

Suitable Binary and Ternary Thermodynamic Conditions for Hydrate Mixtures of CH₄, CO₂, and C₃H₈ for Gas Hydrate-Based Applications

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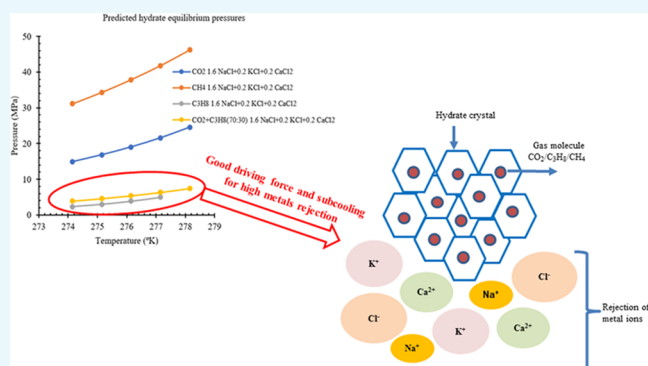


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ABSTRACT: The selection of suitable hydrate formers and their respective gas composition for high hydrate formation, driving force is critical to achieve high water recovery and metal removal efficiency in the hydrate-based desalination process. This study presents a feasibility analysis on the possible driving force and subcooling temperatures for the binary and ternary mixtures of methane, carbon dioxide, and propane for hydrates-based desalination process. The driving force and subcooling for the gas systems was evaluated by predicting their hydrate formation phase boundary conditions in 2 wt % NaCl systems at pressure ranges from 2.0–4.0 MPa and temperatures of 1–4 °C using modified Peng–Robinson equation of state in the PVTsim software package. The results suggest that the driving force of CH₄ + C₃H₈ and CO₂ + C₃H₈ binary systems are similar to their ternary systems. Thus, the use of binary systems is preferable and simpler than the ternary systems. For binary gas composition, CO₂ + C₃H₈ (70:30) exhibited a higher subcooling temperature of 8.07 °C and driving force of 1.49 MPa in the presence of 2 wt % aqueous solution. In the case of the ternary system, CH₄–C₃H₈–CO₂ gas composition of 10:80:10 provided a good subcooling temperature of 12.86 °C and driving force of 1.657 MPa for hydrate formation. The results favor CO₂–C₃H₈ as a preferred hydrate former for hydrate-based desalination. This is attributed to the formation of sII structure and it constitutes 136 water molecules which signifies a huge potential of producing more quantities of treated water.



1. INTRODUCTION

Freshwater is a basic and key resource for existence and is essential for socio-economic growth. The increasing population and economic development demand more fresh water supply in the world. However, only 0.3% freshwater of the 2.5% is accessible by humans.¹ This leads to an urgent need to produce freshwater from saline water which amounts to about 97.5% of the world water resources as readily accessible. The conversion of saline water to freshwater (known as desalination) via removal of dissolved salts from saline water would positively aim to meet the increasing freshwater demands in the world. Desalination techniques are classified into three main types, namely (i) thermal process systems in which evaporation and condensation processes are used to separate the dissolved salts from saline water, (ii) the membrane process systems where either pressure difference or electric field is applied over the saline water to allow it to pass through a permeable membrane, leaving salts behind, and (iii) chemically activated techniques.^{2–4} These water management techniques are mature and robust techniques to treat saline water but faced with limitations like less water recovery, corrosion, scaling issues, and above all they are a highly energy

intensive processes. Because of these limitations, hydrate-based desalination is proposed as a potential method for seawater desalination.

Gas hydrates are icelike, crystalline nonstoichiometric compounds consisting of gas as guest molecule and water as host molecule that are together bonded by a hydrogen bond. Hydrates require two main basic requirements for the hydrate to form, namely water and a gas molecule. Thus, the presence of ion in any system could be excluded since only water would engage in the hydrate formation process. The choice of hydrate forming gas is an additional advantage which could allow a simultaneous seawater desalination while utilizing harmful gases such as CO₂. However, challenging kinetics limitation based on the thermodynamic driving force on the gas systems in seawater is an important concern to enhance the process.

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The presence of a significant temperature and pressure driving force based on different gas mixtures in brine systems would help to determine and develop hydrate-based desalination (HBD) processes that could perform well with minimal operating conditions.

The separation efficiency of metal ions from aqueous salt solution is directly related to the amount of hydrate that could be formed and how fast it can form. The fast hydrate formation and amount of hydrate formation is directly related to the pressure driving force and/or subcooling temperature. Subcooling temperature is determined as the difference between the equilibrium temperature and the system temperature at the system pressure. Driving force is the difference between the Gibbs free energy of the solution and the crystal phase as considered in this work. Several driving forces for the nucleation and growth process of hydrate formation have been discussed elsewhere in the literature.^{4–7} Many significant achievements have been made in gas hydrate thermodynamic, kinetic studies, and research is maturely increasing. So far there has been no study performed in determining the best gas composition that can provide suitable driving force in terms of pressure and subcooling temperature for seawater desalination purpose. Hence, initiating the driving force research in selecting the best gas composition for gas hydrate formation has significant importance to provide guidelines for selecting the best composition for hydrate-based desalination applications. The use of gas such as propane, methane, CO₂ and their mixtures has gained much attention as suitable gas compositions for hydrate-based desalination purposes. These gases are mostly considered because they provide good driving force and form sI and sII hydrates with 46 and 136 water molecules for water removal. Also, in the case of gases such as CO₂, their environmental prohibitive nature in recent times promotes their utilization to produce clean water instead of storing it permanently. However, the selection of the best gas systems by researchers for seawater desalination is trial and error or based on the researcher's choice from literature. This kind of method limits the full potentials of the hydrate-based desalination process, leading to driving force challenge and low efficiency. Therefore, uncovering the boundary conditions of driving force for different gas systems will be useful to choose the best gas composition for seawater desalination.

The use of hydrate phase boundary conditions is the main property that could be used to determine the pressure and temperature driving forces for high water recovery. Aside from the classical thermodynamic models, software packages such as CSMGem and PVTsim are well-known products used by academicians and industries alike to study hydrate behavior of gas components. PVTsim simulator is used as it is well used in oil and gas industries and moreover specifically used for mixed gases and hydrocarbons compared to CSMGem.

Several theoretical studies have been carried out over the years to anticipate phase equilibria of hydrate systems utilizing various formers such as nitrogen, C₂H₆, CO₂, CH₄, C₃H₈, isobutane, and hydrogen sulfide (H₂S).^{8–11} However, these experiments were limited to single and mixed former hydrate production in pure water. Researchers have also looked into the effects of electrolytic salts (such as Na⁺, K⁺, Mg²⁺, Ca²⁺, Fe²⁺, Cl⁻, and SO₄²⁻) on hydrate phase equilibria.^{12–15} Several experimental and simulation studies on the mitigation of natural hydrates on various oil and gas sites across the world have been published.^{16–18} Previous research included hydrate formation studies using simple gases such as methane, carbon

dioxide, and ethane. Gudmundsson et al.¹⁹ studied pure methane and a mixed gas composition (C₁ = 92%, C₂ = 5%, and C₃ = 3%). Bediako²⁰ predicted the hydrate phase boundary of synthetic natural gas composition using PVTsim in the Keta basin of Ghana at pressures and temperatures ranging from 43.09 to 350 bar and 12.87 to 27.29 °C, respectively, in the presence of inhibitors (methanol and glycol). Maekawa et al.²¹ studied equilibrium conditions of hydrate for 100% CH₄ and gas mixtures with compositions of (98.9 vol % CH₄ + 1.1 vol % C₂H₆), (97.9 vol % CH₄ + 2.1 vol % C₂H₆), (95.2 vol % CH₄ + 4.8 vol % C₂H₆) and (90.2 vol % CH₄ + 9.8 vol % C₂H₆) in the presence of pure water and 3.0 wt % NaCl aqueous solution. The study revealed that by addition of ethane the hydrate equilibrium pressure decreased with increase in ethane gas composition. Overall, there was no proper way to implement selecting the gas compositions. According to an experimental study by Mohammadi et al.²² on hydrate formation of CH₄ (99.99%), C₂H₆ (99.99%), C₃H₈ (99.99%), and CO₂ (99.99%), in the presence of various salts different concentrations were compared with the predicted results and were found to be in good agreement. However, pure gas components were used in this study. Seo et al.²³ studied the phase equilibrium of pure CH₄ at 4.5 MPa, pure SF₆ (99.9%) at 0.75 MPa and pure HFC-134a at 0.16 MPa in the presence of NaCl (30 wt %) at 258.15K for its application in desalination where the limitation of pressure was chosen randomly based on the phase equilibrium values. The study revealed a potential to reduce the formation energy by using HFC-134a but requires further studies on better separation to achieve higher quality of desalinated water and also there is no well-defined way of selecting pressures for hydrate formation. Bavoh et al.²⁴ used PVTsim to predict the equilibrium hydrate phase boundaries of synthetic natural gas in Malaysia having higher percentage of CO₂ and H₂S in the presence of inhibitors (methanol and glycol) and compared the results with the experimental data from literature. The study revealed that triethylene glycol inhibited hydrate formation in pure synthetic natural gas system, synthetic natural gas with 30 mol % CO₂, and synthetic natural gas with 30 mol % H₂S. Another study by Babu et al.²⁵ considered that in two mixtures of ternary gas system CO₂ (59.4%) + H₂(59.4%) + C₃H₈(2.5%) and CO₂(80%) + H₂(18.8%) + C₃H₈(2.5%) the hydrate phase equilibrium is estimated at different temperature and pressure. It revealed that the addition of propane reduced the pressure by 66% at 278.4 K, and also there is no well-defined way for the selection of gas composition, pressure, and temperature values. Another researcher²⁶ predicted the phase equilibria and gas solubility in the aqueous phase; simulation studies on the formation of hydrates in pure and saline water (2–8 wt %) for five chosen hydrate forms, CO₂, C₃H₈, C₂H₆, CH₄, and isobutane, were performed to provide an integrated approach to select a suitable hydrate form for hydrate-based desalination. The simulation study favored ethane and propane as suitable hydrate forms for desalination based on enthalpy formation/dissociation and operating conditions of pressure, while methane and carbon dioxide have the potential to form hydrates in saline system but their application is limited because of higher operating pressure at a given temperature.

The gases considered in this study constitute methane, propane, and carbon dioxide. This analysis shows how composition can have a major impact on the hydrate formation process as it affects the water to gas ratio for hydrate formation. Hence, as a result when developing the gas hydrate formation

Table 1. Chronological Order of the Phase Behavior Conditions for Pure and Mixed Hydrocarbons

gas system and reference	temperature/pressure	additives	findings
CH ₄	260–290 K	NaCl	Established a predictive method to predicting hydrate formation conditions in presence of single or mixed electrolytes and also validated with the predicted hydrate forming conditions by calculating water activity by using freezing point depression information.
C ₃ H ₈	2–16 MPa	NaCl	
cyclopropane ¹²	271.15–278 K	CaCl ₂ + KCl	
	0.1–0.6 MPa		
C ₃ H ₈ ²⁷	273.15–277.15 K		
	0.05–0.1 MPa		
	273.10 K		
	172 KPa		
N ₂			
CH ₄			
C ₂ H ₆ ⁹		3 wt % NaCl	The propane–water system's phase behavior was determined from extremely high to very low pressure.
98.9% CH ₄ + 1.1% C ₂ H ₆	275–290 K		Van der Waals and Platteuw's model was used to derive phase diagrams of gas-hydrate mixtures and also studied the effect of lattice cavity size being larger as an uncertainty on the location of the hydrate structures.
97.9% CH ₄ + 2.1% C ₂ H ₆	1.7–11.0 MPa		
95.2 CH ₄ + 4.8 C ₂ H ₆			The addition of ethane stabilized the structure and changed the equilibrium conditions to a higher temperature and lower pressure. A shift in hydrate structure from sI to sII occurred over the methane composition of 99 to 98% based on the pressure versus composition of gas equilibrium curves.
90.2 CH ₄ + 9.8 C ₂ H ₆ ²¹			
C ₃ H ₈ (99.9%) ²⁸	3.6–4.8 bar		Propane hydrate occurs at moderate pressure and temperature conditions. Hydrate formed easily in presence of ice and it took longer duration to form in presence of water.
	2 ± 0.2 °C with water		A thermodynamic model based on the predictive SRK approach is implemented by considering the gas interactions where the fugacity in vapor/liquid and hydrate phase are calculated to determine the mixed gas dissociation behavior. Compared between the modified Huron vidal second order (mHV2) and PSRK for the mixed gas hydrate and found that accuracy is improved for mHV2 for mixed hydrates.
88.65% CH ₄ + 7.17% C ₃ H ₈ + 4.18% H ₂ S	275.15–302 K 0.2–8 MPa		
81.01% CH ₄ + 7.02% C ₃ H ₈ + 11.97% H ₂ S	289–297 K 3–11 MPa		
60.89%CH ₄ + 7.40% C ₃ H ₈ + 31.71% H ₂ S			
82% CH ₄ + 12.6% CO ₂ + 5% H ₂ S			
80% CH ₄ + 12% CO ₂ + 8% H ₂ S			Kinetics was measured using ¹³ CNMR spectroscopy. The hydrate surface reaction growth data revealed that large cages populated by C ₃ H ₈ formed twice as fast as small cages loaded with CH ₄ . A reaction model was developed relating growth rate to particle size and pressure.
72% CH ₄ + 12%CO ₂ + 16%H ₂ S ¹⁰			
CH ₄ + C ₃ H ₈ ²⁹	270 K 0.69 MPa		Developed a model considering the gas and electrolyte interactions and verified the importance of electrolyte in gas hydrate models.
CH ₄	180–298 K	NaCl	A thermodynamic model is proposed using Pitzer model for variation in water activity for predicting methane and carbon dioxide hydrate phase equilibrium in aqueous solutions of high ionic strength and at high pressures.
CO ₂ ¹³	180–283 K	NaCl, KCl, CaCl ₂ , NaCl + KCl, NaCl + CaCl ₂ (0–6 molar strength)	
CH ₄ –H ₂ O	253–311.15 K		Researchers used the temperature pressure analysis based on Clapeyron equation to determine the type of structure formed. The inclusion of CO ₂ lowers the hydrate formation pressure significantly in comparison to pure hydrogen. Addition of propane lowered the pressure even more and hydrogen is found to be in hydrate phase in both situations. CO ₂ +H ₂ formed sI structure CO ₂ +H ₂ +C ₃ H ₈ formed sII structure
CO ₂ –H ₂ O	13.75–2177.95 bar		
CH ₄ /CO ₂ –H ₂ O ¹⁴			The phase equilibrium data for ice + liquid + hydrate + gas rich vapor was analyzed for the systems.
CO ₂ +H ₂ (39.2 mol %/60.8 mol %)	273.9–278.4 K 5.56–10.74 MPa		
(57.9 mol %/42.1 mol %)	274.6–281.4 K 2.77–8.31 MPa		Investigated the dissociation data for each of pure hydrates in the presence of single salts of various concentrations and at various temperatures and suitable agreement was found between the experimental data between the measured and data found in the literature.
(83.3 mol %/16.7 mol %) CO ₂ +H ₂ +C ₃ H ₈	273.9–281.6 K 1.58–5.15 MPa 274–282 K		
(38.3 mol %/58.5 mol %/3.2 mol %) ¹⁰	2.51–9.75 MPa		
CH ₄	0.971 to 2.471 MPa		NaCl (99.5%), KCl (99.5%), and CaCl ₂ (98%)
C ₂ H ₆	0.122 to 0.637 MPa		
C ₃ H ₈	41.0 to 280.0 KPa		CH ₄ , 268–283.6 K for various concentration of salts C ₂ H ₆ , 270–284.7 K for various concentration of salts C ₃ H ₈ , 271.5–276.2 K for various
CO ₂ ¹⁵	0.364 to 0.963 MPa		
methane (99.9%), ethane (99.9%), propane (99.9%), carbon dioxide (99.9%) ²²	CH ₄ , 268–283.6 K for various concentration of salts C ₂ H ₆ , 270–284.7 K for various concentration of salts C ₃ H ₈ , 271.5–276.2 K for various		

Table 1. continued

gas system and reference	temperature/pressure	additives	findings
CO ₂ +H ₂ (40:60) CO ₂ +H ₂ +C ₃ H ₈ (38.2:59.2:2.6)	concentration of salts CO ₂ , 270.2–280.2 K for various concentration of salts 8 MPa and –20 °C 3.8 MPa and –20 °C		CO ₂ +H ₂ formed sI structure. Addition of propane reduced the hydrate formation pressure and formed sII structure at 3.8 MPa.
CH ₄ +CO ₂ ³²	279.1–289.9 K and 2.96–13.06 MPa		At varied CO ₂ concentrations, dissociation conditions for CH ₄ +CO ₂ mixed hydrates were measured and validated with the generated experimental dissociation data with the data available in literature.
CO ₂	276–278 K/1.95–2.96 MPa	NaCl (1 mol %)	The induction times were found to be substantially less for ternary system than binary system. Presence of THF enhanced the hydrate growth and presence of NaCl increased the induction time. The apparent rate constant for these systems was found to be concentration dependent. Furthermore, the mixed hydrate system, showed a greater apparent rate constant.
CO ₂ +(tetrahydrofuran) THF (5 mol %)	284–290 K/1.53–3.76 MPa		Hydrate forming conditions are determined using temperature search method with increasing concentration of CO ₂ . Deviations of van der Waals model increased with increase in CO ₂ concentration whereas deviation by Chen Guo model reduced as found to be superior too and modified using statistical model.
CO ₂ +THF (5 mol %) + NaCl (1 mol %) ³³	284–288 K/1.7–3 MPa –2.6–15 °C 0.5–15 MPa		Thermodynamic modeling is employed to produce phase equilibrium data using CSMGem for single binary and multi component systems and validated with literature experimental data.
natural gas (NG) with high content CO ₂ ¹⁶	273.15–302 K 273.15–283.15 K 273.15–288 K		With increase in CO ₂ concentration from 31.4 to 66.8% it forms sII structure and further increase in CO ₂ concentration from 83.15% formed sI structure as the bigger molecules act as diluents and analyzed using CSMGem.
CH ₄ , CO ₂ CH ₄ –CO ₂ NG with excess CO ₂ (31.40%, 66.85%, 83.15%, 89.62%, 100%) ¹⁷	274–290 K 0.1–8 MPa		Provided the impact of sII and sH forming hydrocarbons on hydrate formation kinetics based on model of hydrate development in terms of their molecular size and shape. Although the size to cavity ratio of n-C ₄ H ₁₀ 98% CH ₄ 2% iso-C ₄ H ₁₀ 98% CH ₄ 2% neo-C ₃ H ₈ 98% CH ₄ 1% iso-C ₃ H ₈ 99% CH ₄ hydrate developed initially and later in coexistence with the CH ₄ hydrate, a 1% iso-C ₃ H ₈ containing structure H hydrates aroused.
natural gas (CH ₄ +C ₂ H ₆ –C ₃ H ₈ +i-C ₄ H ₁₀ +n-C ₄ H ₁₀ +CO ₂) ³⁴	273.15–286 K 0.1–3.8 MPa		The phase equilibrium conditions were determined experimentally and modeled using equation of states and the average deviation is found to be <5%.
2% C ₃ H ₈ 98% CH ₄ 2% iso-C ₄ H ₁₀ 98% CH ₄ 2% n-C ₄ H ₁₀ 98% CH ₄ 2% neo-C ₃ H ₈ 98% CH ₄ 1% iso-C ₃ H ₈ 99% CH ₄ ³⁵	278.6–289.5 K 0.2–0.8 MPa 280.9–285 K 0.2–0.8 MPa 274.15 K <4.5 MPa 274.15 K <3.0 MPa		Addition of propane of 2.5 mol % there was 66% reduction in pressure and based on enthalpy of dissociation it was found to form sII structure.
chlorodifluoromethane 1,1,1,2-tetrafluoroethane ¹¹	40–75 °F 177–4020 psia	H ₂ S(2 and 5 mol %)/ methanol(0.1 and 0.3 mol %)	Presence of high concentration of CO ₂ shift the equilibrium to lower pressure conditions; 1.2 wt % propane acts as a dilutant without any change in the structure.
38.1% CO ₂ + 59.4% H ₂ + 2.5% C ₃ H ₈	41.63–74.93 °F 187.5–2990 psia		Phase behavior is determined by changing the gas compositions using PVTSim. Addition of H ₂ S (5 mol %) to the gas composition expanded the hydrate-forming region, and addition of methanol (0.3 mol %) decreased the hydrate forming region.
80.0% CO ₂ + 18.8% H ₂ + 1.2% C ₃ H ₈ ²⁵	12.87–27.29 °C 43.09–350 bar	methanol (10 wt %)	The threat of hydrate formation decreased as N ₂ composition increased to 10 mol % and increased as H ₂ S composition increased. Methanol showed the highest hydrate inhibition effect using PVTSim.
Case 1: CO ₂ (0.18) C ₁ (87.76), C ₂ (5.49), C ₃ (3.48) nC ₄ (3.09)		ethanol (10 wt %) diethylene glycol (10 wt %) monoethylene glycol (10 wt %)	Case 1: As the concentration of CO ₂ /H ₂ S in the system increases, the hydrate phase equilibrium curves tend to shift toward the hydrate equilibrium curve of pure component.
Case 2: N ₂ (0.652) + C ₁ (86.16)+C ₂ (6.58) +C ₃ (3.63)+C ₄ (1.161) +nC ₄ (1.008), nC ₅ (0.794) ³⁶	2–20 °C 16–200 bar	Case 1: with increasing CO ₂ /H ₂ S concentration synthetic natural gas (SNG) (methanol, ethanol, monoethylene glycol (MEG), triethylene glycol (TEG) and glycerol)	Case 2: TEG is found to be the best inhibitor. The type of gas composition can alter the efficacy of a thermodynamic inhibitor and analyzed using PVTSim.
synthetic natural gas ²⁰			
Malaysia synthetic natural gas (SNG) ²⁴			

Table 1. continued

gas system and reference	temperature/pressure	additives	findings
methane	30.8–55.4 MPa	NaCl (2.8 wt %) + KCl (0.1 wt %) + MgCl ₂ (0.35 wt %) + CaCl ₂ (0.11 wt %) + Na ₂ SO ₄ (0.12 wt %) + NaBr (0.02 wt %)	The hydrate phase equilibria in presence of salt water is predicted using Hydra FLASH and enthalpy is estimated and presence of salt had negligible effect on enthalpy and hydration number.
carbon dioxide	14.6–30.6 MPa		
ethane	5.4–11.4 MPa		
propane	2.3–6.1 MPa		
iso-butane ²⁶	1.5–2 MPa		
CH ₄	258.15 K/4.5 MPa,	30 wt % NaCl	The enthalpies of hydrate dissociation were computed using the Clausius–Clapeyron equation based on phase equilibrium pressure and temperature data. This study shows that the formation energy required using LNG, cold energy and HFC-134a is efficient for desalination but it has a global warming potential of 1410.
SF ₆	0.75 MPa,		
HFC-134a ²³	0.16 MPa		
CH ₄ (93.36) + THF (5.54) + water (1.1.mole%) ³⁷	283.2 K 3.0, 5.0, and 7.2 MPa	3 wt % NaCl (99%) + Amino acid (98% purity) (leucine+arginine)	In the presence of salt, 200 ppm leucine was found to increase the kinetics of mixed hydrate formation. Leucine of 200 ppm exhibited the development of mixed methane/THF hydrates with improved kinetics and significant gas absorption.
C ₂ , C ₃ , n-C ₄	233.15 K/22.81 KPa		In the presence of bigger molecules, it is shown that increasing ethane concentration increases the probability of hydrate formation is lower while making it more stable, whereas decreasing ethane concentration causes unstable hydrates to form and then dissolve. It was determined that raising the concentration of ethane and pentane raises the equilibrium pressure, making hydrate formation difficult and stable and determined the optimum concentration of gas.
i-C ₄	248.15 K/51.90 kPa		
i-C ₅ ³⁸	263.15 K/106.20 kPa.		
CH ₄ , CO ₂ , CH ₄ –CO ₂ ³⁹	261.8–300 K	24.12 wt % NaCl	Database of measured phase behavior of pure and binary mixtures is established. Thermodynamic model to predict phase boundaries is implemented with some reference parameters and impacts of NaCl, temperature, gas composition and phase boundary is considered.

for an upscale process, it is critical to specify the operational conditions, quantities, and design variables. There is no literature available in determining the best natural gas composition using PVTsim based on driving force. So far, there is sufficient literature available for hydrate equilibrium formation conditions of temperature and pressure for natural gas of known compositions/ randomly chosen for pure hydrocarbons or mixed hydrocarbons of as shown in Table 1. But the criteria for selecting the best gas composition of a hydrocarbon that can provide a good driving force is not discussed so far. The present study will help us to utilize CO₂ for capture and utilization and also for the transportation of the natural gas which can be applied for the applications of hydrate-based applications that have a greater ability toward the energy and environmental approach. Though past studies have focused on the practicality of hydrate-based desalination, the criteria for selecting hydrate formers, gas composition, and selecting pressures and temperature conditions for large-scale applications prior to the design stage have not been discussed or examined.

Therefore, in this study the suitable ranges pressure and temperature hydrates driving forces for CO₂, CH₄, and C₃H₈ and their binary and ternary mixtures were evaluated using PVTsim in the presence of 2 wt % salinity (1.6 wt % NaCl, 0.2 wt % CaCl₂, 0.2 wt % KCl). The pressure and temperature driving force were used to study the suitable gas composition that could provide a good driving force to provide high water recovery and metal removal during seawater desalination. The binary mixtures were based on varying concentrations of CO₂-CH₄, CO₂-C₃H₈, and CH₄-C₃H₈, while the ternary system was formulated based on CO₂-CH₄-C₃H₈. The finding in this study would provide the landmarks for selecting the appropriate gas systems for high water production and metals removal from seawater during desalination process.

2. RESULTS AND DISCUSSION

2.1. Validation of Experimental and PVTsim Predicted Data. The accuracy of PVTsim is determined by performing a validation test by predicting the phase behavior of a natural gas from the open literature.^{20,24,36,40} The predicted results were in good agreement with the literature data with a mean absolute percentage error (MAPE) of 4.13% which is less than 5% from the experimental data which confirms PVTsim's accuracy in predicting hydrate phase equilibrium conditions.²⁴ Both the experimental and predicted data results, as seen in Figure 1, overlapped one another in most areas. The mean absolute percentage error of less than 5% is observed between experimental and predicted hydrate formation pressure/temperature values which indicates the uncertainty of the simulation. This clearly proves PVTsim's accuracy in predicting hydrate phase equilibrium conditions. Similarly, Sule and Rahman³⁶ and Broni et al.²⁰ used PVTsim to forecast the hydrate equilibrium phase of synthetic natural gas in the presence of H₂S and inhibitor (methanol) in Canada and Ghana, respectively. This proves that the predicted hydrate equilibrium conditions of temperature and pressures using PVTsim simulation is accurate.

2.2. Hydrate Based-Desalination Feasibility Zone in Binary Gas Systems. The feasibility zone for using binary gas systems for hydrate-based desalination were first evaluated and presented in this section. A decade of research in gas hydrate has profoundly focused at the molecular level using solid state analytical instruments like X-ray diffraction and NMR

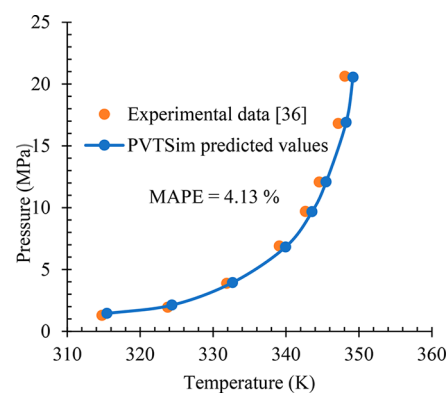


Figure 1. Comparing hydrate equilibrium curves with PVTsim and experimental data.

spectroscopy and Raman spectroscopy to characterize the composition and structure of hydrates formed. Studies based on mixed hydrates using Raman spectroscopy and X-ray diffraction suggest that the reaction kinetics of each hydrate system is different and relies on the type of guest molecule and external pressure-temperature conditions.^{35,41,29} ¹³C NMR studies performed for CH₄ + C₃H₈ during sII hydrate formation was presented by Kini et al.²⁹ They observed that the large cages (5¹²6⁴) were occupied with C₃H₈, and they form twice as fast as small cages (5¹²) with CH₄. Generally small molecules like CH₄ and CO₂ tend to form sI hydrates⁴² where the small cages are filled by CH₄ and larger cages are filled by CO₂ or C₂H₆, while larger molecules like C₃H₈ and C₄H₁₀ form sII hydrates.^{40,29} In the interim, the gas molecules occupying different cavities of gas hydrates would also affect the stability of structure. Some of the properties of the various gas hydrate structures are listed below in Table 2.

Zheng et al.³⁹ presented a thermodynamic model to enhance the accuracy in the prediction of phase boundary of hydrates of pure components, CH₄ and CO₂, and binary mixture, CH₄ + CO₂, in the presence of pure and saline water. They observed that the CH₄ + CO₂ binary hydrates pressure phase boundaries decreased with an increase in CO₂ concentration. In another communication, the clathrate hydrate phase equilibria of CH₄ + CO₂ suggested the stable structure for the binary system to be sI structure.³² Identical perceptions have been addressed.^{44,45} The propane molecule diameter is too large as listed in Table 2 to occupy the small 5¹² cages, therefore it occupies the larger cages of 5¹²6⁴ leaving the smaller 5¹² cages empty.^{29,46,27,28} The small 5¹² cages of sII hydrate can possibly be occupied by the molecules having smaller diameter size like CO₂ and CH₄ at suitable pressure and temperature conditions. Essentially, these smaller guest molecules often stabilize the sII hydrates more than just the C₃H₈ molecule. Because there are usually no additional forces available between the host and the guest molecule, van der Waal forces are thought to be responsible for this stability.²⁹ On the basis of the dissociation enthalpy values from literature it confirms that addition of propane reduces the driving force of the mixed gas system and confirmed the formation of an sII hydrate.³⁰ A study by Kumar et al.³¹ confirms with the help XRD and NMR spectroscopy that the addition of propane reduces the driving force of a mixed gas system and it contributes to the sII structure.

The three binary systems studied were CO₂ + CH₄, CO₂ + C₃H₈, and C₃H₈ + CH₄. To evaluate the feasibility of forming suitable hydrates in the binary systems the driving force and

Table 2. Structural and Cage Occupancy Characteristics of Gas Hydrates^{40,29,42,43a}

properties of cage	sI		sII		sH		
	small	large	small	large	small	medium	large
cavity description	5 ¹²	5 ¹² 6 ²	5 ¹²	5 ¹² 6 ⁴	5 ¹²	4 ³ 5 ⁶ 6 ³	5 ¹² 6 ⁸
number per unit cell	2	6	16	8	3	2	1
average cavity radius (Å)	3.95	4.33	3.91	4.73	3.91	4.06	5.71
coordination number ^b	20	24	20	28	20	20	36
lattice type	cubic		face-centered cubic		hexagonal		
water molecules per unit cell	46		136		34		
ratio of diameter of guest molecule to diameter of cage for hydrate former							
guest	diameter (Å)	diameter (Å)	diameter (Å)	diameter (Å)	diameter (Å)	diameter (Å)	diameter (Å)
CH ₄	4.36	0.886 ^c	0.757 ^c	0.889	0.889	0.675	0.675
CO ₂	5.12	1.041	0.889 ^c	1.044	1.044	0.792	0.792
C ₃ H ₈	6.28	1.276	1.090	1.280	1.280	0.971 ^c	0.971 ^c

^aData was adapted from Sloan, 2007, Kini et al., 2004, Avaldsnes, 2014 and Lal, B. et al., 2019. ^bNumber of oxygen atoms at the end of each cavity. ^cIndicates cage occupied by guest species.

subcooling temperatures were estimated. The average driving force at 2.0 MPa for 1–4 °C was reported, while the average subcooling temperatures for pressure ranging from 2.0–4.0 MPa at 4 °C were reported. The selection of 2.0 MPa and 4 °C was to ensure the evaluation of the minimum conditions suitable to form more hydrates with less energy and pressure required.

Figure 2 shows the average driving force subcooling temperature for CH₄ + C₃H₈ system at 2 wt % concentration

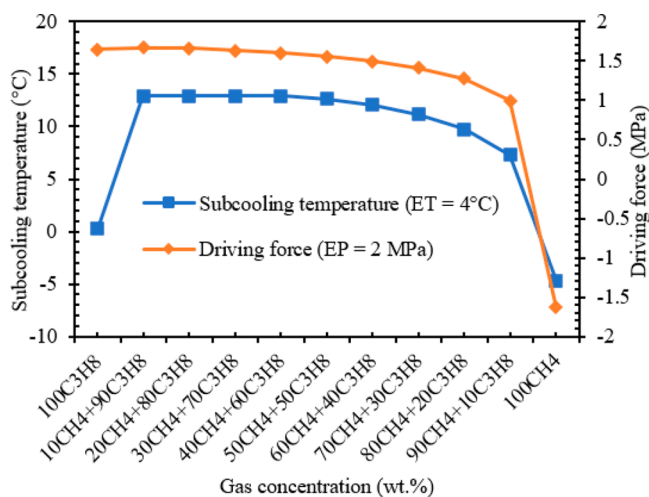


Figure 2. Driving forces versus various CH₄–C₃H₈ gas concentrations.

of aqueous synthetic solution (1.6 wt % NaCl, 0.2 wt % KCl, 0.2 wt % CaCl₂) used for this study. This system is suitable for the utilization of natural gas constituents for desalination. In Figure 2, the subcooling temperatures for pure CH₄ and C₃H₈ at experimental temperature (ET) of 4 °C are –4.7 and 0.28 °C, respectively. The system with 90CH₄ + 10C₃H₈ raises the pure CH₄ systems subcooling temperature by 12 °C. Increasing the propane concentration up to 30 wt % increases the subcooling temperature of pure CH₄. Propane concentrations above 30 wt % show a slight negligible impact on the subcooling temperature for CH₄ + C₃H₈ systems. The driving force for CH₄ + C₃H₈ mixtures behavior is similar as their subcooling temperatures, however pure C₃H₈ exhibits a higher driving force than its mixture with CH₄ at all concentrations

(Figure 2). The pure C₃H₈ systems have a less subcooling temperature which is a limitation for its application.^{47–49,28} Propane forms a hydrate at milder conditions of temperature and pressure; hence when these hydrate equilibrium values are deducted from experimental temperatures (1–4 °C) and experimental pressures (2.0, 2.5, 3.0, 3.5, 4.0 MPa), the driving force available is less which means not enough driving force is available for hydrate formation. From Figure 2, it is clear that the binary system 10CH₄ + 90C₃H₈ exhibits the highest subcooling temperature of 12.932 °C and driving force of 1.668 MPa. Therefore, 10CH₄ + 90C₃H₈ binary system is a suitable system that could provide a significant driving force and subcooling temperature for hydrate-based desalination/water treatment at minimal/average energy intensity conditions of 4 °C and experimental pressure (EP) of 2.0 MPa. The binary gas system 10CH₄ + 90C₃H₈ is about 68% and 77.5% higher than the driving force and subcooling temperature of 90CH₄ + 10C₃H₈ system as shown in Figure 2. This process shows that by the small addition of propane there is a pressure increase which is caused by the hydrate crystal change from sI to sII as propane can only fit into a larger 5¹²6⁴ cavity of sII; therefore, more pressure is required to fit into the cage as C₃H₈ is too large to occupy any other cavity, as listed in Table 2. However, increasing the C₃H₈ composition in the C₃H₈ + CH₄ system increases the subcooling temperature and driving force as shown in Figure 2.

On the other hand, CO₂ and C₃H₈ mixtures also behave similarly to CH₄ + C₃H₈ (Figures 2 and 3). The subcooling temperature for CO₂ + C₃H₈ is averaging about 0.39 °C lower than CH₄ + C₃H₈ but about 0.05 MPa higher than the CH₄ + C₃H₈ systems. This suggests that the hydrate formation behavior and the water recovery/metals removal in mixing C₃H₈ with CO₂ is highly influenced by the pressure differential driving force. The subcooling temperature highly controls the hydrate formation behavior and the water recovery/metals removal efficiency in C₃H₈ + CH₄ systems. The binary mixtures of C₃H₈, CH₄, and C₃H₈, CO₂ at 70–80%/20–30% would averagely provide a suitable subcooling temperature and driving force for metals removal via hydrate-based desalination or water treatment methods at relatively moderate temperature and pressure conditions. Hence, the process could occur and run efficiently with low energy intensity. Because CO₂ and C₃H₈ can form hydrates at significantly lower pressures than methane, they have a wide range of potential applications.^{50–52} However, increasing the C₃H₈ composition in the CO₂ + C₃H₈

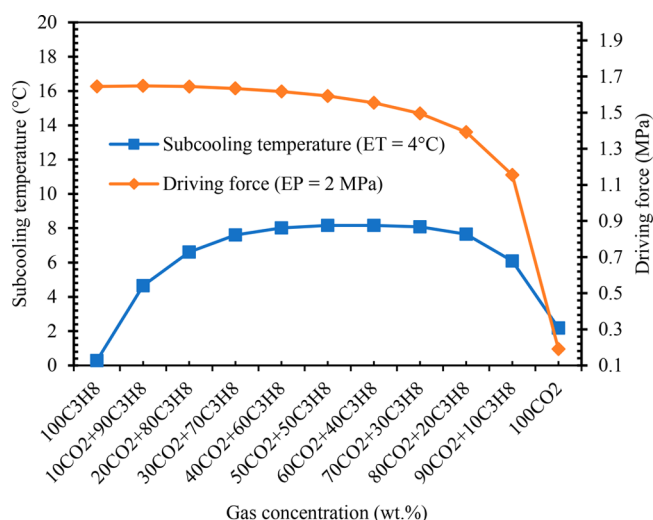


Figure 3. Driving force versus various $\text{CO}_2\text{-C}_3\text{H}_8$ gas concentrations.

system increases the subcooling temperature and driving force. As the concentration of propane addition to CO_2 is increased for the binary system from $90\text{CO}_2 + 10\text{C}_3\text{H}_8$ to $50\text{CO}_2 + 50\text{C}_3\text{H}_8$, there has been 34.18% increase in subcooling temperature which signifies that these binary system combinations are suitable systems that could provide a significant driving force and subcooling temperature for hydrate-based desalination/water treatment at minimal/average energy intensity conditions of 4°C and 2.0 MPa. For the binary system $90\text{CO}_2 + 10\text{C}_3\text{H}_8$ the subcooling temperature and driving force are 6.08°C and 1.155 MPa. The subcooling temperature and driving force at $50\text{CO}_2 + 50\text{C}_3\text{H}_8$ are 8.16°C and 1.592 MPa. Beyond this further addition of propane to carbon dioxide resulted in decrease in the subcooling temperature by 42%. On the other hand, the driving force increased by 42.6% with increase in concentration of propane to CO_2 . The system with 70–80% $\text{CO}_2 + 30\text{--}20\%$ C_3H_8 exhibits the highest driving force of 1.495 MPa and subcooling temperature of 8.07°C , respectively. This is about 29.45% and 32.73% higher than the driving force and subcooling temperature for $90\text{CO}_2 + 10\text{C}_3\text{H}_8$ system as shown in Figure 3.

Figure 4 the $\text{CO}_2 + \text{CH}_4$ gas composition exhibits a poor hydrate formation subcooling and driving force at low pressure and temperature conditions. Thus, using $\text{CO}_2 + \text{CH}_4$ mixed gas systems for desalination or metal removal would require very high pressure and lower temperature conditions. These conditions would increase the energy demand for the process to occur. Increasing the concentration of CH_4 in $\text{CO}_2 + \text{CH}_4$ systems linearly reduces the subcooling and driving force of pure CO_2 by 3 and 8 times, respectively (Figure 4). Generally, in the presence of electrolytes, the hydrate formation is delayed.³³ There is extensive literature^{53–59,37} available with experimental data, models, and simulations of hydrate formation and dissociation in the presence of electrolytes. All of these studies show that the presence of salt in water produces an increase in hydrate equilibrium pressure and/or a drop in the hydrate equilibrium temperature. As a result, the formation of water cages is impeded, and the stability of the hydrate structure is decreased.^{58,59} In essence, using pure CO_2 would yield suitable conditions to form hydrate than with mixed $\text{CO}_2 + \text{CH}_4$ systems, however, the driving force and subcooling for pure CO_2 must be at lower temperature condition ($<4^\circ\text{C}$) and higher pressures (>2.0 MPa). This

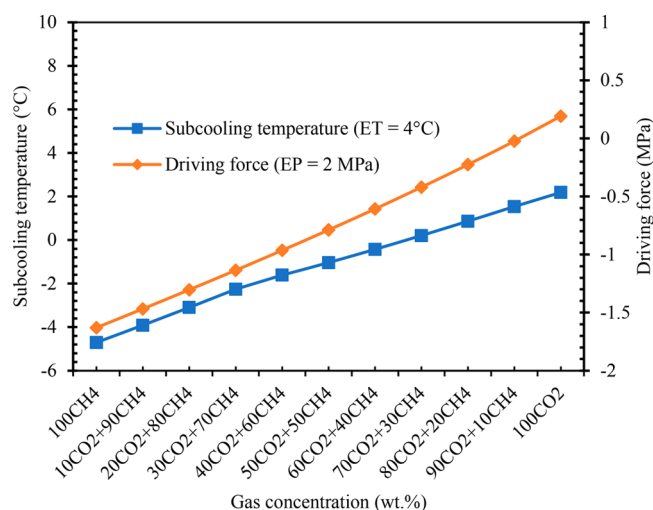


Figure 4. Driving force versus various concentrations of $\text{CO}_2\text{-CH}_4$.

would be due to the double hydrate formation of $\text{CH}_4 + \text{CO}_2$, where majority of the large cages might be accommodated by both guest species, though there is less occupancy of CH_4 in the large cages because CO_2 can only occupy the large cage, whereas CH_4 can occupy both the large and small cages. This holds in good agreement with the study performed by few researchers^{60,61} using NMR spectroscopy. In this case $\text{CH}_4 + \text{CO}_2$ binary system with significantly high-pressure driving force is required which might not be economical for hydrate-based desalination.

2.3. Hydrate Based-Desalination Feasibility Zone in Ternary Gas Systems. The hydrate formation driving force and subcooling behavior of the ternary system for $\text{CH}_4 + \text{C}_3\text{H}_8 + \text{CO}_2$ was further investigated in this work. Figures 5–7

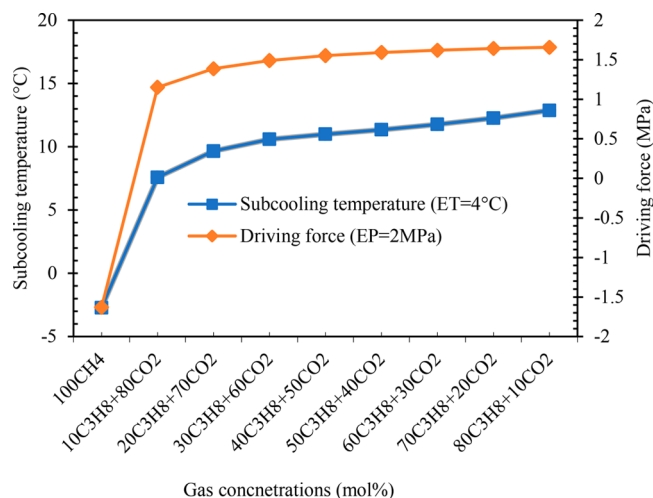


Figure 5. Driving force versus concentrations of $\text{C}_3\text{H}_8 + \text{CO}_2$ at 10 wt % CH_4 concentration.

shows the results for the ternary systems. Generally, all the ternary systems exhibited higher subcooling temperatures and driving forces that are suitable for high hydrate formation kinetics at low-pressure and high-temperature conditions (Figures 5–7).

The driving force of the ternary systems in Figures 5 and 6 are similar to the binary systems in Figures 2 and 3 except for $\text{CH}_4\text{-CO}_2$ systems (Figure 4). This implies that using binary

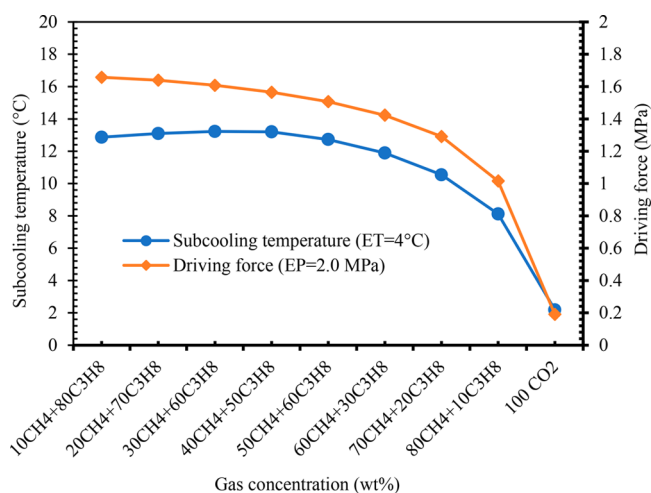


Figure 6. Driving force versus concentrations of CH_4 – C_3H_8 at 10 wt % CO_2 concentration.

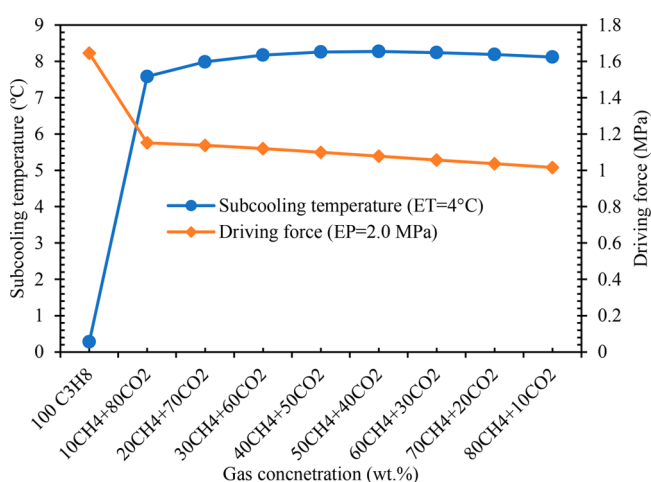


Figure 7. Driving force versus concentrations of CH_4 – CO_2 at fixed 10 wt % C_3H_8 concentration.

systems for desalination or metals removal purpose is preferable in terms of driving forces. The subcooling temperature for the ternary systems varied significantly. This provides an added advantage to easily form hydrate when using ternary systems compared to the binary systems. However, the ternary system with constant C_3H_8 (10 wt %) and varying CO_2 and CH_4 exhibited subcooling temperature conditions similar to the binary systems of $\text{CO}_2 + \text{C}_3\text{H}_8$ and $\text{CH}_4 + \text{C}_3\text{H}_8$. This might be because a small addition of C_3H_8 causes an increase in the subcooling temperature and a decrease in the driving force due to structural change from sI to sII and also follows literature.^{40,43} Propane can only occupy larger cages of sII due to its large size as listed in Table 2 and $\text{CH}_4 + \text{CO}_2$ forms a sI structure. A few researchers^{44,45} have made similar observations. For constant 10 wt % CH_4 and varying $\text{C}_3\text{H}_8 + \text{CO}_2$, the ratio of (10:80:10) exhibits highest subcooling temperature and driving force of 12.86 °C and 1.657 MPa at 4 °C and 2.0 MPa as shown in Figure 5. From Figure 6 with constant 10 wt % CO_2 and varying concentrations of $\text{CH}_4 + \text{C}_3\text{H}_8$, the ratio of (10:30:60) exhibits the highest subcooling temperature of 13.22 °C and at (10:10:80) provides a high driving force of 1.6575 MPa at 4 °C and 2.0 MPa as shown in Figure 6. However, the ternary systems with either constant CO_2 or CH_4

and varying C_3H_8 composition exhibited higher subcooling temperatures up to 4 °C higher than the binary systems. Instead of using binary system $\text{CH}_4 + \text{CO}_2$ it is better to use a ternary system with a small addition of propane as 10 wt % C_3H_8 addition to this system provides good driving force for hydrate-based desalination system as shown in Figure 6. The ternary system $\text{C}_3\text{H}_8 + \text{CH}_4 + \text{CO}_2$, having compositions of (10:40:50) or (10:50:40), provides a high subcooling temperature of 8.25 °C which is about 96.5% increase from pure C_3H_8

3. CONCLUSION

The hydrate equilibrium pressures and temperatures for binary and ternary gas system are predicted for the given temperatures (1–4 °C) and pressures (2.0–4.0 MPa) using PVTsim. From this study the suitable gas composition of mixtures which can provide good driving force in terms of subcooling temperature and pressure are evaluated. From this study the findings are

- $\text{CH}_4 + \text{C}_3\text{H}_8$ gas combination gave higher subcooling temperature of 12.93 °C for gas composition (10:90) and also provided significant average driving force of 1.668 MPa.
- $\text{CO}_2 + \text{C}_3\text{H}_8$ binary gas mixture gave higher subcooling temperature of 8.07 °C and driving force average of 1.495 MPa at the gas composition (70:30). This gas system is appropriate for high water production and metals removal from seawater during desalination process as it forms an sII structure with 136 water molecules at milder conditions of temperature and pressure which signifies the potential to produce more treated water.
- $\text{CO}_2 + \text{CH}_4$ gas combination gave higher subcooling temperature of 2.18 °C with gas composition (100:0) and driving force of 0.19 MPa for gas composition CO_2 – CH_4 (0:100). As a result, using $\text{CO}_2 + \text{CH}_4$ mixed gas systems for desalination or metal removal would demand extremely high pressures and temperatures. These conditions would raise the energy requirement for the process to take place.
- $\text{CH}_4 + \text{C}_3\text{H}_8 + \text{CO}_2$ gas combination having gas composition of (10:30:60/10:80:10) by varying C_3H_8 concentration and keeping CH_4/CO_2 concentration constant at 10 wt % gave a higher subcooling temperature that averaged at 12.86 °C and a higher driving force of 1.657 MPa

On the basis of the findings from this work, the suitable gas combination in the case of binary system is determined to be $\text{CO}_2 + \text{C}_3\text{H}_8$ (70:30) having a subcooling temperature, driving force of 8.07 °C and 1.495 MPa at 4 °C and 2.0 MPa. For a ternary system, the gas combination that provides good driving force is $\text{CH}_4 + \text{C}_3\text{H}_8 + \text{CO}_2$ (10:80:10) having a subcooling temperature, and a driving force of 12.86 °C and 1.657 MPa can be selected in the presence of salt solution for hydrate-based desalination application.

4. METHODOLOGY

4.1. Gas and Brine Systems. The gas system used in this work are CO_2 , CH_4 , and C_3H_8 . The simulated systems were made from binary and ternary mixtures of these gases. They were selected to represent CO_2 utilization applications produced from high CO_2 content natural gas systems as Malaysian oil reserves contain more than 70% carbon dioxide in the natural gas. On the other hand, C_3H_8 was selected for its

ability to form sII hydrates, which consist of 136 water molecules, and thus could lead to higher water recovery. CH₄ is the dominant gas in natural gas, hence as such its usage in desalination was tested for binary and ternary combination with CO₂ and C₃H₈ to determine the best gas combination that could provide suitable driving force to achieve higher water recovery and metals removal efficiency. Details on the various gas combination compositions used in this work are presented in Table 3. There are so many optimizations that can be performed, but for simplicity we considered 36 gas combination mixtures as shown in Table 3.

Table 3. Studied Gas Systems in This Study

Composition (wt %)					
binary			ternary		
CH ₄	CO ₂	C ₃ H ₈	CH ₄	CO ₂	C ₃ H ₈
100			10	80	10
90	10		10	70	20
80	20		10	60	30
70	30		10	50	40
60	40		10	40	50
50	50		10	30	60
40	60		10	20	70
30	70		10	10	80
20	80		20	70	10
10	90		20	60	20
	100		20	50	30
	90	10	20	40	40
	80	20	20	30	50
	70	30	20	20	60
	60	40	20	10	70
	50	50	30	60	10
	40	60	30	50	20
	30	70	30	40	30
	20	80	30	30	40
	10	90	30	20	50
		100	40	50	10
10		90	40	40	20
20		80	40	30	30
30		70	40	20	40
40		60	40	10	50
50		50	50	40	10
60		40	50	30	20
70		30	50	20	30
80		20	50	10	40
90		10	60	30	10
			60	20	20
			60	10	30
			70	20	10
			70	10	20
			80	10	10

The hydrate formation driving force for the gas systems were predicted in a synthetic brine system. This is to mimic the influence of the salts on the hydrate formation conditions as used in typical desalination process and as seawater has higher concentration of sodium chloride 2 wt % aqueous salt solution is considered in this study. The synthetic brine systems used in this work consist of the composition having 1.6 wt % NaCl + 0.2 wt % KCl + 0.2 wt % CaCl₂ aqueous solution.

4.2. Hydrate Equilibrium Phase Predictions using PVTsim. In this study, PVTsim was initially used to determine the phase behavior conditions of the gas systems (Table 3). The obtained phase behavior data for the PVTsim simulations was used to estimate the driving force and subcooling for all the gas systems. PVTsim is used to simulate hydrate formation conditions for gases and oil mixtures and can be dealt with the most used thermodynamic hydrate inhibitors like methanol, ethanol, glycols, and salts. To predict the hydrate phase behavior in PVTsim, the desired fluid (gas systems in Table 3) is entered and selected from the PVTsim with their composition and fluid characterization based on the plus fraction. The plus fraction option is used because the molecular weight of the chosen alkanes is always higher due to the presence of other compounds. Peng–Robinson Penenloux equation of state was used for all of the predictions with the desired brine systems as stated earlier. The hydrate equilibrium data for the gas were then predicted by following two stages. The first was determining the hydrate equilibrium temperatures at constant pressures of 2.0, 2.5, 3.0, 3.5, and 4.0 MPa. This allowed the estimation of the subcooling temperatures at the experimental pressure conditions. Also, these pressures were selected for select a system that can form hydrates at low pressure conditions for practical applicability with less energy consumptions. Second, the pressure driving force was determined by predicting the hydrate equilibrium pressures of the gas systems at 1, 2, 3, and 4 °C. PVTsim enables one to predict the hydrate equilibrium formation temperature values at desired pressures and hydrate equilibrium pressure values at the desired temperatures. The subcooling temperature is the difference between the hydrate equilibrium formation temperature values and the experimental temperature (1, 2, 3, and 4 °C) and the driving force is determined as the difference between the hydrate equilibrium formation pressures and the experimental pressures (2.0, 2.5, 3.0, 3.5, and 4.0 MPa) using excel. These temperatures represents suitable conditions to form hydrates for desalination purposes with relatively less energy.

4.3. Estimation of Driving Force Parameters. The driving force measurement in this work was based on pressure and subcooling temperature. These parameters were used since they are critical fundamental parameters for hydrate formation kinetics and ensure the possibility of forming a substantial amount of hydrate with less metastability in the system. Generally, the driving force for the formation of hydrate is a function of pressure, temperature, and gas composition. The driving force is calculated as the difference between the equilibrium pressure and temperature values and their respective experimental pressure and temperature conditions. The use of this property to describe the driving force for hydrate formation is well established and acceptable in literature. The subcooling temperatures and driving force in this study were estimated using eqs 1 and 2. For each system, the average values were reported.

$$\Delta T_{\text{avg},i,j,k} = \frac{\sum_{i,j,k}^P (T_{\text{eq}} - T_{\text{expt}})_{i,j,k}}{n_{i,j,k}} \quad (1)$$

$$\Delta P_{\text{avg},i,j,k} = \frac{\sum_{i,j,k}^T (P_{\text{eq}} - P_{\text{expt}})_{i,j,k}}{n_{i,j,k}} \quad (2)$$

where $\Delta T_{\text{avg},ijk}$ corresponds to the average driving force/subcooling temperature at the respective gas compositions of i, j, k for $\text{CH}_4, \text{CO}_2, \text{C}_3\text{H}_8$ as listed in Table 3 and refers to the difference between the hydrate equilibrium temperature values determined at 2.0, 2.5, 3.0, 3.5, and 4.0 MPa and experimental temperature values at (1, 2, 3, 4 °C). Taking their average value provides the average subcooling temperature (driving force), $n_{i,j,k}$ represents the number of data points, that is, five in this case at compositions of i, j, k for $\text{CH}_4, \text{CO}_2, \text{C}_3\text{H}_8$ as shown in Table 3. Similarly, $\Delta P_{\text{avg},ijk}$ corresponds to the average pressure driving force at the respective compositions of i, j, k of $\text{CH}_4, \text{CO}_2, \text{C}_3\text{H}_8$ as listed in Table 3. The driving force is the difference between the hydrate equilibrium pressure values determined at (1, 2, 3, 4 °C) and the experimental pressure values (2.0, 2.5, 3.0, 3.5, and 4.0 MPa) and $n_{i,j,k}$ corresponds to number of data points, that is, four in this case at compositions i, j, k for $\text{CH}_4, \text{CO}_2, \text{C}_3\text{H}_8$.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.1c06186>.

(Table S1) contains binary system data for methane + propane equilibrium hydrate formation temperatures at experimental pressures and their hydrate formation pressures at experimental temperatures; (Table S2) contains binary system data for Carbon dioxide + propane equilibrium hydrate formation temperatures at experimental pressures and their hydrate formation pressures at experimental temperatures; (Table S3) contains binary system data for Carbon dioxide + Methane Equilibrium hydrate formation temperatures at experimental pressures and their hydrate formation pressures at experimental temperatures; (Table S4) contains ternary gas system data for $\text{CH}_4 + \text{C}_3\text{H}_8 + \text{CO}_2$ the equilibrium hydrate formation temperatures at 25, 30, 35, and 40 bar and equilibrium hydrate formation pressures at 1,2,3,4 °C; (Table S5) consolidated average driving force data for $\text{CH}_4 + \text{C}_3\text{H}_8 + \text{CO}_2$ at experimental temperatures and pressures; (Table S6) consolidated average driving force data for $\text{CO}_2 + \text{C}_3\text{H}_8 + \text{CH}_4$ at experimental temperatures and pressures; (Table S7) consolidated average driving force data for $\text{C}_3\text{H}_8 + \text{CH}_4 + \text{CO}_2$ at experimental temperatures and pressures (PDF)

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Notes

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■ REFERENCES

- (1) Ranjan, S. P.; Kazama, S.; Sawamoto, M. Effects of climate and land use changes on groundwater resources in coastal aquifers. *J. Environ. Manage.* **2006**, *80* (1), 25–35.
- (2) Glueckauf, E. Sea Water Desalination—in Perspective. *Nature* **1966**, *211* (5055), 1227–1230.
- (3) Thu, K.; Chakraborty, A.; Saha, B. B.; Ng, K. C. Thermophysical properties of silica gel for adsorption desalination cycle. *Appl. Therm. Eng.* **2013**, *50* (2), 1596–1602.
- (4) Vysniauskas, A.; Bishnoi, P. R. A kinetic study of methane hydrate formation. *Chem. Eng. Sci.* **1983**, *38* (7), 1061–1072.
- (5) Englezos, P.; Kalogerakis, N.; Dholabhai, P. D.; Bishnoi, P. R. Kinetics of formation of methane and ethane gas hydrates. *Chem. Eng. Sci.* **1987**, *42* (11), 2647–2658.
- (6) Natarajan, V.; Bishnoi, P. R.; Kalogerakis, N. Induction phenomena in gas hydrate nucleation. *Chem. Eng. Sci.* **1994**, *49* (13), 2075–2087.
- (7) Skovborg, P.; Rasmussen, P. A mass transport limited model for the growth of methane and ethane gas hydrates. *Chem. Eng. Sci.* **1994**, *49* (8), 1131–1143.

- (8) Fakharian, H.; Ganji, H.; Naderifar, A. Desalination of high salinity produced water using natural gas hydrate. *J. Taiwan Inst. Chem. Eng.* **2017**, *72*, 157–162.
- (9) Lundgaard, L.; Mollerup, J. Calculation of phase diagrams of gas hydrates. *Fluid Phase Equilib.* **1992**, *76*, 141–149.
- (10) Yoon, J. H.; Yamamoto, Y.; Komai, T.; Kawamura, T. PSRK method for gas hydrate equilibria: I. Simple and mixed hydrates. *AIChE J.* **2004**, *50* (1), 203–214.
- (11) Karamoddin, M.; Varaminian, F. Experimental measurement of phase equilibrium for gas hydrates of refrigerants, and thermodynamic modeling by SRK, VPT and CPA EOSs. *J. Chem. Thermodyn.* **2013**, *65*, 213–219.
- (12) Englezos, P.; Bishnoi, P. R. Prediction of gas hydrate formation conditions in aqueous electrolyte solutions. *AIChE J.* **1988**, *34* (10), 1718–1721.
- (13) Marion, G. M.; Catling, D. C.; Kargel, J. S. Modelling gas hydrate equilibria in electrolyte solutions. *Calphad: Comput. Coupling Phase Diagrams Thermochem.* **2006**, *30* (3), 248–259.
- (14) Duan, Z.; Sun, R. A model to predict phase equilibrium of CH₄ and CO₂ clathrate hydrate in aqueous electrolyte solutions. *Am. Mineral.* **2006**, *91* (8–9), 1346–1354.
- (15) Yasuda, K.; Ohmura, R. Phase equilibrium for clathrate hydrates formed with methane, ethane, propane, or carbon dioxide at temperatures below the freezing point of water. *J. Chem. Eng. Data* **2008**, *53* (9), 2182–2188.
- (16) Sun, R.; Li, C.; Yu, S.; Wang, Sun, O.; Liu, E. Hydrate formation conditions of natural gas with high content of carbon dioxide and the calculation model. *Soc. Pet. Eng.* **2010**, *3*, 2407–2414.
- (17) Huang, M. Simulation of hydrate formation and inhibition in submarine wet-gas pipeline. *Proc. Twent. Int. Offshore Polar Eng. Conf.* **2010**, *7*, 20–25.
- (18) Gupta, G.; Singh, S. K. Hydrate inhibition - Optimization in deep water field. *Soc. Pet. Eng. J.* **2012**, 311–317.
- (19) Gudmundsson, J.; Andersson, V.; Levik, O.; Parlaktuna, M. H. Hydrate concept for Capturing Associated Gas. *Proc. Soc. Pet. Conf.* **1998**, DOI: 10.2118/50598-MS.
- (20) Broni-Bediako, E.; Amorin, R.; Bavoh, C. B. Gas hydrate formation phase boundary behaviour of synthetic natural gas system of the keta basin of Ghana. *Open Pet. Eng. J.* **2017**, *10* (1), 64.
- (21) Maekawa, T. Equilibrium conditions for gas hydrates of methane and ethane mixtures in pure water and sodium chloride solution. *Geochem. J.* **2001**, *35* (1), 59–66.
- (22) Mohammadi, A. H.; Afzal, W.; Richon, D. Gas hydrates of methane, ethane, propane, and carbon dioxide in the presence of single NaCl, KCl, and CaCl₂ aqueous solutions: Experimental measurements and predictions of dissociation conditions. *J. Chem. Thermodyn.* **2008**, *40* (12), 1693–1697.
- (23) Seo, S. D.; Hong, S. Y.; Sum, A. K.; Lee, K. H.; Lee, J. D.; Lee, B. R. Thermodynamic and kinetic analysis of gas hydrates for desalination of saturated salinity water. *Chem. Eng. J.* **2019**, *370*, 980–987.
- (24) Bavoh, C. B.; Khan, M. S.; Ting, V. J.; Lal, B.; Ofei, T. N.; Ben-Awuah, J.; Ayoub, M.; Shariff, A. B. M. The effect of acidic gases and thermodynamic inhibitors on the hydrates phase boundary of synthetic Malaysia natural gas. *IOP Conf. Ser.: Mater. Sci. Eng.* **2018**, *458* (1), 012016.
- (25) Babu, P.; Yang, T.; Veluswamy, H. P.; Kumar, R.; Linga, P. Hydrate phase equilibrium of ternary gas mixtures containing carbon dioxide, hydrogen and propane. *J. Chem. Thermodyn.* **2013**, *61*, 58–63.
- (26) Sahu, P.; Krishnaswamy, S.; Ponnani, K.; Pande, N. K. A thermodynamic approach to selection of suitable hydrate formers for seawater desalination. *Desalination* **2018**, *436*, 144–151.
- (27) Harmens, A.; Sloan, E. D. The phase behaviour of the propane-water system: A review. *Can. J. Chem. Eng.* **1990**, *68* (1), 151–158.
- (28) Giavarini, C.; Maccioni, F.; Santarelli, M. L. Formation kinetics of propane hydrates. *Ind. Eng. Chem. Res.* **2003**, *42* (7), 1517–1521.
- (29) Kini, R. A.; Dec, S. F.; Sloan, E. D. Methane+ propane structure II hydrate formation kinetics. *J. Phys. Chem. A* **2004**, *108* (44), 9550–9556.
- (30) Kumar, R.; Wu, H. J.; Englezos, P. Incipient hydrate phase equilibrium for gas mixtures containing hydrogen, carbon dioxide and propane. *Fluid Phase Equilib.* **2006**, *244* (2), 167–171.
- (31) Kumar, R.; Englezos, P.; Moudrakovski, I.; Ripmeester, J. A. Structure and composition of CO₂/H₂ and CO₂/H₂/C₃H₈ hydrate in relation to simultaneous CO₂ capture and H₂ production. *AIChE J.* **2009**, *55* (6), 1584–1594.
- (32) Belandria, V.; Mohammadi, A. H.; Richon, D. Phase equilibria of clathrate hydrates of methane+ carbon dioxide: New experimental data and predictions. *Fluid Phase Equilib.* **2010**, *296* (1), 60–65.
- (33) Sabil, K. M.; Duarte, A. R. C.; Zevenbergen, J.; Ahmad, M. M.; Yusup, S.; Omar, A. A.; Peters, C. J. Kinetic of formation for single carbon dioxide and mixed carbon dioxide and tetrahydrofuran hydrates in water and sodium chloride aqueous solution. *Int. J. Greenhouse Gas Control* **2010**, *4* (5), 798–805.
- (34) Azmi, N.; Mukhtar, H.; Sabil, K. M. Purification of natural gas with high CO₂ content by formation of gas hydrates: Thermodynamic verification. *J. Appl. Sci.* **2011**, *11* (21), 3547–3554.
- (35) Luzi, M.; Schicks, J. M.; Naumann, R.; Erzinger, J. Systematic kinetic studies on mixed gas hydrates by Raman spectroscopy and powder X-ray diffraction. *J. Chem. Thermodyn.* **2012**, *48*, 28–35.
- (36) Sule, I.; Rahman, A. Phase behaviour of hydrate formations in oil and gas production in subsea conditions. *Proc. IEEE* **2014**, 1–6.
- (37) Veluswamy, H. P.; Kumar, A.; Kumar, R.; Linga, P. Investigation of the kinetics of mixed methane hydrate formation kinetics in saline and seawater. *Appl. Energy* **2019**, *253*, 113515.
- (38) Fazlali, A.; Ghalekhondabi, V.; Ranjbaran, T. Prediction of liquid propane hydrate formation conditions in the presence of light hydrocarbons (C₂-C₅): Experimental investigation and thermodynamic modeling. *Fluid Phase Equilib.* **2021**, *529*, 112756.
- (39) Zheng, R.; Fan, Z.; Li, X.; Negahban, S. Phase boundary of CH₄, CO₂, and binary CH₄-CO₂ hydrates formed in NaCl solutions. *J. Chem. Thermodyn.* **2021**, *154*, 106333.
- (40) Sloan, E. D., Jr; Koh, C. A. *Clathrate hydrates of natural gases*; CRC Press, 2007.
- (41) Uchida, T.; Takeya, S.; Kamata, Y.; Ikeda, I. Y.; Nagao, J.; Ebinuma, T.; Narita, H.; Zatsepina, O.; Buffett, B. A. Spectroscopic observations and thermodynamic calculations on clathrate hydrates of mixed gas containing methane and ethane: Determination of structure, composition and cage occupancy. *J. Phys. Chem. B* **2002**, *106* (48), 12426–12431.
- (42) Avaldsnes, O. G. An Analysis of CO₂, CH₄ and Mixed CO₂-CH₄ Gas Hydrates: Experimental Phase Equilibria Measurements and Simulations with State-of-the-Art Software. Master's Thesis, The University of Bergen, 2014.
- (43) Lal, B.; Nashed, O. *Chemical additives for gas hydrates*; Springer Nature, 2019.
- (44) Takeya, S.; Uchida, T.; Kamata, Y.; Nagao, J.; Kida, M.; Minami, H.; Sakagami, H.; Hachikubo, A.; Takahashi, N.; Shoji, H.; Khlystov, O.; Grachev, M.; Soloviev, V. Lattice expansion of clathrate hydrates of methane mixtures and natural gas. *Angew. Chem., Int. Ed.* **2005**, *117* (42), 7088–7091.
- (45) Sloan, E. D. Fundamental principles and applications of natural gas hydrates. *Nature* **2003**, *426* (6964), 353–359.
- (46) Gaudette, J.; Servio, P. Measurement of dissolved propane in water in the presence of gas hydrate. *J. Chem. E/10.1002/anie.200501845ng. Data.* **2007**, *52* (4), 1449–1451.
- (47) Abbondondola, J. A.; Fleischer, E. B.; Janda, K. C. Propane clathrate hydrate formation accelerated by xenon. *J. Phys. Chem. C* **2009**, *113* (11), 4717–4720.
- (48) Klauda, J. B.; Sandler, S. I. Phase behavior of clathrate hydrates: a model for single and multiple gas component hydrates. *Chem. Eng. Sci.* **2003**, *58* (1), 27–41.
- (49) Adeniyi, K. I. Thermodynamic formation conditions for propane hydrates in equilibrium with liquid water. Masters Thesis, University of Calgary, Alberta, Canada, 2016.

- (50) Eslamimanesh, A.; Mohammadi, A. H.; Richon, D.; Naidoo, P.; Ramjugernath, D. Application of gas hydrate formation in separation processes: A review of experimental studies. *J. Chem. Thermodyn.* **2012**, *46*, 62–71.
- (51) Nambiar, A.; Babu, P.; Linga, P. CO₂ capture using the clathrate hydrate process employing cellulose foam as a porous media. *Can. J. Chem.* **2015**, *93* (8), 808–814.
- (52) Fan, S.; Li, S.; Wang, J.; Lang, X.; Wang, Y. Efficient capture of CO₂ from simulated flue gas by formation of TBAB or TBAF semiclathrate hydrates. *Energy Fuels* **2009**, *23* (8), 4202–4208.
- (53) Gambelli, A. M.; Castellani, B.; Filippini, M.; Nicolini, A.; Rossi, F. Chemical inhibitors as potential allied for CO₂ replacement in gas hydrates reservoirs: Sodium chloride case study. 6th World Congress on Mechanical, Chemical, and Material Engineering, Aug. 16–18, 2020; Avestia Publishing, **2020**.
- (54) Cha, M.; Hu, Y.; Sum, A. K. Methane hydrate phase equilibria for systems containing NaCl, KCl, and NH₄Cl. *Fluid Phase Equilib.* **2016**, *413*, 2–9.
- (55) Hu, Y.; Makogon, T. Y.; Karanjkar, P.; Lee, K. H.; Lee, B. R.; Sum, A. K. Gas hydrates phase equilibria and formation from high concentration NaCl brines up to 200 MPa. *J. Chem. Eng. Data* **2017**, *62* (6), 1910–1918.
- (56) Nallakukkala, S.; Lal, B. Seawater and Produced water treatment via gas hydrate. *J. Environ. Chem. Eng.* **2021**, *9*, 105053.
- (57) Nallakukkala, S.; Kassim, Z.; Othman, N. A.; Lal, B. Advancement in Gas Hydrate Water Based Produced Water Desalination: An Overview. *Adv. Eng. Res.* **2020**, *200*, 190–197.
- (58) Nallakukkala, S.; Lal, B.; Shariff, M. A. Influence of water volume on CO₂ hydrate-based desalination of brine solution. *Mater. Today: Proc.* **2021**, DOI: 10.1016/j.matpr.2021.11.495.
- (59) Lu, H.; Matsumoto, R.; Tsuji, Y.; Oda, H. Anion plays a more important role than cation in affecting gas hydrate stability in electrolyte solution? —a recognition from experimental results. *Fluid Phase Equilib.* **2001**, *178* (1–2), 225–232.
- (60) Ripmeester, J. A.; Ratcliffe, C. I.; Klug, D. D.; Tse, J. S. Molecular perspectives on structure and dynamics in clathrate hydrates. *Ann. N.Y. Acad. Sci.* **1994**, *715* (1), 161–176.
- (61) Koh, C. A. Towards a fundamental understanding of natural gas hydrates. *Chem. Soc. Rev.* **2002**, *31* (3), 157–167.