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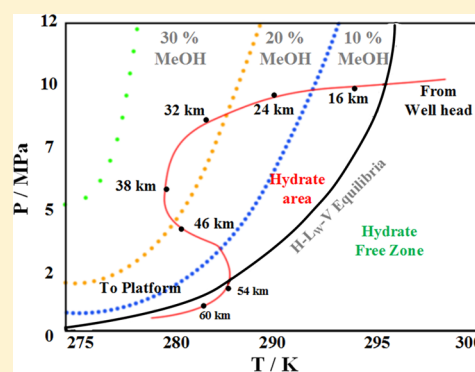
Hydrate Dissociation Condition Measurement of CO₂-Rich Mixed Gas in the Presence of Methanol/Ethylene Glycol and Mixed Methanol/Ethylene Glycol + Electrolyte Aqueous Solution

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ABSTRACT: In this work, the hydrate dissociation condition for carbon dioxide rich gas mixture in the presence of methanol, methanol + sodium chloride or calcium chloride, and ethylene glycol, ethylene glycol + sodium chloride or calcium chloride aqueous solution, were measured and reported. The measurements are carried out at temperature and pressure range of (263.85 to 284.75) K and (2.76 to 12.08) MPa. All data were measured using the isochoric pressure search method. In order to exhibit the inhibition effect of above-mentioned aqueous solution, a comparison was made between experimental data of carbon dioxide rich gas mixture in the presence of pure water and aqueous solutions consist of inhibitor and electrolytes. Furthermore, a thermodynamic model was used to correlate the experimental values.



1. INTRODUCTION

Natural gas serves as an important and growing part of global energy stream. However, for the past half of century, the growth in global demand of natural gas along with its limited resource has gained market share. The rapid build-up in natural gas prices and perception of long-term shortage creates incentives for the development of infrastructure to produce natural gas from carbon dioxide (CO₂) rich gas reservoir. These types of reservoirs are located across the globe.^{1–6} The gas produced from such reservoir are economically unviable and not suitable to use as a feedstock for LNG plant and hence need to be treated in inside multistage separation processes which runs at low temperature and high pressure.

One of the main concerns for the natural gas production from CO₂-rich gas is its increasing susceptibility to form gas hydrate. Gas hydrate is a major flow assurance problem in gas production, especially for deep water gas reservoirs where hydrate formation cause pipe blockage and rise safety concerns.^{1–3} Since CO₂ is more favorable to form gas hydrate as compared to methane, so it is quite imperative that gas mixture with rich CO₂ contents are more prone to form gas hydrate. One of the common preventive measures to avoid gas hydrate formation is to ensure the working condition either in the pipeline or top facility is set above the hydrate formation condition. This is usually done by insulating the pipeline or active heating. Other methods include the dehydration of the natural gas and more commonly used option is the injection of thermodynamic inhibitors. The water-soluble solvents reduce the activity of water effectively shifts the hydrate equilibrium condition to high pressure and low temperature.

Produce gas contains a significant amount of formation water mixed with various type of salt of different quantities, which reduces the ability of gas hydrate formation. Cases where saline water inhibition is insufficient, aqueous solution consists of methanol, and ethylene glycol are injected into the pipeline create a system contains both inhibitors and salts.⁷ In this regard, accurate knowledge for gas hydrate dissociation condition in the presence of salt and methanol/ethylene glycol is vital to avoid formation of gas hydrate. This could benefit safe and economical plant design, production, processing facilities, and pipeline operations.

The study is the extension of our previous work⁸ and is carried out further to consider the potential importance and limited availability of experimental data for carbon dioxide (CO₂) rich gas system in the presence of aqueous solution of methanol/ethylene glycol and salt. Numerous experimental data of hydrate dissociation condition are reported,^{7,9–17} previously for single methane (CH₄) and carbon dioxide (CO₂) in the presence of alcohol or salt aqueous solution; however, experimental data for the mixed system containing both alcohol and electrolyte in aqueous solution are limited.^{12–15,18–21} Also limited reported data of hydrate dissociation condition are available for binary (CH₄–CO₂) and natural gas system in the presence of aqueous solution of alcohol and electrolyte.²² To the best of our knowledge, no such work has been reported for CO₂-rich gas mixture in the presence of aqueous solution salt and organic inhibitors.

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In this work, three-phase, hydrate–liquid water–vapor ($H-L_W-V$) hydrate dissociation condition of CO_2 -rich mixed gas hydrates were carried out in absence⁸ and in the presence of aqueous solution of (methanol, ethylene glycol) and combination of (methanol/ethylene glycol + sodium chloride/calcium chloride). Aqueous solution was prepared at various concentration (mass fraction) of inhibitors and salt. The measurements were carried out at temperature and pressure ranges from (263.85 to 284.75) K and (2.76 to 12.08) MPa, respectively. All experimental data obtained in this work were reported using a pressure-search method.^{23–25} To exhibit the inhibition effect of the studied solution, hydrate dissociation data of CO_2 rich gas mixture in pure water⁸ are compared with CO_2 rich gas mixture in the presence of aqueous solution containing of single methanol or ethylene glycol and mixed (methanol, ethylene glycol + electrolyte). Finally the experimental data were compared with the correlated result generated by a thermodynamic model.²⁶

2. EXPERIMENTAL SECTION

2.1. Materials. The chemicals used in this work were purchased from Merck Company. The purity grades (expressed in mass fraction) of chemical reagents (confirmed with gas chromatography) are shown in Table 1. The CO_2 -rich mixed gas were purchased from Gas Walkers SDN BHD. All chemicals and gases were used without any further purification. The aqueous solution was prepared by following the gravimetric method, using a digital analytical balance calibrated with uncertainty of ± 0.0001 g (in term of mole fraction < 0.001).

Table 1. Composition of Gas Mixture Used in This Work

component	mole fraction		chemicals	mass fraction purity
	Mix A	Mix B		
carbon dioxide	0.70353	0.69103	sodium chloride	0.995
nitrogen	0.03096	0.03100	calcium chloride	0.995
methane	0.26551	0.26197	methanol	0.995
ethane		0.00900	ethylene glycol	0.995
propane		0.00300		
iso-butane		0.00200		
<i>n</i> -butane		0.00200		

2.2. Apparatus. A mercury-free PVT-equilibrium cell, specifically designed to study the hydrate dissociation condition, was used in this work.⁸ The schematic diagram of the apparatus is shown in Figure 1.

MA major part of the equipment includes the high pressure equilibrium sapphire cell with inner volume of 60 cm^3 and a maximum operating pressure of 20 MPa in a temperature range of (253.15 to 338.15) K. Pressure, temperature, and volume are measured and recorded uninterruptedly in 2 s intervals with an accuracy of ± 0.1 K, ± 0.01 MPa, and $\pm 0.001\text{ cm}^3$, respectively. The temperature of the cell was cooled by circulating ethanol by means of Lauda + DLK45 thermostats. To achieve proper mixing of sample inside the equilibrium cell, a magnetic torque stirrer was placed inside the equilibrium cell, which can be operated up to 2000 rpm. The gas sample in the mixed tank was transferred to the equilibrium cell using Haskel AG-303 air driven booster compressor runs with maximum outlet pressure of 31 MPa. Deionized water was injected into the equilibrium cell using a variable volume displacement manual pump. Moreover, a video recorder with image enlargement options was available and used to visually monitor any changes to the sample placed in the equilibrium cell.

2.3. Experimental Method. Hydrate dissociation condition in this work was measured using an isochoric pressure search method.²³ To ensure the system is free from air and any other gases, the sapphire cell and all external pipings were vacuumed using a vacuum pump. The cell was charged first with 25 cm^3 of aqueous solution prepared earlier, followed by gas sample. The conditions of temperature and pressure were first set outside the hydrate stability boundary zone. Then the system temperature was decreased until the hydrate is formed which could be observed as a rapid drop in pressure at nearly constant temperature. Hydrate formation is supposed to be completed when there is no change in pressure and temperature versus time. The cell was heated up by increasing the temperature of system with a stepwise interval method of 0.2 K/step.

The length of each step varies between (2 to 4) hours maximum in order to ensure equilibrium is archived at every condition imposed on the system.²³ The temperature ramp was continued until the final set point was reached. A pressure

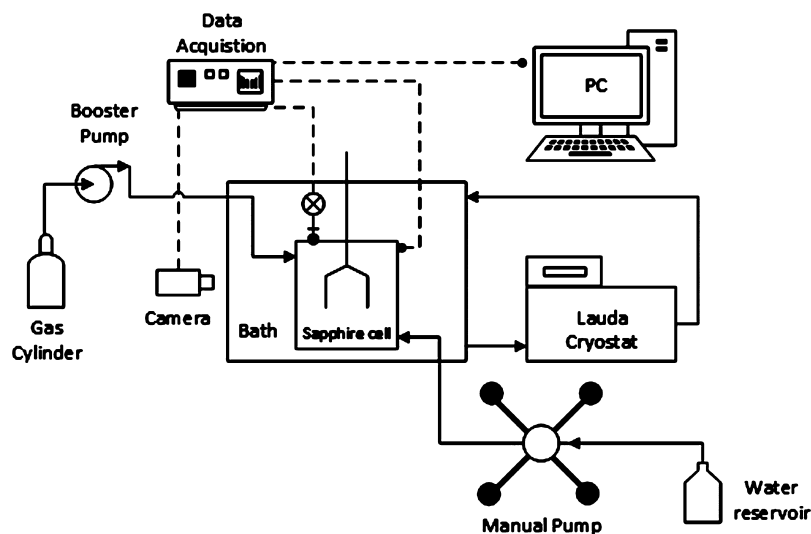


Figure 1. Schematic diagram of the experimental apparatus.

versus temperature plot were constructed, and the point where pressure–temperature curve changes or in other words a point of intersection between cooling and heating curves was known as the hydrate dissociation point.²⁷

3. THERMODYNAMIC MODEL

The detailed description of thermodynamic model used in this study was provided elsewhere.²⁶ From the thermodynamic point of view, the model is mainly based on the equality of chemical potential of various component in the existing phases, which can also be stated as the equality of fugacity of various components in different phases. For the hydrate phase, the van der Waals–Platteeuw²⁸ approach was used, whereby the gas phase was modeled using the Peng–Robinson equation of state.²⁹ The activity of water in the aqueous phase was calculated as the sum of the activity contributions from both alcohol and electrolyte, along with it was assumed that they have no

effect on each other.³⁰ The combined activity is written as follows:

$$\ln a_{w,\text{mix}} = \ln a_{w,\text{el}} + \ln a_{w,\text{al}} \quad (1)$$

where $a_{w,\text{mix}}$ is the activity of water in the mixture and $a_{w,\text{el}}$ and $a_{w,\text{al}}$ are the activities of electrolyte and alcohol which are calculated separately.

4. RESULTS AND DISCUSSION

4.1. Simple CO₂ Hydrates. To verify the reliability of the apparatus used and experimental procedure, hydrate dissociation points for single carbon dioxide hydrate in the presence of pure water were measured and compared with literature data.^{31–34} The hydrate–liquid water–vapor (H–L_w–V) equilibrium conditions were measured with temperature and pressure ranges from (274.35 to 281.55) K and (1.38 to 3.29) MPa. The results are presented in Figure 2. As shown in Figure 2, the results obtained in this work are in good agreement with experimental values reported earlier in literature data.

4.2. Mixed Hydrates. Similarly, hydrate dissociation conditions were measured for the carbon dioxide rich gas mixture in the presence of aqueous solution of methanol (MeOH), methanol (MeOH) + sodium chloride (NaCl)/calcium chloride (CaCl₂), and ethylene glycol (MEG), ethylene glycol (MEG) + sodium chloride (NaCl)/calcium chloride (CaCl₂). For Mix A + MeOH/MEG, the equilibrium data were collected with temperature and pressure ranges from (272.55 to 284.15) K and (2.97 to 7.30) MPa, whereas for Mix B + MeOH/MEG, the equilibrium data are collected with temperature and pressure ranges from (268.85 to 284.75) K and (2.76 to 12.08) MPa, respectively. Similarly, for a mixed system such as Mix A + (MeOH/MEG + NaCl/CaCl₂), the equilibrium data were collected with temperature and pressure ranges from (264.95 to 280.95) K and (2.84 to 7.44) MPa, whereas for Mix B + (MeOH/MEG + NaCl/CaCl₂), the equilibrium data were collected with temperature and pressure ranges from (263.85 to 277.85) K and (2.90 to 8.30) MPa, respectively. The measured data points are tabulated in Tables 2 to 3 and Tables 5 to 7,

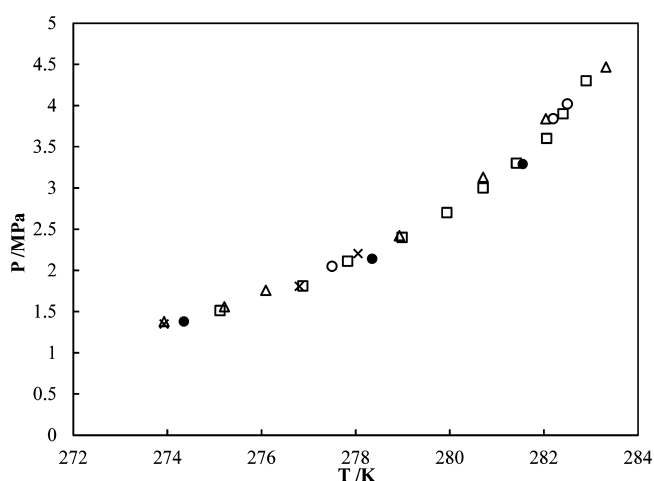


Figure 2. Hydrate dissociation condition of carbon dioxide hydrate in the presence of pure water: Δ , ref 31; \circ , ref 32; \times , ref 33; \square , ref 34; \bullet , this work.

Table 2. Mix A, Hydrate Dissociation Condition in the Presence of Aqueous Solution (Mass Fraction) of Methanol (MeOH) and Ethylene Glycol (MEG) at Temperature T and Pressure P

0.10 MeOH		0.20 MeOH		0.10 MEG		0.20 MEG	
T^a/K	P^b/MPa	T^a/K	P^b/MPa	T^a/K	P^b/MPa	T^a/K	P^b/MPa
279.35	3.35	272.55	2.97	279.45	3.21	276.85	3.12
281.35	4.84	275.45	4.22	282.35	4.87	279.45	4.62
282.75	6.19	277.45	5.89	283.85	6.1	281.35	5.86
283.25	7.30	278.15	6.94	284.15	7.18	281.85	6.92

^aStandard uncertainty $u_i(T) = \pm 0.05$ K. ^bStandard uncertainty $u_i(P) = \pm 0.002$ MPa.

Table 3. Mix B, Hydrate Dissociation Condition in the Presence of Aqueous Solution (Mass Fraction) of Methanol (MeOH) and Ethylene Glycol (MEG) at Temperature T and Pressure P

0.10 MeOH		0.20 MeOH		0.10 MEG		0.20 MEG	
T^a/K	P^b/MPa	T^a/K	P^b/MPa	T^a/K	P^b/MPa	T^a/K	P^b/MPa
274.55	2.76	268.85	2.77	278.15	3.21	276.15	3.58
277.25	3.84	270.45	3.70	280.55	4.45	278.25	4.96
280.15	6.06	275.25	5.98	282.85	6.48	280.15	7.12
281.95	8.85	277.05	8.50	284.05	8.35	281.15	9.64
283.45	12.08	277.95	10.82	284.75	10.06	282.05	10.82

^aStandard uncertainty $u_i(T) = \pm 0.05$ K. ^bStandard uncertainty $u_i(P) = \pm 0.002$ MPa.

Table 4. Average Absolute Error (AAE) between Measured and Predicted Hydrate–Liquid Water–Vapor (H–L_w–V) Line in the Presence of Methanol (MeOH) and Ethylene Glycol (MEG)

system	concentration mole fraction	no. data point	temperature range	AAE/K
Mix A				
MeOH	0.10	4	279.35 to 283.25	0.29
	0.20	4	272.55 to 278.15	0.49
MEG	0.10	4	279.45 to 284.15	0.35
	0.20	4	276.85 to 281.85	0.25
Mix B				
MeOH	0.10	5	274.55 to 283.45	0.27
	0.20	5	268.85 to 277.95	0.41
MEG	0.10	5	278.15 to 284.75	0.20
	0.20	5	276.15 to 282.05	0.15

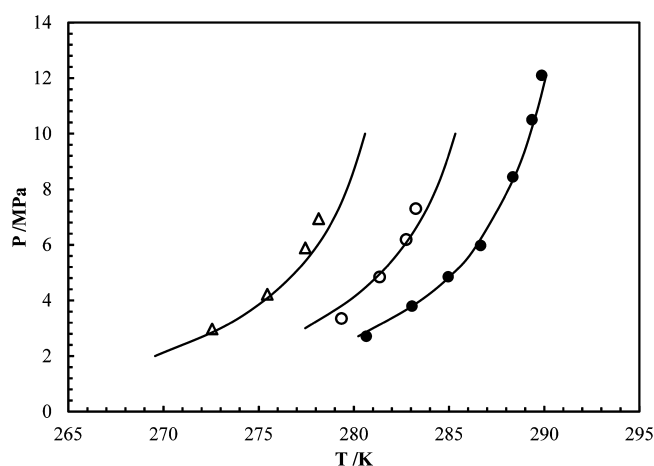


Figure 3. Mix A, hydrate dissociation condition in the presence of aqueous solution containing methanol. Symbols represent experimental dissociation conditions: ●, Mix A + pure water;⁸ ○, Mix A + 0.10 mass fraction methanol (MeOH); △, Mix A + 0.20 mass fraction methanol (MeOH) and lines (—) represent the model prediction.

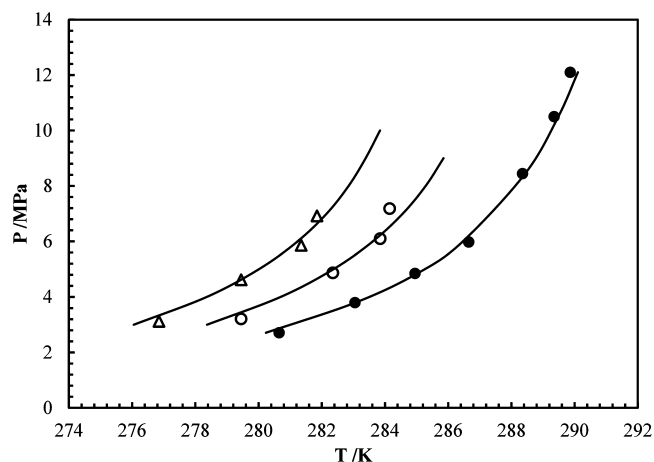


Figure 4. Mix A, hydrate dissociation condition in the presence of ethylene glycol aqueous solution. Symbols represent experimental dissociation conditions: ●, Mix A + pure water;⁸ ○, Mix A + 0.10 mass fraction ethylene glycol (MEG); △, Mix A + 0.20 mass fraction ethylene glycol (MEG) and lines (—) represent the model prediction.

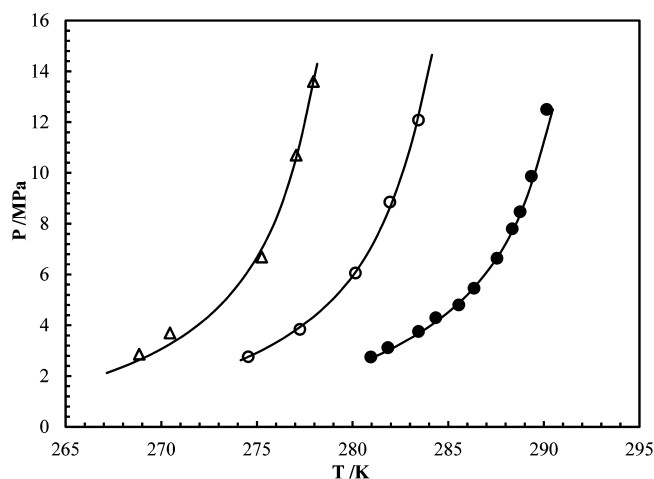


Figure 5. Mix B, hydrate dissociation condition in the presence of aqueous solution containing methanol. Symbols represent experimental dissociation conditions: ●, Mix B + pure water;⁸ ○, Mix B + 0.10 mass fraction methanol (MeOH); △, Mix B + 0.20 mass fraction methanol (MeOH) and lines (—) represent the model prediction.

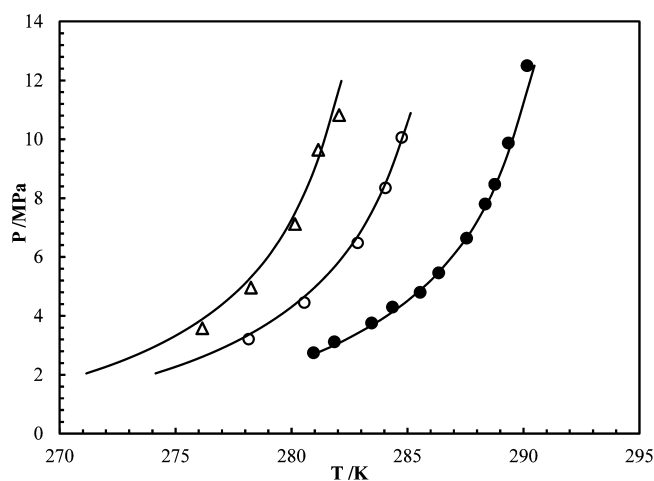


Figure 6. Mix B, hydrate dissociation condition in the presence of aqueous solution containing ethylene glycol. Symbols represent experimental dissociation conditions: ●, Mix B + pure water;⁸ ○, Mix B + 0.10 mass fraction ethylene glycol (MEG); △, Mix B + 0.20 mass fraction ethylene glycol (MEG) and lines (—) represent the model prediction.

respectively. The average absolute deviation between measured and predicted results are tabulated in Table 4. Furthermore, as shown in Figures 3 to 6, the measured data points were compared with the predicted data points of the thermodynamic model. To get an insight into inhibition effect of the latter aqueous solution, previously reported data points for CO₂ rich gas mixture hydrate (Mix A and Mix B) in the presence of pure water⁸ are also presented in Figures 3 to 6 for comparison purposes.

Based on these figures, the presence of aqueous solutions studied in this work has a considerable inhibition effect on the hydrate dissociation condition of CO₂ rich mixed gas system. As shown in Figures 3 and 4, for aqueous solution of methanol/ethylene glycol, the results obtained are in good agreement with thermodynamic model prediction. Moreover, for aqueous solution of methanol/ethylene glycol + sodium chloride/calcium chloride, the results are tabulated in Tables 5 to 7 and illustrated together with the prediction of thermodynamic model in Figures 7 to 10, respectively. As shown in these

Table 5. Mix A, Hydrate Dissociation Condition in the Presence of Aqueous Solution (Mass Fraction) of Methanol (MeOH) + Sodium (NaCl)/Calcium Chloride (CaCl₂) and Ethylene Glycol (MEG) + Sodium Chloride (NaCl)/Calcium Chloride (CaCl₂) at Temperature *T* and Pressure *P*

0.20 MeOH + 0.10 NaCl		0.20 MeOH + 0.10 CaCl ₂		0.20 MEG + 0.10 NaCl		0.20 MEG + 0.10 CaCl ₂	
<i>T</i> ^a /K	<i>P</i> ^b /MPa	<i>T</i> ^a /K	<i>P</i> ^b /MPa	<i>T</i> ^a /K	<i>P</i> ^b /MPa	<i>T</i> ^a /K	<i>P</i> ^b /MPa
264.95	2.84	272.65	3.67	268.35	3.01	276.45	3.84
266.75	3.94	274.15	5.33	270.75	4.32	278.45	5.30
268.55	5.32	274.95	6.45	272.35	5.58	279.05	6.43
269.65	6.12	275.75	7.10	273.95	6.45	280.95	7.44

^aStandard uncertainty $u_r(T) = \pm 0.05$ K. ^bStandard uncertainty $u_r(P) = \pm 0.002$ MPa.

Table 6. Mix B, Hydrate Dissociation Condition in the Presence of Aqueous Solution (Mass Fraction) of Methanol (MeOH) + Sodium Chloride (NaCl)/Calcium Chloride (CaCl₂) and Ethylene Glycol (MEG) + Sodium Chloride (NaCl)/Calcium Chloride (CaCl₂) at Temperature *T* and Pressure *P*

0.20 MeOH + 0.10 NaCl		0.20 MeOH + 0.10 CaCl ₂		0.20 MEG + 0.10 NaCl		0.20 MEG + 0.10 CaCl ₂	
<i>T</i> ^a /K	<i>P</i> ^b /MPa	<i>T</i> ^a /K	<i>P</i> ^b /MPa	<i>T</i> ^a /K	<i>P</i> ^b /MPa	<i>T</i> ^a /K	<i>P</i> ^b /MPa
266.95	4.30	263.85	2.90	271.95	5.38	273.75	3.06
268.75	5.94	267.05	4.00	272.15	6.06	275.05	3.79
270.25	7.92	267.95	5.20	273.35	7.01	276.55	4.80
270.25	8.30	268.65	6.18	273.15	7.87	277.15	5.66
		269.55	6.96	274.55	7.72	277.85	6.76

^aStandard uncertainty $u_r(T) = \pm 0.05$ K. ^bStandard uncertainty $u_r(P) = \pm 0.002$ MPa.

Table 7. Average Absolute Error (AAE) Obtained between Measured and Predicted Hydrate–Liquid Water–Vapor (H–L_W–V) Line in the Presence of Methanol (MeOH)/Ethylene Glycol (MEG) + Sodium Chloride (NaCl)/Calcium Chloride (CaCl₂)

system	concentration (weight fraction)	no. data point	temperature range	AAE/K
Mix A	0.20 MeOH + 0.10 NaCl	4	264.95 to 269.65	0.27
	0.20 MEG + 0.10 NaCl	4	268.35 to 273.95	0.41
	0.20 MeOH + 0.10 CaCl ₂	4	272.65 to 275.75	0.54
	0.20 MEG + 0.10 CaCl ₂	4	276.45 to 279.95	0.47
Mix B	0.20 MeOH + 0.10 NaCl	4	266.95 to 270.25	0.20
	0.20 MEG + 0.10 NaCl	5	270.35 to 274.65	0.45
	0.20 MeOH + 0.10 CaCl ₂	5	263.85 to 269.55	0.81
	0.20 MEG + 0.10 CaCl ₂	5	273.75 to 277.85	0.53

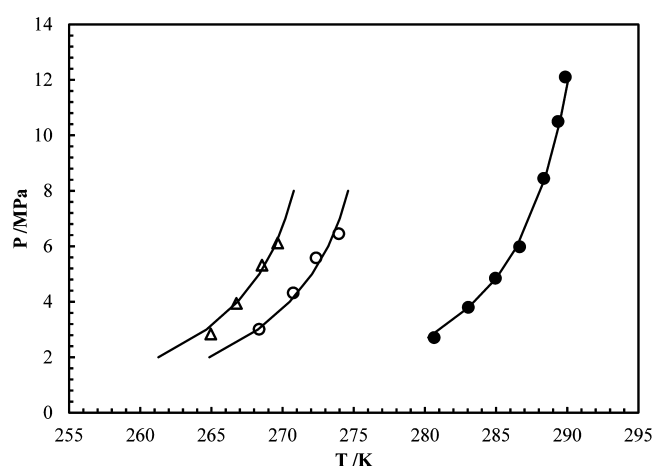


Figure 7. Mix A, hydrate dissociation condition in the presence of methanol/ethylene glycol + sodium chloride aqueous solution. Symbols represent experimental dissociation conditions: ●, mixed gas + pure water;⁸ △, mixed gas + 0.20 mass fraction methanol (MeOH) + 0.10 mass fraction sodium chloride (NaCl); ○, mixed gas + 0.20 mass fraction ethylene glycol (MEG) + 0.10 mass fraction sodium chloride (NaCl), lines (—) represent the model prediction.

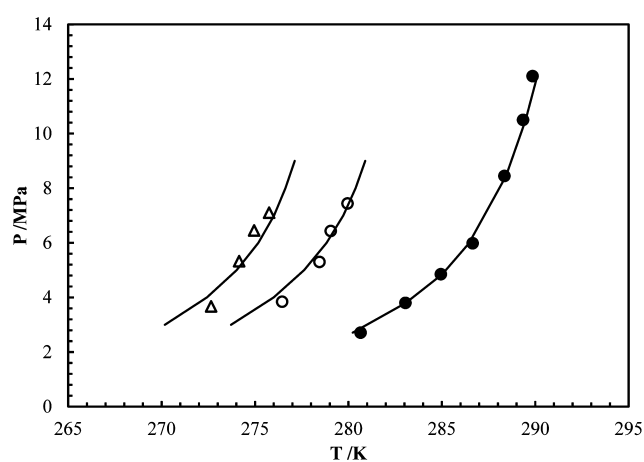


Figure 8. Mix A, hydrate dissociation condition in the presence of methanol (MeOH)/ (MEG) ethylene glycol + calcium chloride (CaCl₂) aqueous solution. Symbols represent experimental dissociation conditions: ●, mixed gas + pure water;⁸ △, mixed gas + 0.20 mass fraction methanol (MeOH) + 0.10 mass fraction calcium chloride (CaCl₂); ○, mixed gas + 0.20 mass fraction ethylene glycol (MEG) + 0.10 mass fraction calcium chloride (CaCl₂), lines (—) the model prediction.

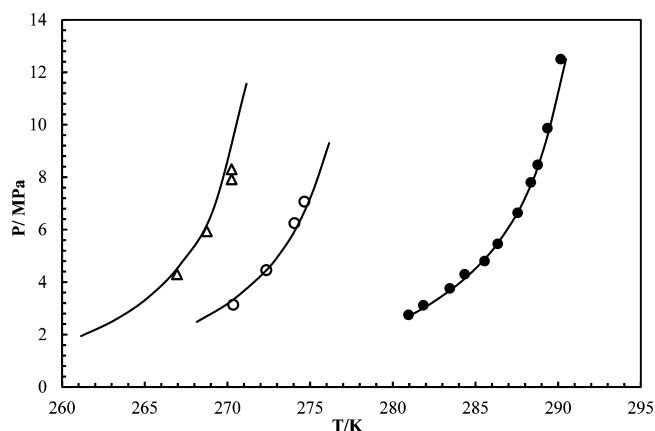


Figure 9. Mix B, hydrate dissociation condition in the presence of methanol (MeOH)/ethylene glycol (MEG) + sodium chloride (NaCl) aqueous solution. Symbols represent experimental dissociation conditions: ●, mixed gas + pure water;⁸ △, mixed gas + 0.20 mass fraction methanol (MeOH) + 0.10 mass fraction sodium chloride (NaCl); ○, mixed gas + 0.20 mass fraction ethylene glycol (MEG) + 0.10 mass fraction sodium chloride (NaCl), lines (—) represent the model prediction.

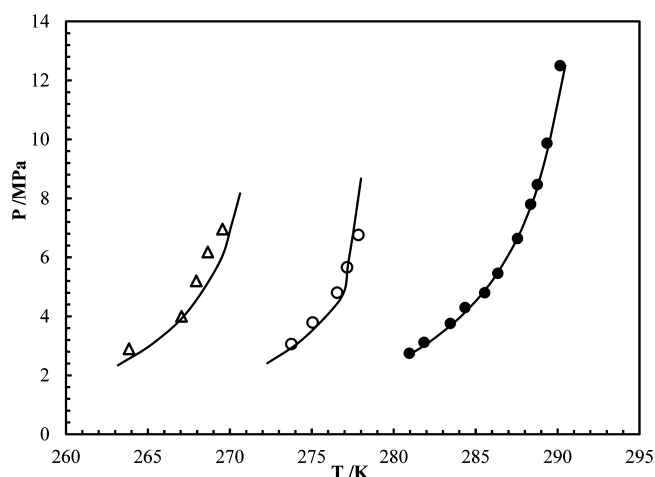


Figure 10. Mix B, hydrate dissociation condition in the presence of methanol (MeOH)/ethylene glycol (MEG) + calcium chloride (CaCl₂) aqueous solution. Symbols represent experimental dissociation conditions: ●, mixed gas + pure water;⁸ △, mixed gas + 0.20 mass fraction methanol (MeOH) + 0.10 mass fraction calcium chloride (CaCl₂); ○, mixed gas + 0.20 mass fraction ethylene glycol (MEG) + 0.10 mass fraction calcium chloride (CaCl₂), lines (—) represent the model prediction.

figures, the model prediction and measured data points shows excellent agreement in the studied pressure and temperature range.

5. CONCLUSION

Hydrate dissociation conditions of CO₂ rich gas mixture in the presence of aqueous solution of methanol (methanol + sodium chloride/calcium chloride) and ethylene glycol (ethylene glycol + sodium chloride/calcium chloride) were reported in this work. Furthermore, to show the inhibition effect comparison was made between measured hydrate dissociation values of CO₂ rich mixed gas in the presence of pure water and with the presence of organic inhibitor, salt + organic inhibitor. Also indicated in this work, the established thermodynamic model

predicts the hydrate dissociation condition of CO₂ rich gas mixture with the presence of aqueous solution of organic inhibitor well; however, the discrepancy were observed between measured and predicted values for a mixed aqueous solution of salt + organic inhibitor.

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Notes

The authors declare no competing financial interest.

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