dissociation of the CO_2 hydrate in the presence of selected inhibitors. The average CO_2 hydrate dissociation enthalpies for the selected inhibitors in oil and gas flow assurance are listed in Table III.

Table III shows that the average dissociation enthalpy of methanol and MEG is relatively larger than that of ethanol because CO_2 hydrate formation in the presence of methanol and MEG under these conditions maintains slightly higher cage occupancy than ethanol hydrate formation [38]. Additionally, as the percentage of inhibitors increases, the average enthalpy of dissociation also increases. Furthermore, as the pressure increases, the average dissociation enthalpy also increases. Thus, in CO_2-CH_4 synthetic seawater, methanol, ethanol, and MEG have a smaller impact on the methane hydrate structure. Moreover, the presence of the selected inhibitors resulted in slightly lower cage occupancy. Overall, the crystalline structure of the gas hydrate remained largely unaffected by methanol, ethanol, and MEG.

TABLE III. ENTHALPY OF DISSOCIATION OF HYDRATE INHIBITORS FOR CO_2-CH_4 SYNTHETIC SEAWATER

Pressure (MPa)	Methanol	Ethanol	MEG
5 mol%			
1.5	73.48	72.61	73.39
2	75.18	74.12	74.82
2.5	76.71	75.59	76.30
3	78.20	76.98	77.72
3.5	75.89	74.82	75.56
Average	73.48	72.61	73.39
7 mol%			
1.5	73.65	72.31	73.45
2	75.08	73.81	74.74
2.5	76.79	75.28	76.31
3	78.30	76.66	77.80
3.5	75.96	74.51	75.58
Average	73.65	72.31	73.45
10 mol%			
1.5	73.62	71.87	73.07
2	75.51	73.36	74.53
2.5	77.08	74.82	76.19
3	78.66	76.31	77.63
3.5	76.22	74.09	75.35
Average	73.62	71.87	73.07

IV. CONCLUSIONS

A CO_2 and CH_2 salty water mixture was used for simulation studies. Hydrate-Liquid-Vapor Equilibrium (HLVE) curves were generated for salty water and for systems containing methanol, ethanol, and Mono-Ethylene Glycol (MEG) inhibitors. Based on the HLVE curves, it was concluded that all selected inhibitors were effective. However, methanol at a 7 mol% concentration was identified as the most suitable commercial inhibitor, as the corresponding HLVE curve was lower than the 273.15 K temperature threshold. Hydrate formation occurs at or above 273.15 K; below this temperature, ice formation dominates.

The average temperature depression caused by methanol, ethanol, and MEG inhibitors was also calculated. The average temperature depression ranged from 1.184 to 4.314 K., with methanol at 10 mol% producing the highest average temperature depression of 4.314 K. It was found that increasing the concentration of methanol enhanced its inhibition performance, as indicated by the greater temperature depression.

The enthalpy of dissociation for methanol, ethanol, and MEG was determined using the Clausius-Clapeyron equation. It was found that CO_2 hydrate formation in the presence of the selected inhibitors showed relatively small differences in guest-cage occupancy and hydrate structure. In summary, the crystalline structure of the gas hydrate exhibited minimal changes when exposed to methanol, ethanol, or MEG.

In conclusion, all the studied inhibitors exhibited effective inhibition performance. However, 7 mol% methanol was identified as the most suitable inhibitor.

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DATA AVAILABILITY

Simulation data will be provided upon reasonable request.

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