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Methane Hydrate-in-Oil Systems in the Presence of Natural Amino Acid-Equilibrium Phase Condition Measurements

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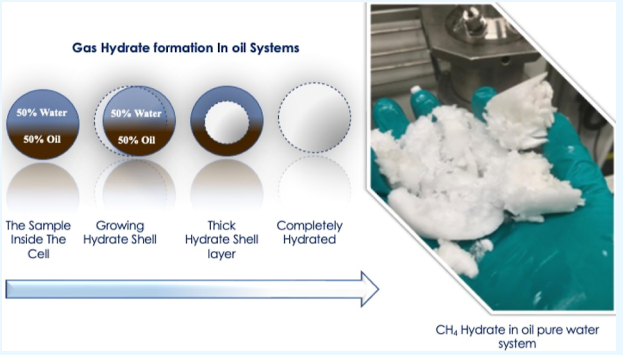
ABSTRACT: This experimental study reports the thermodynamic influence of three different amino acids on methane hydrate in oil-dominated systems, namely, glycine, proline, and alanine. To thoroughly examine the effect of selected amino acids on methane (CH_4) hydrate formation compared to the commercial inhibitor monoethylene glycol (MEG) in the presence of oil, the hydrate liquid−vapor equilibrium (H-Lw-Lo-V) curve is used to measure amino acid aqueous solutions. All experiments are performed at a concentration of 10 wt % by using the isochoric T-cycle technique in a high-pressure reactor cell at the selected range of pressures with temperatures of 4.0−9.0 MPa and 276.5−286.0 K, respectively. Results show that all studied amino acids inhibit hydrate formation of methane; the inhibition trend shows as glycine > alanine > proline in both systems; in the brine water system, the inhibition performance was higher than in the pure water system due to the presence of NaCl. Glycine showed the highest inhibition strength in both systems with an average reduced temperature in pure and brine water of 0.92 and 1.75 K, respectively, at 10 wt %, making the inhibition performance of glycine comparable to the commercial inhibitor MEG. The inhibition effect is attributed to the amino acid's hydrogen bonding energies and side group alkyl chain. Calculating the dissociation enthalpies of methane hydrates in the presence of amino acids using the Clausius−Clapeyron equation implies that the amino acids do not occupy the cage structures during methane hydrate formation.



1. INTRODUCTION

Gas hydrates are solid crystals that form when water molecules trap small gas molecules like methane, ethane, carbon dioxide, nitrogen, and hydrogen sulfide under high-pressure and low-temperature conditions.[1−3] Forming hydrates is a challenge in the oil and gas industry, as they can cause blockages, delays in operations, and safety issues. To prevent these issues, it is crucial to ensure safe flow practices.

Currently, there are multiple techniques available for mitigating the effects of gas hydrates, including chemical inhibitors, water removal, isobaric thermal heating, and depressurization. One of the most effective and feasible techniques applied in the oil and gas industries for hydrate inhibition is the use of chemical additives.[4] There are two main types of gas hydrate inhibitors; low-dosage gas hydrate inhibitors (LDHIs) and thermodynamic inhibitors (THIs). LDHIs are further categorized into two types, which are kinetic hydrate inhibitors (KHIs) and antiagglomerates (AAs). KHIs mainly delay the formation of the gas hydrate by increasing the induction time to delay the crystallization within the pipeline, requiring concentrations in the range of 1−2 wt %.[5,6] However, at high subcooling, their performances are poor.[7−10] THIs, which mainly consist of alcohols such as ethylene glycol, monoethylene glycol (MEG), and methanol, are used as active THIs to prevent the formation of hydrate in pipelines by shifting the phase boundary of hydrate formation to higher pressures and lower temperatures via disrupting hydrogen-bonded water molecules desirable for hydrate formation.[11] However, they require much larger quantities (10−50 wt %) compared to KHIs[12−14] and are harmful to the environment. THIs are also volatile and may evaporate in the hydrocarbon stream, leading to expensive chemical losses during hydrocarbon refining.[15,16]

Due to its high concentration requirement and concerning environmental impact, efforts are being made to find new THIs that are as effective as commercial inhibitors and are safer for the environment and more economical for industrial use. Such recent discoveries are in the so-called organic, green inhibitors known as amino acids.[3] Amino acids are known primarily as molecules that are building blocks for proteins. The living

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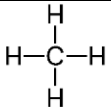
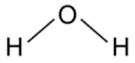
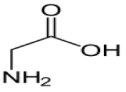
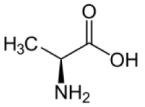
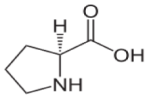
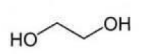
Table 1. List of Chemicals Used in This Study

Chemical Name	Purity	Formula	Structure	Mol.Wt. (g.mol^{-1})	Cas Number	Supplier
Methane	99.97%	CH_4		16.04	74-82-8	LMG-UTP
Water	Deionized	H_2O		18.02	7732-18-5	UTP
Brine Water	3.5%	ClH_2NaO	-	76.46	7732-18-5 74-95	Self-prepared
Glycine	99.99%	C_2H7NO_3		75.07	56-40-6	Benua Sains Sdn. Bhd
Alanine	99.9%	$C_3H_7NO_2$		89.09	56-41-7	Benua Sains Sdn. Bhd
Proline	99.9%	$C_5H_9NO_2$		115.13	147-85-3	Benua Sains Sdn. Bhd
Mono Ethylene glycol	99%	$C_2H_6O_2$		62.07	107-21-1	LMG-UTP
Drilling Oil	99.0%	-	-	-	-	PETRONAS Sdn Bhd

organism has 20 naturally occurring amino acids. All amino acids are made up of a carboxylic acid (−COOH) and an amine ($-NH_2$) functional group as well as a distinct side chain, which may range from a polar alkyl chain to a positively or negatively charged moiety. The physical and chemical characteristics of amino acids are heavily influenced by their side chains.[17−20] Since most amino acids function as zwitterions in aqueous conditions, they may be regarded as possible gas hydrate inhibitors.[21−23] The zwitterionic nature of amino acids results in a "potent electrostatic interaction between the electrical charges of the amino acids and water molecules", which could hinder the formation of hydrates by water molecules. Additionally, the presence of amine groups and carboxylic acids in amino acids enables them to form hydrogen bonds with molecules of water. Experimental studies using neutron scattering[24] demonstrate that amino acids significantly alter the local water environment through the enhancement of the hydrogen bond network between water molecules and the amino acids. In brief, amino acids are promising for gas hydrate inhibition because they are nontoxic, biodegradable, physiologically active,[25] and simple to produce larger quantities in low cost.

Multiphase pipelines differ significantly from normal gas pipelines and are affected via numerous variables such as the composition of the oil and gas (such as heavy hydrate formers, asphaltenes, resins, naphthenic acids, phenols, and wax), the physical and chemical properties of the oil (such as viscosity and solubility of oil fractions), the properties of the water (such as pH and salinity), and many other unknown factors. A comprehensive examination of the literature reveals that inconsistent conclusions have been reported regarding hydrate formation in oil-dominated systems and the impact of oil on hydrate formation.[26−28] This is most likely due to the significant variation in oil sources and their underlying (and usually unidentifiable) effects on other components in the systems, as well as the subcomponents' solubility. This further complicates any attempt to understand whether it promotes or inhibits hydrate formation.[28,29] Water cuts may differ from one well to another and are often greater in older oil/gas wells. Because the quantity of a hydrate inhibitor is proportional to the volume of water, a large water cut will result in a large amount of hydrate in the pipeline, culminating in a full blockage. As a result, more inhibitors will be required to stop hydration, raising the total cost of additives. Furthermore, data suggests that systems with severe water shortages respond differently than systems with minor water cuts.[30]

Based on the literature, no studies have reported on the thermodynamic effect of green inhibitor amino acids on CH_4 hydrate formation in the oil system. A recent kinetics study conducted using glycine in the presence of crude oil in natural gas hydrate formation was done by Mu and von Solms,[31] where green inhibitor glycine was tested with other inhibitors.

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The inhibition strength was found as the following: starch < chitosan < glycine < PVP. Few studies have reported amino acids as novel thermodynamics inhibitors in the gaseous system. Bavoh et al.[32,33] tested glycine, alanine, proline, arginine, and serine for CO_2 and CH_4 hydrate using a sapphire cell with an inhibitor concentration of 10 wt %. Reportedly, glycine showed the best inhibition performance with an average temperature reduction of 1.83 K, followed by alanine, proline, serine, and arginine. Both systems of CO_2 and CH_4 showed a similar trend in inhibitor performance, with the only difference being that CO_2 demonstrated higher inhibition strength than the CH_4 system. Sa et al.[34] were the first to present the H-Lw-Lo-V curve of CO_2 hydrates for valine, glycine, and alanine in the 0.1−3.0 mol % range. According to the findings, amino acids significantly reduce the amount of CO_2 hydrates. The inhibition performance was discovered to be valine > alanine > glycine (in mol %). They suggested that the thermodynamic inhibition potency rises as the hydrophobicity of amino acids increases. Most amino acids have now been reported as KHIs for CH_4, CO_2, natural gas, and tetrahydrofuran.

Another study on the thermodynamic and kinetic effect was done by Sa et al.[35] on CH_4 and natural gas hydrate in the presence of the amino acids glycine, serine, alanine, and proline. It was suggested that they thermodynamically and kinetically inhibit hydrate in both systems. At 1.3 mol %, the order of thermodynamic inhibitory influence in both systems was proline > serine > alanine > glycine. The inhibitory effects were associated with the electrostatic force and hydrogen bonding of attraction between water molecules and amino acids through zwitterion interactions.

Although most amino acids have been studied kinetically and thermodynamically on different gas systems, data on kinetics remain scarce, while thermodynamics studies on the effect of green inhibitor amino acids in oil-dominated systems are also lacking. Therefore, additional research on the impact of amino acids on gas hydrate in oil systems' former phase equilibrium condition and structural cage occupancy is required. In this article, the influence of three natural amino acids on the H-Lw-Lo-V curve of methane hydrate formation in two systems, pure and brine water, is presented in an oil system. The Clausius−Clapeyron equation was also used to calculate the hydrate dissociation enthalpy of methane hydrate in the absence and presence of amino acids as well as its comparison to the commercial inhibitor MEG.

2. METHODOLOGY

2.1. Materials. The list of chemicals, purity, formula, CAS number, structure, and molecular weight of all the chemicals used during this experimental study is shown in Table 1. Green inhibitor chemicals used in this study, namely, glycine, alanine, and proline, were supplied by Benua Sains Sdn. Bhd, and the commercial inhibitor ethylene glycol was supplied by LMG-UTP. All chemicals are used without further purification. Drilling oil used during this study with a purity of 99.0% was provided by PETRONAS Sdn Bhd, with the composition of the drilling oil shown in Table 2. The experiment was conducted on methane gas with a purity of 99.995%, which was purchased from LMG-UTP, Malaysia. Deionized and brine water were used in preparing all solutions.

2.2. Experimental Setup. In this study, a high-pressure stainless steel cell reactor was used to determine the phase boundaries of green inhibitors on CH_4 hydrates in the presence of the inhibitor amino acid solutions. The apparatus features a 650.0 cm^3 high-pressure cell that operates within a temperature range of 253.0−323.0 K and up to 20.0 MPa pressure. It also includes a magnetic stirring system and two PT-100 sensors for monitoring.[36−39] One is installed inside the cell, and the other is located 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. A gas booster compressor injects methane into the cell, and 100 mL of the amino acid solutions loads into the cell manually. As illustrated in Figure 1, the whole apparatus 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.

Table 2. Drilling Oil Compositions

component		mol %
C1	methane	0.88
C3	propane	1.8
C6	cyclohexane	2.03
C10	decane	10.85
C11	undecanes	13.94
C12	dodecanes	19.07
C13	tridecanes	12.32
C14	tetradecanes	16.49
C15	pentadecanes	5.55
C16	hexadecanes	2.3
C17	heptadecane	1.13
C18	octadecanes	0.52
C19	nonadecanes	9.84
C22	docosanes	0.71
C26	hexacosanes	0.39
C29	nonacosanes	2.18
total		**100%**

2.3. Experimental Process for H-Lw-Lo-V Point Measurement. The desired pressure is applied once the chemicals are injected into the cell. Figure 2 displays a T-cycle method for achieving the hydrate dissociation temperature, which correlates to the hydrate phase equilibrium.[36,40] The reactor's temperature was immediately reduced to (273.0 K)/1 °C and held until the hydrate formation was complete. When the pressure immediately drops, it indicates the formation of hydrates. A gradual heating rate is required to detect the right hydrate dissociation temperature. Initially, hydrate formations occur in the system, which is then gradually heated to around 6 K above the dissociate point, at a stepwise heating rate of 0.5 K/h until complete gas hydrate dissociation. To determine the hydrate equilibrium point accurately, the length of every step usually needs 2.0 to 6.0 h. The completion of each THI experiment required approximately 48 h. The equilibrium point of the hydrate is determined at the intersection of the temperature−pressure curve and the cooling curve during the heating process. The equilibrium curve was calculated by conducting tests at four different pressure levels. The measurement uncertainties were calculated using the standard uncertainty type B evaluation with taking into consideration accuracy of standard equipment, normal distribution, and 95% level of confidence using GUM Workbench.

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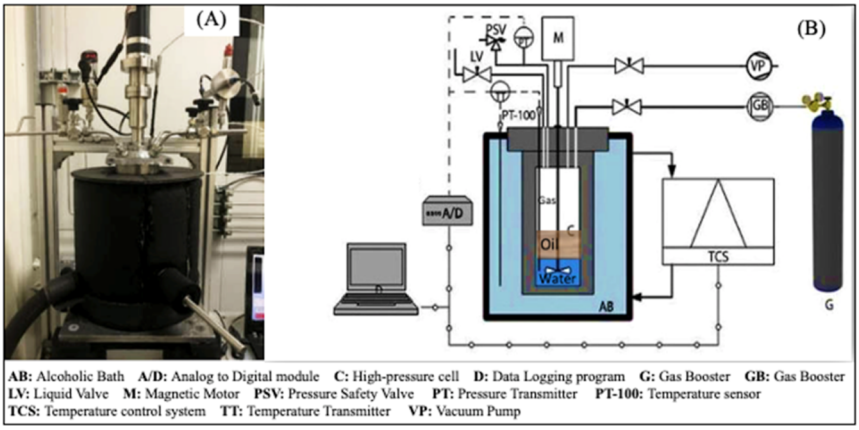

Figure 1. (A) High-pressure cell reactor used in this study. (B) Schematic diagram of the high-pressure reactor ("replotted from Almashwali Copyright 2023."[22]).[21]

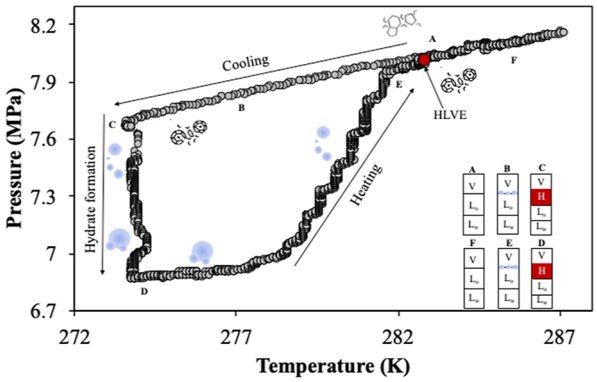

Figure 2. T-cycle plot generated during the experiment used to indicate the impact of the inhibitors on the hydrate phase equilibrium (Almashwali Copyright 2023."[22]).[21]

2.4. Hydrate Dissociation Enthalpy (ΔH_{diss}) and the Average Reduced Temperature. The phase equilibrium temperature of CH_4 gas in the presence of amino acids was designated by $T_{1,pi}$, while $T_{0,pi}$, represented the equilibrium temperature of CH_4 gas in water. Dissociation pressures and temperatures should be monitored simultaneously. The number of pressure points is denoted by n for this analysis. Integrating the observed H-Lw-Lo-V values into a single Clausius−Clapeyron equation is the usual practice to get gas hydrate dissociation enthalpies (H_{diss}). In addition, it also is used to determine the slope of H-Lw-Lo-V data, and the resulting values are referred to as H_{diss}[41−43]

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

The thermodynamic inhibitory activity of the above systems containing amino acids in the two different systems of pure and brine water in the oil system was obtained by calculating the average inhibition temperatures. The calculation of average reduced temperature ($\underline{T}$) is obtained from eq 2 using an established method.[36,44−46]

$$\underline{T} = \frac{\Delta T}{n} = \frac{\sum_{i=1}^{n}(T_{0,pi} - T_{1,pi})}{n} \tag{2}$$

where R is the universal gas constant, z is the compressibility factor of the investigated gas, and P and T represent the conditions at equilibrium. This is achieved by solving the Peng−Robinson equation of state. The Peng−Robinson equation of state is used to determine the value of z. Several studies have followed the literature's approach in calculating dissociation enthalpy.[47,48]

2.5. Thermodynamic Model. Predicting gas hydrate phase equilibria using thermodynamic models is challenging due to the presence of chemical inhibitors as well as the oil. A model was provided by Quinby-Hunt and Dickens that considers the impact of chemical additives on water activity and generates more accurate predictions. As a result, this model may be used to make approximations about the CH_4 hydrate equilibrium data points.[49] Pieroen's model[50] discovered a correlation between the enthalpy of formation, water activity, and the suppression temperature. The following eq 3 may be used to determine the activity level of this solution[49,51]

$$\ln a_w = \frac{\Delta H_{FUS(i)}}{R}\left[\frac{1}{T_{f(i)}} - \frac{1}{T_f}\right] \tag{3}$$

where a_w denotes the water activity, $\Delta H_{FUS(i)}$ is the heat of fusion of ice (6.008 kJ/mol), and $T_{f(i)}$ and T_f are the freezing point temperatures of water (273.15 K) and water + AAs solutions. T_f is calculated as proposed by Dickens and Quinby-Hunt in eq 4, using a cryoscopic constant of water as 1.853 K·kg/mol.[49]

$$\Delta T_f = K_F \times m \times i \tag{4}$$

K_F is the cryoscopic constant, which is 1.86 K (kg/mol) for water, m is the molality (mol/kg), and i is the van't Hoff factor, where T_f is the freezing point depression. The freezing point of amino acid solutions has been estimated in the literature using a van't Hoff factor of (1).[3,52,53] The system's ideality improves due to the cooperation between amino acids, oil, and water. This has led to a change in the degree to which the temperature drops below freezing.[11,49] Here, the freezing point depression for the brine system was calculated using the van't Hoff factor of mixed inhibitor solutions, which was 1.35 in the brine water system, whereas in a pure water system, it was 1. The partial ionization of glycine into two ions while maintaining the glycine concentration necessitates setting the van't Hoff factor for the brine system between 1 and 1.35, which is consistent with the observation that a weak electrolyte might have a van't Hoff factor of 1 to 2. Equation 5 below may

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be used to calculate how the presence of THIs affects the dissociation temperature of CH_4 hydrate

$$\ln a_w = \frac{\Delta H_d}{nR}\left[\frac{1}{T_w} - \frac{1}{T_{THI}}\right] \quad (5)$$

where T_w and T_{THI} are the hydrate dissociation temperatures in both systems of T_W water and T_{THI} aqueous amino acid solution, a_w denotes the water activity, n represents for CH_4 hydrates hydration number 5.75,[54] ΔH_{diss} represents the experimental dissociation enthalpy of methane (58.882 kJ/mol), and R is the universal gas constant; the phase transition temperature for CH_4 hydratase is higher than the ice−water equilibrium temperature, as shown by the combination of eqs 5−7. Temperature of THI (T_{THI}) may be determined using the formula in eq 6 below

$$\left[\frac{1}{T_w} - \frac{1}{T_{THI}}\right] = \frac{n\Delta H_{FUS(i)}}{\Delta H_d}\left[\frac{1}{T_{f(i)}} - \frac{1}{T_f}\right] \quad (6)$$

Therefore, the equation determines the temperature at which hydrates dissociate when inhibitors are present. The average absolute error determines whether the model is appropriate for a given system (AAE). Equation 7 is use to determine the AAE.[49]

$$AAE = \frac{1}{n}\sum_{i=1}^{n}[T_{exp} - T_{cal}] \quad (7)$$

2.6. Average Reduced Temperature in the Presence of THI Solution. To evaluate the inhibitory impact of THIs, eq 8 is used to calculate the average reduced CH_4 hydrate equilibrium temperature.[55,56] The estimated average temperature drop, as illustrated in Figure 5, is as follows

$$T = \frac{1}{n}\sum_{i=1}^{n}\Delta T \quad (8)$$

where in the presence of amino acids for pure or brine water in oil-dominated systems, the difference in equilibrium points at a given pressure is illustrated by ΔT.

3. RESULTS AND DISCUSSION

3.1. H-Lw-Lo-V Points on Methane Hydrate in Oil-Dominated Systems. The reported results of CH_4 H-Lw-Lo-V points in oil-dominated systems in the presence of the 3 selected amino acids in pure and brine 3.5 wt % systems are presented in Table 3. The three selected amino acids inhibit CH_4 hydrate formation via shifting the CH_4 H-Lw-Lo-V curve to higher-pressure and lower-temperature conditions, as illustrated in Figure 3. The efficacy of the investigated amino acids in suppressing hydrate formation is quantified by calculating the average reduction in temperature (T), as specified in eq 2. In addition, the average depression temperature (T) is estimated to evaluate the effectiveness of the amino acids in inhibiting hydrate formation, as outlined in eq 2. The results of these calculations for the amino acids studied are listed in Table 3. According to the data presented in Table 3, the inhibition performance in the brine water system is higher than in the pure water system, the presence of the oil provides extra time in delaying the hydrate formation, and the impact of the amino acids at a concentration of 10 wt % is listed in the descending order of magnitude for both systems of pure and brine water: glycine > alanine > proline.

Table 3. HLVE Data for CH_4 Hydrate under Different Inhibitors for Both (Pure/Brine) Water-in-Oil Systems[a]

deionized water		brine water	
T (K)	P (MPa)	T (K)	P (MPa)
285.41	8.95	285.04	8.96
284.75	8.01	284.25	8.01
280.65	5.49	280.19	5.4
278.25	4	277.65	3.9
deionized water + oil		brine water + oil	
T (K)	P (MPa)	T (K)	P (MPa)
285.5	8.85	284.74	9
284.1	8.02	283.8	8.1
280.2	5.40	279.53	5.39
277.9	4.05	277.16	4.04

	deionized water		brine water	
	T (K)	P (MPa)	T (K)	P (MPa)
glycine (10 wt %)	284.27	8.8	282.95	8.95
	283.2	7.82	281.86	7.95
	279.51	5.43	278.09	5.61
	277.25	4.25	275.81	4.23
proline (10 wt %)	284.7	8.84	283.45	8.9
	283.5	7.89	282.2	7.95
	279.7	5.5	278.15	5.5
	277.44	4.2	275.9	4
alanine (10 wt %)	284.5	8.79	283.6	9
	283.4	7.9	281.92	7.85
	279.55	5.3	278.5	5.7
	277.3	4.21	276.13	4.12
MEG (10 wt %)	283.9	8.84	282.91	9.1
	282.6	7.99	281.92	8
	278.72	5.482	277.9	5.65
	276.77	4.24	275.5	4.1

[a]Expanded uncertainties. $U(T)$ = ±0.1 K; $U(P)$ = ±0.01 MPa; U(mass fraction) = ±0.0001 g (0.95 level of confidence).

The difference between both systems is the greater inhibition performance of the solution with 3.5 wt % NaCl. As salt is a known THI, this affirms its ability in strengthening the inhibition performance of even green inhibitors, by shifting the equilibrium curve. In contrast, a similar inhibition trend is reported by Bavoh et al.,[33] but in a methane gas system whereby the gas is at a molarity basis, of 1.3 mol %.

The investigated concentration unit selected by many researchers is directly connected to the molecular weight of the amino acids being inhibited, which may depend on the system.[13,57] Because of this, the impact of hydrate inhibition might differ depending on the concentration unit used to study it, which can lead to conflicting interpretations of the influence of amino acids. For instance, 1.3 mol % is comparable to around 5.01 wt % of glycine. Given the large reported fluctuations in wt %, it may be difficult to assess the inhibitory effect on the basis of wt % alone. Typically, the inhibitory influence on the mole percent basis is greater for substances with larger molecular weights and vice versa.[13] Nevertheless, the wt % unit is preferable, as pointed out by Yousif, since it is often used in real-world gas hydrate inhibition applications.[58] So, translating the effects of hydration inhibition in that way will add more to the advancement of real-world applications.

THIs (alcohols) typically inhibit the formation of gas hydrates by vying for water molecules and disrupting water activity in the formation process through hydrogen bonding.[59]

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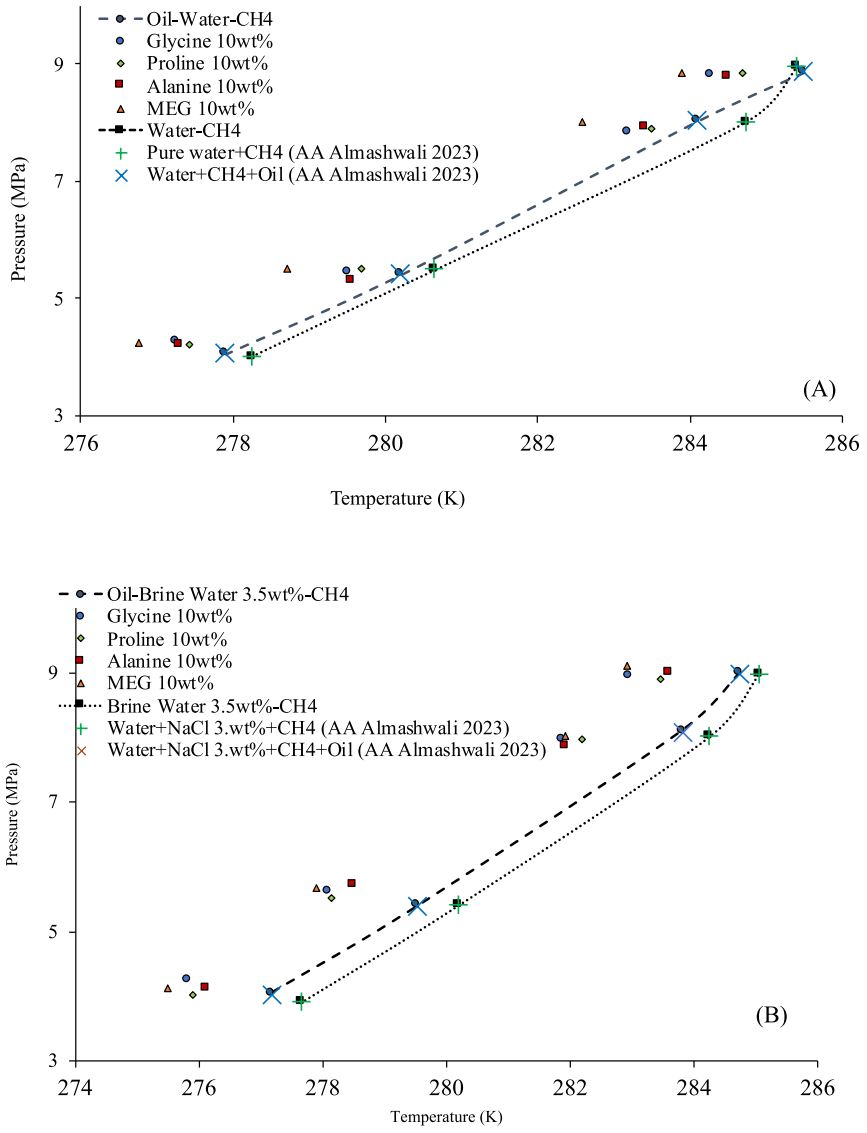

Figure 3. Phase equilibrium of CH_4 hydrate-in-oil systems: (A) pure water system and (B) brine water system (Almashwali[22,53]).

Similarly, amino acids disrupt the reorientation dynamics of bulk water by reducing the hydration shell through hydrogen bonding interactions with water molecules, altering the water solvation dynamics. According to the literature,[24,60,61] amino acids primarily produce a decrease in water reorientation structure dynamics, which may be advantageous for hydrate inhibition. Water molecules rotate during hydrate formation to create cages that house the guest molecules. As shown by a molecular dynamic (MD) simulation research,[62−64] amino acid molecules influence the reorientation behavior of water molecules through hydrogen bonding, resulting in a hydrate inhibitory effect. As a result, the variance in the amino acid inhibitory effect might be attributed to their hydrogen bonding interaction energy with water molecules and the side group alkyl chain. Furthermore, salt additions in brine water systems create additional disruptive water activity in hydrate formation, resulting in an improved gas hydrate inhibition performance.

As the concentration of sodium chloride (NaCl) increases, the efficacy of glycine in disrupting the arrangement of water molecules also augments. This enhancement is due to the additional perturbation that glycine causes in the bulk water reorientation dynamics, which are favorable for hydrate inhibition. As a result, the inhibition performance of CH_4 hydrate formation is improved.

The CH_4 H-Lw-Lo-V curve points of the selected amino acids are represented by using the mark point, and the pure water/brine systems with/without an inhibitor use the dashed lines as a reference to indicate the impact of the present amino acids in both systems. Amino acids are more effective in pure water, while their efficiency is reduced in brine due to competitive ionic interactions. Oil acts as a physical barrier and alters surface tension, influencing hydrate formation in both systems. All amino acids were compared with the conventional inhibitor MEG at 10 wt %, as illustrated in Figure 3, where the hydrate inhibition performance of glycine is within a similar range of MEG. Their closeness in performance highlights how amino acids carry potential as innovative gas hydrate inhibitors, particularly THIs, for industrial uses. In addition, compared to ionic liquids, amino acids are more affordable and friendlier to the environment.[65,66]

3.2. Hydrate Dissociation Enthalpy (ΔH_{diss}). The impact of amino acids on the occupancy and structure of the CH_4 hydrate formation cage is determined by using the Clausius−Clapeyron equation to calculate the dissociation

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Table 4. ΔH_{diss} (kJ/Mol) Values for Glycine, Proline, Alanine, and MEG at 10 wt % Concentration for Both Systems Pure/Brine Water[a]

pressure (MPa)	deionized water + oil	glycine	proline	alanine	MEG
		10 wt %			
9	66.826	66.063	65.310	66.085	65.511
8	66.929	66.165	65.420	66.190	65.607
5.5	67.255	66.488	65.709	66.515	65.917
4	67.440	66.670	65.883	66.658	66.088
average	**67.113**	**66.346**	**65.580**	**66.362**	**65.781**
pressure (MPa)	brine water + oil	glycine	proline	alanine	MEG
		10 wt %			
9	66.702	65.345	65.936	66.007	65.455
8	66.811	65.467	66.048	66.140	65.593
5.5	67.147	65.757	66.352	66.409	65.881
4	67.332	65.947	66.564	66.630	66.098
average	**66.998**	**65.629**	**66.225**	**66.297**	**65.757**

[a]Expanded uncertainties. $U(P)$ = ±0.01 MPa; U(mass fraction) = ±0.0001 g; $U(H)$ = ±1.2 kJ·mol^{-1} (0.95 level of confidence).

Table 5. Average Reduced Temperature (K) of THIs in Different Systems[a]

inhibitors	concentrations	pure water + drilling oil	brine water (3.5 wt %) + drilling oil
glycine	10 wt %	0.92	1.75
proline		0.65	1.31
alanine		0.73	1.32
MEG		1.52	1.89

[a]Expanded uncertainties. $U(T)$ = ±0.1 K.

enthalpy of methane hydrate in the presence of amino acids.[45,53,67] The average methane hydrate dissociation enthalpies for amino acids in oil systems of both systems are shown in Table 4.

Table 4 shows that there is almost no difference in the average dissociation enthalpy of methane hydrates between the presence and absence of amino acids in the oil system. This means that methane hydrate formation in the presence of amino acids under the conditions studied in this paper maintains the same guest cage occupancy and hydrate structure as those of simple methane hydrate. Thus, in oil-dominated systems, amino acids show almost no significant impact on the methane hydrate structure. Furthermore, the cage occupancy was not noticeably different in the presence of amino acids. In brief, the crystalline structure of the gas hydrate shows little change when under the effect of amino acids.

3.3. Average Reduced Temperature in the Presence of THI Solution. To assess the inhibitory effect of THIs, eq 8 is applied to determine the average reduction in the CH_4 hydrate equilibrium temperature. The resulting average temperature decrease, depicted in Figure 5, is as follows: in oil-dominated systems, with pure or brine water and the presence of amino acids, the difference in equilibrium temperatures at a given pressure is represented by ΔT.

Table 5 summarizes the average reduction in temperature of three different amino acids (Gly, Pro, and Ala) compared to the commercial inhibitor MEG in terms of the total average reduced temperature of the pure components in two oil-dominated systems.

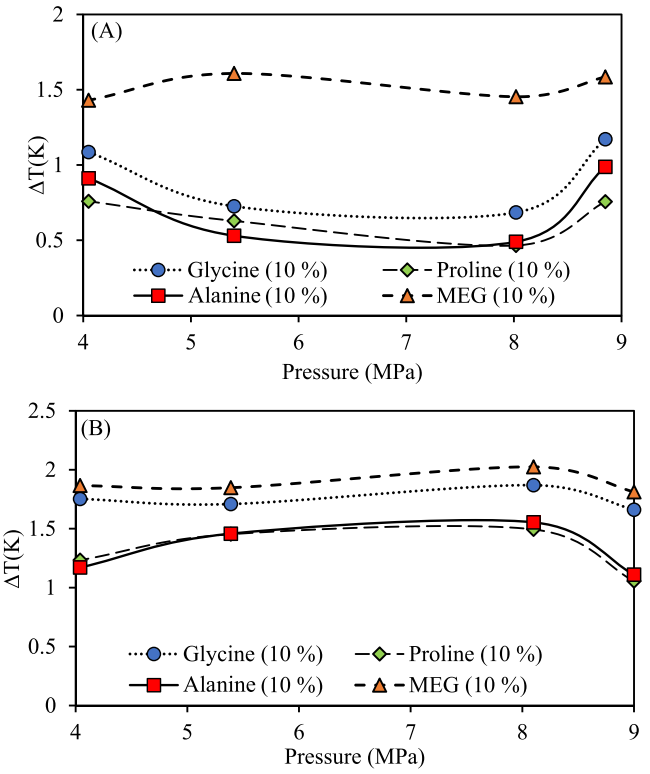

Figure 4. Average reduced temperature at different pressure set points: (A) pure system and (B) brine water-in-oil system.

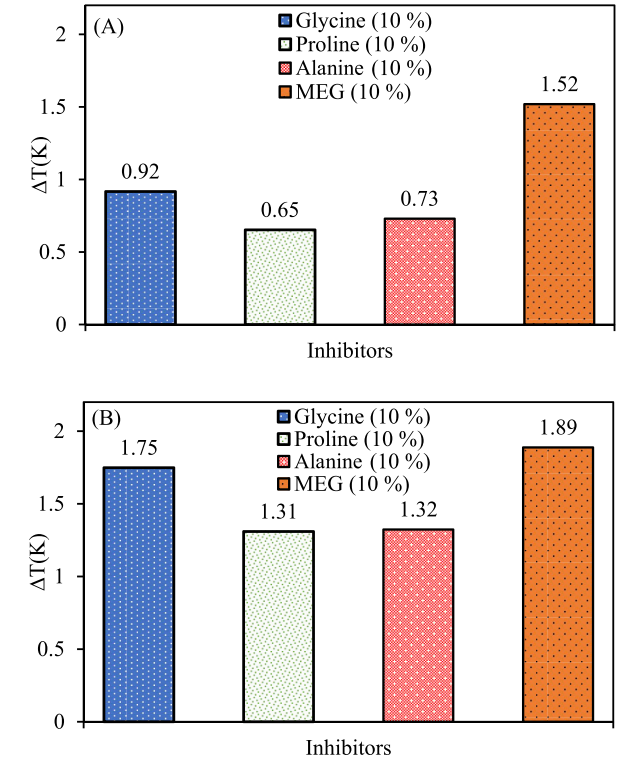

Figure 5. Total average reduced temperature of the selected three amino acids: (A) pure water- and (B) brine water-in-oil system.

Figure 4 details the different sets of points at different pressures and temperatures of the reported inhibitors, showing

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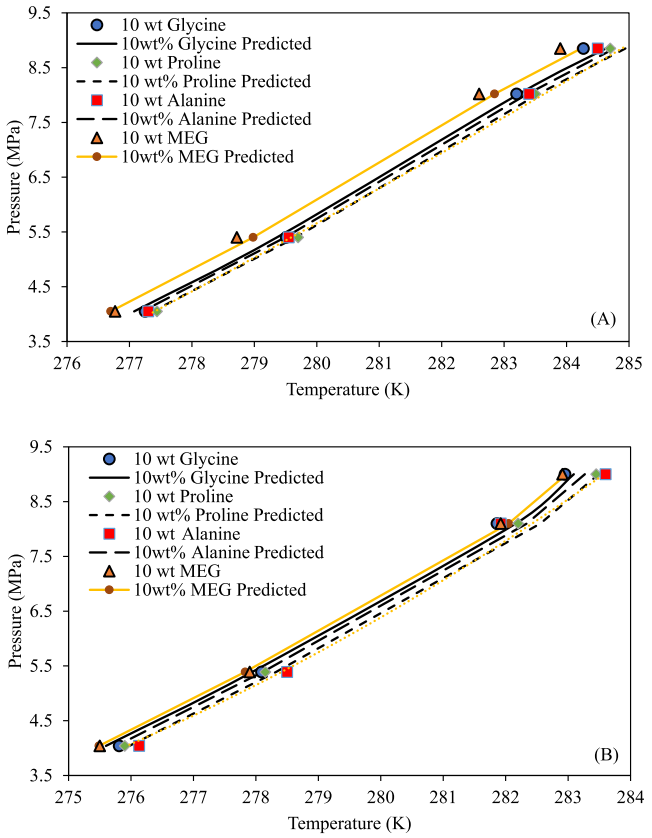

Figure 6. Experimental and predicted values for CH_4 hydrate dissociation temperatures in oil systems: (A) pure water and (B) brine water.

the trend in the inhibition performance for both systems. The brine water (3.5 wt %) + drilling oil system shows a better inhibition effect than the pure water + drilling oil system due to the presence of the salt, further improving the performance of the listed inhibitors. Figure 5 shows the inhibitor's average temperature reduction ΔT compared to MEG. Overall, amino acids show comparable inhibition performance with MEG, with the brine system besting the pure water system. Glycine surprisingly shows the highest inhibition performance among the green inhibitors, where the difference is only 0.14 K against MEG. In addition, all inhibitors perform more favorably at higher pressures and temperatures. In the pure system, the average reduced temperatures for amino acids of glycine, proline, and alanine are 0.92, 0.65, and 0.74 K, respectively, whereas in the brine system, they are 1.75, 1.31, and 1.32 K, respectively. Methane hydrates are stable under specific conditions of temperature and pressure, and inhibitors are chemicals that are added to water in order to prevent the formation of hydrates. At high pressure, the likelihood of hydrate formation increases, making it more difficult for inhibitors to prevent the formation of hydrates, as shown in Figure 4. In some cases, the use of inhibitors at high pressure may not be effective and other methods may need to be used. It is suggested that experiments be conducted at higher concentrations in order to determine the range where a synergistic effect is most effective.

3.4. Thermodynamic Modeling of Amino Acids Compared with MEG. Experimental and predicted values of the equilibrium phase data points for CH_4 hydrate in the presence of amino acids were compared and are shown in Figure 6. Experiments at the studied systems were found to be in good agreement with the prediction model for all of the systems analyzed under the Quinby-Hunt and Dickens models.[49] Furthermore, using the Quinby-Hunt and Dickens model, its efficacy may be estimated by assuming that it lowers the solution's freezing point in the presence of the inhibitor.[15,36]

Table 6 encompasses the AAE values, which were computed for CH_4 hydrates in the oil system in the presence of the green inhibitor together with MEG. Four data points were used in calculating the AAE and R^2 values.

Figure 6 compares the experimental hydrate dissociation temperatures to extrapolated temperatures from the model.

Table 6. Phase Equilibrium Temperature Prediction in the Presence of THI Solutions for CH_4 Hydrate-in-Oil (Pure/Brine) Systems[a]

inhibitors	system	T_{exp}	T_{cal}	$T_{cal} - T_{exp}$ (K)	AAE (%)
glycine	pure water	284.27	284.63	0.36	−0.12
		283.20	283.24	0.03	−0.01
		279.51	279.36	−0.15	0.05
		277.25	277.07	−0.18	0.06
		average =		0.0180	−0.0057
proline		284.70	284.94	0.24	0.08
		283.50	283.55	0.04	0.01
		279.70	279.66	−0.03	0.01
		277.44	277.37	−0.06	0.02
		average =		0.0989	0.0393
alanine		284.50	284.77	0.26	0.10
		283.40	283.37	−0.02	0.01
		279.55	279.49	−0.05	0.02
		277.30	277.20	−0.09	0.03
		average =		0.1111	0.0393
MEG		283.90	284.23	0.33	0.11
		282.60	282.84	0.24	0.08
		278.72	278.98	0.26	0.09
		276.77	276.70	−0.06	0.02
		average =		0.2276	0.080
inhibitors	system	T_{exp}	T_{cal}	$T_{cal} - T_{exp}$ (K)	AAE (%)
glycine	brine water	282.95	283.09	0.14	−0.05
		281.86	282.16	0.30	−0.10
		278.09	277.94	−0.14	0.05
		275.81	275.59	−0.21	0.07
		average =		0.2012	−0.0066
proline		283.45	283.48	0.03	0.01
		282.20	282.55	0.35	0.12
		278.15	278.32	0.17	0.06
		275.90	275.97	0.07	0.02
		average =		0.1601	0.0570
alanine		283.6	283.26	−0.33	0.11
		281.92	282.33	0.41	0.14
		278.50	278.11	−0.38	0.13
		276.13	275.76	−0.36	0.13
		average =		0.3758	0.1342
MEG		282.91	282.97	0.06	0.02
		281.92	282.04	0.12	0.04
		277.90	277.82	−0.07	0.02
		275.50	275.48	−0.01	0.004
		average =		0.06	0.0245

[a]Expanded uncertainties. $U(T)$ = ±0.1 K; (0.95 level of confidence).

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The proposed model was then used to predict the impact of amino acids on the methane hydrate in the oil systems and for comparison with the equilibrium phase condition point. The predicted and experimental methane hydrate equilibrium points are presented in Table 6 and Figure 6. As shown in Figure 6, the model predictions are in good agreement with the experimental data; in the pure system, the AAE for the 4 points in glycine, proline, alanine, and MEG are 0.18, 0.09, 0.11, and 0.227 K, respectively, and the determined R^2 value is 0.998Δ, whereas in the brine water system, they are 0.20, 0.16, 0.375, and 0.06 K, respectively, with an R^2 value of 0.997Δ. The THI solution had a concentration of 10 wt % and was in accordance with the data for all the systems examined. Table 5 shows the AAE(K) values obtained from CH_4 hydrates in the oil system, in which the experimental findings and the developed model are similar. Based on the predicted and experimental H-Lw-Lo-V temperatures, the greatest mean average absolute error for alanine was 0.375 K. This suggests that the predicted and experimental hydrate formation temperatures are in excellent agreement.

4. CONCLUSIONS

In this study, the methane H-Lw-Lo-V points in the presence of amino acids in oil systems, inside of two aqueous systems of pure water and brine, were investigated using an isochoric method by conducting the experiments using a high-pressure cell reactor at pressures ranging from 4.0 to 9.0 MPa and temperatures ranging from 273.15 to 286.00 K. All amino acids showed inhibition of methane hydrate formation. The hydrogen bonding energies of amino acids and the side group alkyl chain have been discovered to influence their inhibitory effect. Glycine had the greatest inhibitory effect of all of the amino acids tested in both systems, which is equivalent to MEG and slightly greater than alanine. Furthermore, the calculated methane dissociation enthalpy in the presence of amino acids shows that amino acids and drilling oil are not involved in the hydrate structure cage occupancy. Because amino acids are biodegradable and economically viable for industrial use, this study proposes amino acids as a possible innovative gas hydrate inhibitor in oil-dominated systems over environmental inhibitors to replace current THIs.

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Notes

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NOMENCLATURE

AA	amino acids
AAs	antiagglomerates
LDHIs	low-dosage gas hydrate inhibitors
THIs	thermodynamic hydrate inhibitors
KHIs	kinetic hydrate inhibitors
CO_2	carbon dioxide
CH_4	methane
ΔH_{diss}	dissociation enthalpies
HLVE	hydrate liquid vapor equilibrium
ΔT	average reduced temperature
$\underline{T}$	reduced temperature
AAE	average absolute error
Gly	glycine
Ala	alanine
Pro	proline
MEG	monoethylene glycol

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