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Kinetic and Thermodynamic Influence of NaCl on Methane Hydrate in an Oil-Dominated System

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ABSTRACT: This experimental study reports the kinetic and thermodynamic inhibition influence of sodium chloride (NaCl) on methane (CH_4) hydrate in an oil-dominated system. To thoroughly examine the inhibition effect of NaCl on CH_4 hydrate formation, kinetically by the induction time and relative inhibition performance and thermodynamically by the hydrate liquid−vapor equilibrium (HL_wVE) curve, enthalpy (ΔH_{diss}) and suppression temperature are used to measure the NaCl inhibition performance through this experimental study. All kinetic experiments are performed at a concentration of 1 wt % under a pressure and temperature of 8 MPa and 274.15K, respectively, whereby for the thermodynamic study, the concentration was 3 wt % by using the isochoric T-cycle technique at the selected range of pressures and temperatures of 4.0−9.0 MPa and 276.5−286.0K, respectively; both studies were conducted using a high-pressure reactor cell. Results show that kinetically, NaCl offers slightly to no inhibition in both systems with/without oil; however, the presence of drilling oil contributes positively by increasing the induction time; thermodynamically, NaCl contributes significantly in shifting the equilibrium curve to higher pressures and lower temperatures in both systems. In the oil system, the contribution of the THI to the equilibrium curve increases the pressure with a range of 0.04−0.15 MPa and reduces the temperature with a range of 1−3 K, which is due to the NaCl presence in the systems that reduces the activity of water molecules by increasing the ionic strength of the solution. At a high pressure of 9 MPa, the NaCl inhibition performance was greater than that at lower pressures <5.5 MPa because, at the high pressure, NaCl increases the activity of water, which means that more water molecules are available to form hydrate cages around gas molecules.
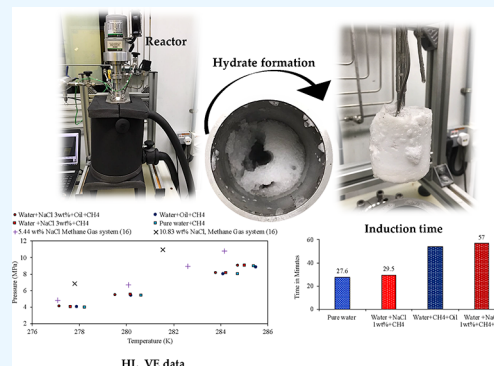
1. INTRODUCTION

Oil and gas production is essential to the global energy supply chain. However, the transportation of hydrocarbons from production sites to processing facilities has significant challenges. One of the most critical challenges is the formation of gas hydrates in pipelines, which can lead to severe flow assurance problems.[1−3] Gas hydrates are ice-like crystalline solids that form from natural gas and water molecules under high-pressure and low-temperature conditions.[4−6] These solids can block pipelines, increase pressure drops, and cause pipeline ruptures. As a result, the oil and gas industry has invested significant resources in developing effective methods to inhibit gas hydrate formation and mitigate the associated flow assurance problems.[7]

Kinetic and thermodynamic inhibitors are commonly used to prevent gas hydrate formation in oil pipelines.[8,9] These inhibitors work by altering the physical and chemical properties of the water phase, which reduces the concentration of hydrate-forming molecules and disrupts the growth and stability of gas hydrates. However, these inhibitors have limitations, including high cost, toxicity, and environmental

impact. Therefore, there is a need for more sustainable and cost-effective methods for inhibiting gas hydrate formation.[10]

One promising method for inhibiting gas hydrate formation is using NaCl as a kinetic and thermodynamic inhibitor. Brine is a solution of water and dissolved salts, and it has been found to effectively inhibit gas hydrate formation in laboratory experiments.[11] NaCl inhibits gas hydrate formation by reducing the concentration of hydrate-forming molecules in the water phase and disrupting the growth and stability of gas hydrates by altering the interfacial properties of the hydrate−water interface. The use of NaCl as a gas hydrate inhibitor is attractive due to its low cost, nontoxicity, and sustainability.[12]

Several studies have investigated the effectiveness of NaCl as a kinetic and thermodynamic inhibitor of gas hydrate

formation in gas systems.[13,14] Still, limited studies have studied the role of NaCl in oil systems and that due to the different properties of oil and gas, the effects of impurities, and the complex interactions between oil, gas, and water.[15] These studies have demonstrated the potential of NaCl to inhibit gas hydrate formation and mitigate flow assurance problems in gas and oil pipelines. Cha et at.[16] conducted a study on the impact of NaCl, KCl, and NH_4Cl in a gas system on methane hydrate with a concentration of 10 wt % using a high-pressure DSC; the study shows that the hydrate inhibition strength by the sodium cation was slightly stronger than that of potassium and ammonium cations. Holzammer et al.[17] studied how NaCl inhibits hydrate on CO_2 hydrate formation through a thermodynamic experimental study using a high-pressure cell under a concentration of 20 wt %; the results reveal that NaCl lowers the temperature of gas hydrate formation by 12 K and the solubility of CO_2 is reduced by 70%. On the other hand, Daraboina et al.[18] investigated the influence of NaCl kinetically in an oil system in the presence of crude oil using a rocking cell (RC-5) apparatus; the result shows that the KHIs' inhibition strength was not affected by NaCl but decreased significantly in the presence of crude oil. However, significant challenges and limitations are still associated with using NaCl as a gas hydrate inhibitor in oil systems.

Therefore, this paper aims to investigate the role of NaCl as a thermodynamic and kinetic gas hydrate inhibitor thermodynamically by (HL_wVE, enthalpy, and suppression temperature) and kinetically by (induction time and relative inhibition performance) on methane hydrate in an oil system. The paper will provide an overview comparison of the use of NaCl in a pure system compared to an oil system in terms of the inhibition strength in both systems.

2. METHODOLOGY

2.1. Materials. The list of chemicals, purity, formula, structure, and molecular weight of all the chemicals used during this experimental study is shown in Table 1. NaCl, used

Table 1. List of Chemicals Used in This Study

Chemical Name	Purity	Formula	Structure	Mol.Wt. (g.mol⁻¹)	Supplier
Methane	99.9%	CH_4		16.04	LMG-UTP
Water	Deionized	H_2O		18.02	UTP
Sodium chloride	99.9%	NaCl	-	58.44	LMG-UTP
Drilling Oil	99.0%	-	-	-	PETRONAS Sdn Bhd

as a hydrate inhibitor in this study, was supplied by LMG UTP. The inhibitor was used without further purification. PETRONAS Sdn Bhd provided the drilling oil used during this study with a purity of 99.0%; further explanation on the composition of the drilling oil has been reported in our previous study.[11] The experiment was conducted on methane gas with a purity of 99.9%, purchased from LMG-UTP, Malaysia. Deionized water was used in preparing all solutions with a water cut of 50%.

2.2. Drilling Oil Characterization. This study utilizes methane gas, drilling oil, and deionized water to replicate fluids in real oil transmission pipelines. Figure 1 displays the carbon compositions of drilling oil by using a gas chromatograph—mass spectrometer (GCMS). The testing was carried out at the Centralized Analytical Laboratory (CAL) at the University Technology PETRONAS (GCMS-DIPPC; model: Agilent 7890A). The results indicate a significant presence of C10—C14 carbons, with nonadecane (C12) being the most abundant. PETRONAS supplied the drilling oil used in the experiment, chosen for its low viscosity and clarity. The low viscosity ensures that it can easily flow in the cell, while its transparency allows for visual monitoring and safe disposal as it poses no harm.

2.3. Experimental Setup. In this study, a high-pressure stainless steel cell reactor was used to determine the kinetic and thermodynamic parameters of NaCl on CH_4 hydrates in the presence of oil. The apparatus features a 650.0 cm³ high-pressure cell that operates within a 253.0—323.0 K temperature range and up to 20.0 MPa pressure. It also includes a magnetic stirring system and two PT-100 sensors for monitoring.[19−22] One is installed inside the cell, and the other is in the alcoholic bath to record the temperature outside. In the cell interior, a 500 rpm motor is used to ensure sufficient sample agitation within the testing cell under designed conditions. The cell is submerged in a thermostatic bath using ethanol as a coolant, equipped with a PID controller for controlling the bath temperature.[23,24] A gas booster compressor injects methane into the cell, and 100 mL of NaCl and oil solutions manually load 50 mL of oil and 50 mL of NaCl solutions into the cell. Figure 2 shows the apparatus and schematic diagram that is linked to a data acquisition system that continuously logs the pressure and temperature inside the cell every 5 s with a precision of ±0.01 MPa and ±0.1 K.

2.3.1. Determination of the Induction Time. The induction time t_i is used to evaluate the performance of kinetic hydrate inhibitors. It describes the ability of KHIs to prolong the hydrate formation and/or crystal growth.[25] It is defined in practice as the time taken for the formation of a detectable volume of the hydrate phase or the time taken for an inhibitor to fail. A high induction time indicates more significant inhibition.[26,27] In this experimental study, induction time was calculated based on the relationship between time and pressure, as depicted in Figure 3, using the method described in previous literature studies.[25,28]

$$t_i = (t_s - t_h) \tag{1}$$

where t_s is the time taken for the system pressure to stabilize at experimental pressure and t_h is the time when detectable hydrate begins to form and grow rapidly, indicated by a sharp pressure drop due to gas consumption into hydrate. However, the initial pressure drop between t_s and t_h in Figure 3 is the amount of gas consumed in gas hydrate nucleation.

2.3.2. Relative Inhibition Performance (RIP). The calculation of relative inhibition performance was adopted from Koh et al.'s[29] procedure. It is used in this study to show the inhibition performance of NaCl in the presence of oil system. The RIP values determine the kinetic inhibitory efficacy of the KHIs; an RIP > 0 corresponds to a better inhibitory performance of KHI. The relative inhibition performance was calculated by using eq 2.
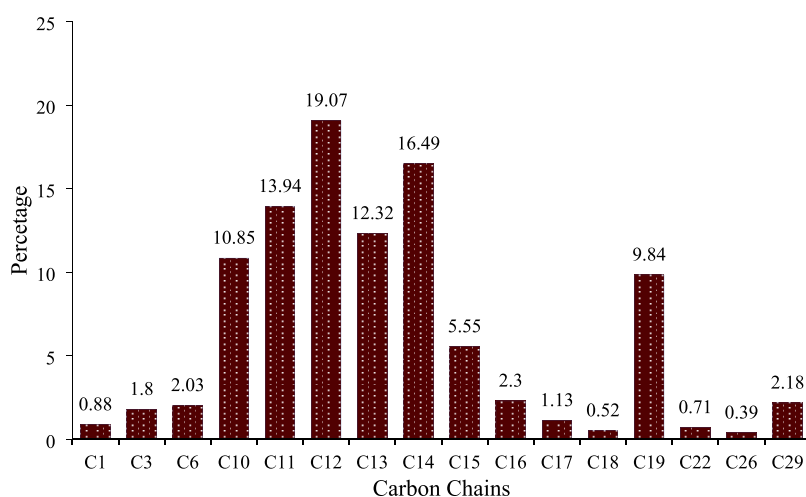
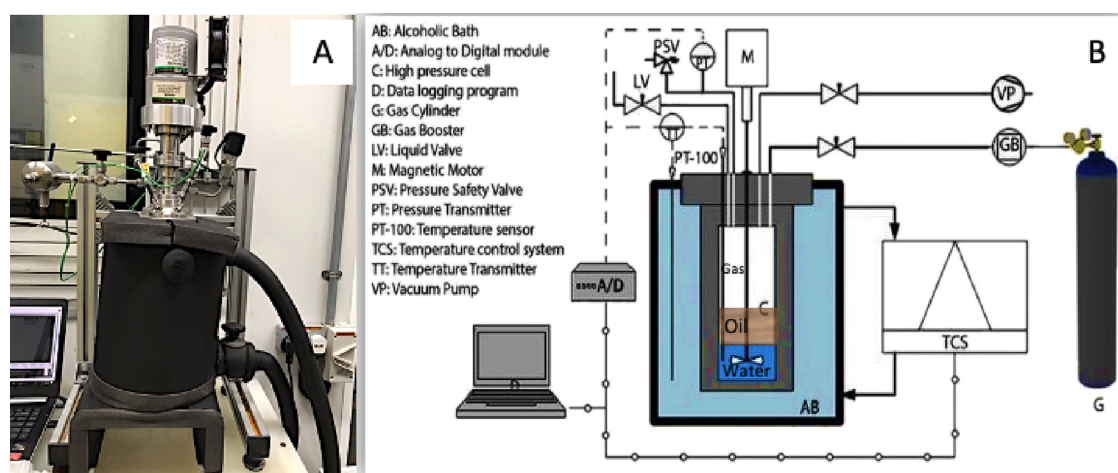**Figure 1.** Carbon chain characterization using GCMS for a drilling oil sample.[11]

Figure 2. (A) High-pressure cell reactor used in this study. (B) Schematic diagram of the high-pressure reactor.[11] Copyright [2022] [ELSEVIER].
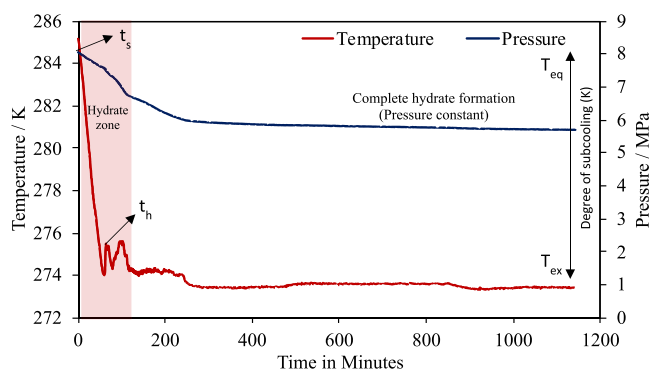

Figure 3. Temperature vs pressure plot indicating the hydrate formation using a high pressure reactor cell.[11] Copyright [2022] [ELSEVIER].

$$\text{RIP}_{\text{induction}} =$$

$$\frac{\text{inductiontime}_{\text{inhibitor}} - \text{inductiontime}_{\text{pure system}}}{\text{inductiontime}_{\text{pure system}}} \quad (2)$$

2.4. Experimental Process for HLwVE Point Measurement.
The experiments are conducted using the isochoric T-cycle method. Prior to each experiment, the cell is thoroughly cleaned with deionized water to ensure that there are no contaminants. After that, the temperature of the system is set slightly above the expected equilibrium temperature at the experimental pressure, with the thermo-stated bath. Following this, the cell is filled with 200 mL of the desired solution and pressurized using CH_4 to the desired experimental pressure. The stirrer is activated, and the system is left to reach stabilization.

Once the pressure stabilizes, the temperature is gradually lowered to 274.15 K at a rate of 4 K per hour. This temperature is maintained for 5 h to facilitate the formation of hydrates. The presence of hydrates is confirmed by noting a sudden decrease in pressure. When hydrates are formed, the system's temperature is rapidly increased at a rate of 8 K per hour until it reaches a point about 6 K below the target dissociation temperature. Then, the temperature is increased incrementally in steps of 0.5 K and kept constant for 3 h at each step. This approach is based on the method proposed by Tohidi et al.[30] The processes of hydrate formation and dissociation are depicted in Figure 4.

2.5. Hydrate Dissociation Enthalpy (ΔH_{diss}) and Average Reduced Temperature.
The determination of gas hydrate dissociation enthalpies (ΔH_{diss}) involves applying the Clausius−Clapeyron equation to phase equilibrium data. This is achieved by differentiating the data as follows:
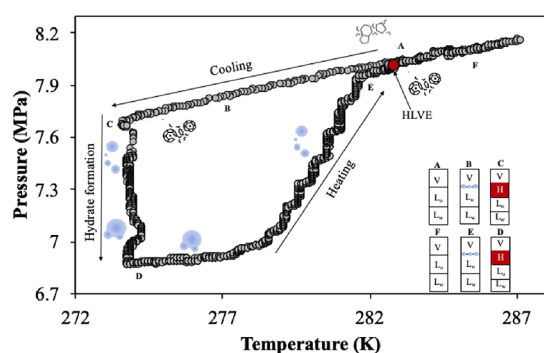
Figure 4. T-cycle plot generated during the experiment used to indicate the impact of the inhibitors on the hydrate phase equilibrium.

$$\frac{\mathrm{d}\ln P}{\mathrm{d}\left(\frac{1}{T}\right)} = \frac{\Delta H_{\mathrm{diss}}}{zR} \tag{3}$$

where P and T are the equilibrium pressure and temperature, respectively, z represents the compressibility factor of respective gas for average gas temperature and pressure (to calculate the compressibility factor z, the real gas equation was used from the Peng−Robinson equation of state), R denotes the universal gas constant, and ΔH_{diss} is the dissociation enthalpy of gas hydrates.

The thermodynamic inhibitory activity of the above systems containing NaCl in the two different systems of pure and oil systems was obtained by calculating the average inhibition temperatures. The calculation of average reduced temperature $(\Delta \mathcal{F})$ is obtained from eq 4 using an established method[19,31−33]

$$\underset{-}{T} = \frac{\Delta T}{n} = \frac{\sum_{i=1}^{n}(T_{0,Pi} - T_{1,Pi})}{n} \tag{4}$$

The average suppression temperature, $\Delta \mathcal{F}$, which is a measure of the average inhibition ability of THI, is calculated for all concentrations by the equation presented by Xiao et al.,[34] where $\Delta \mathcal{F}$ is the suppression temperature at a constant pressure of P_i, $T_{0,Pi}$ represents the hydrate equilibrium temperature of CH_4 in pure water (without NaCl), while $T_{1,Pi}$ is the equilibrium temperature of CH_4 in the presence of NaCl.[35,36]

3. RESULTS AND DISCUSSION

In this experiment, we study the effect of the presence of NaCl on CH_4 hydrate in an oil system kinetically through estimating the induction time and the relative inhibition performance at the studied conditions of a pressure of 9 MPa and temperature of 274.15 K (all kinetic experiments were repeated for three runs) and thermodynamically through investigating the impact of the presence of 3 wt % NaCl toward the pressure and temperature presented by the HL_wVE point under four different pressures (9, 8, 5.5, and 4 MPa), enthalpy, and average reduced temperature. All experiments were conducted with and without NaCl to investigate the role of oil in delaying hydrate formation and shifting the equilibrium curve. The details of the study of the mentioned parameters will be further explained in the following sections.

3.1. Induction Time and Relative Inhibition Performance (RIP).
The induction time can be a valuable indicator of hydrate formation kinetics, particularly when experiments are performed under high pressure and subcooling conditions, as

in this study.[37] Nonetheless, the induction time sometimes misleads the evaluation of the KHI performance since hydrate formation is a probabilistic process.[34] The induction time findings are meticulously tabulated in Table 2, while Figure 5

Table 2. Reported Induction Time Data for a Pure System and Aqueous NaCl Systems with/without Oil on CH_4 Hydrate Formation at 1 wt %

system	pure water	water + NaCl 1 wt % + CH_4	water + CH_4 + oil	water + NaCl 1 wt % + CH_4 + oil
induction time (min)	27.6	29.5	54	57
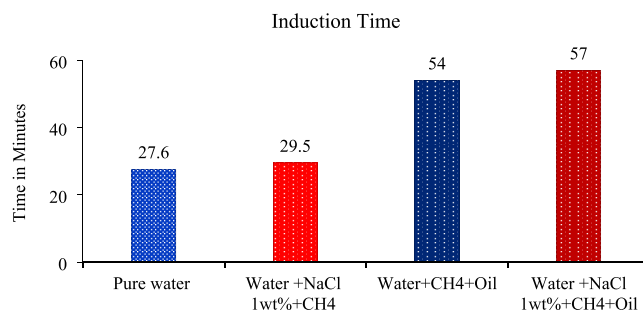
Figure 5. Influence of 1 wt % NaCl on the average induction time of CH_4 hydrate in pure and oil systems.

provides a graphical representation of the effects of various solutions on the induction time. Together, these visual and tabular presentations offer detailed insights into the influence exerted by the solutions on the induction time. The oil system showed a better performance in delaying the hydrate formation than the system of NaCl without oil, which provided an extra 27 min. In the oil system, the added NaCl contributed to the delay of the hydrate formation by 3 min only, and NaCl does not exhibit a substantial effect in terms of delaying the formation of hydrates, indicating its limited impact as a kinetic hydrate inhibitor. Figure 6 shows the relative inhibition
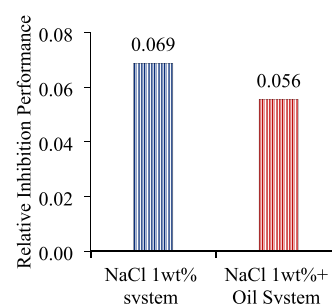
**Figure 6.** Relative inhibition performance comparison of NaCl with/without oil.

performance of NaCl in pure and oil systems presented in Table 3, which shows that NaCl is more effective in the NaCl system than in the oil system. NaCl can still work as a hydrate

Table 3. Comparison of the Relative Inhibition Performance with/without Oil

system	brine water system	brine oil system
RIP	0.069	0.056

Table 4. Hydrate Phase Equilibrium Data of Aqueous NaCl for CH$_4$ Hydrates at 3 wt %

pure water + CH$_4$		water + NaCl 3 wt % + CH$_4$		water + CH$_4$ + oil		water + NaCl 3 wt % + CH$_4$ + oil	
T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)
285.41	8.94	285.04	8.97	285.50	8.85	284.74	9.00
284.75	8.00	284.25	8.09	284.10	8.00	283.80	8.12
280.65	5.40	280.19	5.49	280.20	5.39	279.53	5.41
278.25	3.90	277.65	4.00	277.90	4.02	277.16	4.06
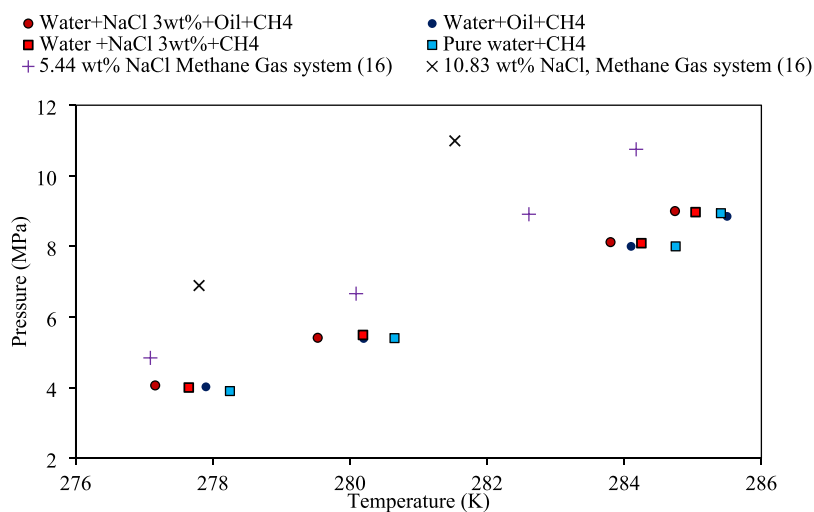
Figure 7. HL$_w$VE data of NaCl in the aqueous solution at 3 wt % on CH$_4$ hydrates in both systems with/without oil.

inhibitor in oil systems, but it may not be as effective as in gas systems due to the lower diffusivity of the oil molecules and the potential for the oil phase to act as a barrier.[38]

The hydrate nucleation temperatures and strength of NaCl were also measured in the oil system by Daraboina et al.[18] at a concentration of 5 wt %. The presence of salt did not influence the strength of the inhibitor, although the combined use of salt and inhibitor has a cumulative effect on inhibition of hydrate formation. Moreover, the ranking of inhibitors follows the same order observed in the absence of salts.

Overall, NaCl is reported effective as a thermodynamic inhibitor and is considered a better thermodynamic inhibitor than a kinetic inhibitor in gas hydrate formation because it can shift the thermodynamic equilibrium conditions of the gas mixture, which prevents hydrate formation by lowering the hydrate formation temperature.[39,40]

3.2. HL$_w$VE Points of NaCl on Methane Hydrate. The influence of NaCl on the equilibrium curve is presented in the presence and absence of oil to evaluate the role of the mentioned THI in both systems at moderate temperature and pressure ranges of 274−286 K and 4.0−9.0 MPa, respectively, as shown in Table 4.

Figure 7 shows the hydrate phase equilibrium data of NaCl at different pressure sets on the CH$_4$ hydrate. The obtained results show that NaCl provided thermodynamic inhibition by shifting the HL$_w$VE points toward higher pressures and lower temperatures for both systems with/without oil, especially at high pressures. Figure 7 shows the difference in temperature and pressure with the presence of water + NaCl + oil + CH$_4$ and water + NaCl + CH$_4$; the added NaCl provided a clear contribution by inhibiting the hydrate, which reflected positively in shifting the equilibrium points. In the oil system, the contribution of the THI to the equilibrium curve increases the pressure with a range of 0.04−0.15 MPa and reduces the

temperature with a range of (1−4 K) due to the NaCl presence in the systems that reduces the activity of water molecules by increasing the ionic strength of the solution. Additionally, the added oil contributes slightly in increasing the pressure and reducing the temperature since oil could inhibit or break down the hydrate.

In the study conducted in gas systems by Hu et al.,[41] at very high pressures up to 200 MPa to study the influence of NaCl at high pressures and under different concentrations (12 wt−26 wt %) compared to the pure system by taking the concentration 12 wt % at 40 MPa in comparison to a pure system; it shows comparable results to our study with a slight increase in pressure and reduction in temperature that is due to the high concentration of NaCl that increases the pressure by 1−3 MPa and lowers the temperature by 3−5 K. Cha et al.[16] studied the influence of NaCl at higher concentrations of 5.44 and 10.83 wt % in a methane gas system, depicting a larger deviation drift toward higher pressures and lower temperatures, as shown in Figure 7, whereby this study was performed at lower concentration 3 wt %; thus, the difference of shifting the pressure and temperature from the pure system was seen minimal as compared to the higher concentration.

3.3. Hydrate Dissociation Enthalpy (ΔH_{diss}). The calculated ΔH_{diss} values for the considered systems (H$_2$O + CH$_4$, H$_2$O + CH$_4$, and NaCl+Oil) are presented in Table 5. It is already assumed that in the HL$_w$VE condition the system primarily contained only gas and liquid phases. Therefore, the extent of the hydrate phase could be negligible.[42,43] The findings showed that the enthalpy information for NaCl in the CH$_4$ system was similar to that of the pure water+oil system. This suggests that NaCl does not participate in gas hydrate formation as salts are rejected. Because CH$_4$ creates S$_1$ hydrate under moderate conditions, only one S$_1$ hydrate structure could form for all of the systems examined.

Table 5. Calculated Dissociation Enthalpies ΔH_{diss} (kJ/mol) in the Presence of Oil at Different Systems with/without NaCl at Various Equilibrium Pressures for CH_4 Hydrates

System	Pure water + oil	Water+NaCl 3 wt % + Oil
Enthalpy	ΔH(kJ/mol)	ΔH(kJ/mol)
	66.83	66.70
	66.93	66.81
	67.26	67.15
Average Enthalpy	67.44	67.33

3.4. Average reduced temperature in the presence of NaCl solution. Figure 8 represents the suppression and
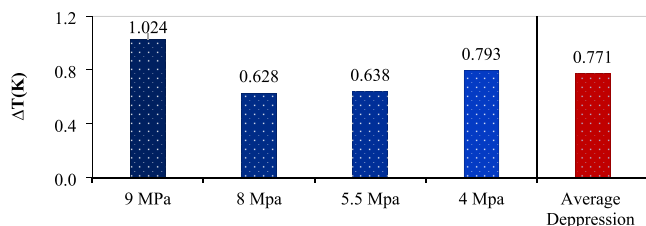
Figure 8. Influence of NaCl on reduced temperature ($\Delta \mathcal{F}$) at 3 wt % on CH_4 gas hydrate in an oil system.

reduced temperature ($\Delta \mathcal{F}$) for aqueous concentrations of NaCl on CH_4 gas hydrate in the oil system at various experimental pressures. From Table 6 the inhibition impact

Table 6. Reduced Temperature ($\Delta \mathcal{F}$) of 3 wt % concentration of NaCl on CH_4 gas hydrate in oil system at different experimental pressures

Pressure (MPa)	9.0	8.0	5.5	4.0	Average Depression
Reduced T (K)	1.024	0.628	0.638	0.793	0.771

also seems to be pressure dependent, as maximum inhibition is obtained at around 9 MPa pressure. At lower pressures ($P <$ 5.5 MPa), the inhibition influence of NaCl is diminished compared to higher-pressure conditions ($P <$ 5.5 MPa) at a concentration of 3 wt % due to its effect on the thermodynamics of hydrate formation. At high pressure, NaCl increases the activity of water, which means that more water molecules are available to form hydrate cages around gas molecules.[44−46] This increase in water activity can lead to more hydrate formation. The average suppression temperature ($\Delta \mathcal{F}$) for NaCl at 3 wt % on CH_4 in oil system is 0.771 K which is quite acceptable since the drilling oil slightly contributes in inhibiting the hydrate compared to the commercial inhibitor ILs in gas systems where the average suppression temperature ($\Delta \mathcal{F}$) values between (0.70−1.42 K).[22]

4. CONCLUSION

In this experimental study, the inhibition effect of NaCl on methane hydrate in an oil system has been investigated kinetically and thermodynamically and compared to the influence of NaCl in the pure system; both studies were studied using an isochoric method by hiring the high-pressure reactor cell.

The two studies (kinetic and thermodynamic) were conducted at different pressures and temperatures, where the kinetic study; was tested at a pressure of 8 MPa and a temperature of 274.15K; the later thermodynamic experiments were performed at 4 different pressures (9,8,5.5 and 4 MPa) and temperatures ranging from 274.15 to 286.00K. The results reveal that NaCl has no significant impact as a kinetic inhibitor on induction time; there was a very slight difference compared to the pure water system. On the other hand, NaCl shows a significant influence as a thermodynamic inhibitor by shifting the equilibrium curve toward higher pressures and lower temperatures in both arrangements with/without oil systems whereby the added oil slightly contributes in shifting the equilibrium curve. Moreover, The findings showed that the enthalpy measurements for system containing NaCl and pure system in CH_4 hydrate in oil systems were similar, implying that NaCl + Oil does not function as a semiclathrate hydrate and does not create polyhedral hydrate cages as salts are rejected during hydrate formation.

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Notes

The authors declare no competing financial interest.

■ NOMENCLATURE

KHI Kinetic hydrate inhibitor
THI Thermodynamic hydrate inhibitor
NaCl Sodium chloride
CH_4 Methane
RIP Relative inhibition performance
$\Delta \mathcal{F}$ Average suppression temperature
HL_wVE Hydrate liquid−vapor equilibrium
GCMS Gas Chromatograph−Mass Spectrometer

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