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Prediction of Phase Equilibrium Conditions and Thermodynamic Stability of CO_2-CH_4 Gas Hydrate

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Abstract: With the large-scale promotion and application of CO_2 flooding, more and more engineering problems have emerged. Due to the high CO_2 mole fraction, the associated gas of CO_2 flooding very easily forms solid hydrates, compared to conventional natural gas. This has resulted in production decline or shutdown. Understanding the phase equilibrium conditions for hydrate formation in production fluids is crucial for hydrate prevention and control. In this study, accurate predictions of CO_2-CH_4 mixed gas hydrate formation conditions were performed using theoretical models. The temperature and pressure ranges for hydrate formation were calculated for different CO_2 mole fraction, ranging from −11.5 °C to 20.85 °C and from 0.81 MPa to −28.1 MPa, respectively. Based on the calculated phase equilibrium data, a multi-parameter empirical model was developed using polynomial fitting. The calculation errors for the multi-parameter empirical model were 3.09%. The multi-parameter empirical model established in this study can avoid complex thermodynamic equilibrium calculations and has the advantages of simplicity, high accuracy, and wide coverage of downhole conditions. Based on the calculated phase equilibrium data, the dissociation enthalpy of CO_2-CH_4 hydrate below and above the freezing point of water was calculated. The results showed that an increase in CO_2 mole fraction led to an increase in hydrate dissociation enthalpy and enhanced thermodynamic stability, making hydrate prevention more challenging. Our work can contribute to the optimization of CO_2 production fluid treatment processes and the development of hydrate prevention and control technologies.

Keywords: gas hydrates; CO_2-CH_4 mixed gas; formation conditions; prediction

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1. Introduction

In 2020, China proposed the goal of peaking carbon emissions by 2030 and achieving carbon neutrality by 2060. Carbon capture, utilization, and storage (CCUS) technology is a key means to achieve these "dual carbon" goals [1–3]. Major oil fields in China are actively developing CO_2 flooding in low-permeability reservoirs to achieve both emission reduction and enhanced oil recovery [4–6]. However, with the large-scale promotion and application of CO_2 flooding, more and more engineering problems have emerged. One of the challenges in oil and gas field development is the formation of hydrate blockages in the production fluid [7].

Gas hydrate refers to the ice-like crystal structure material formed between water molecules and guest molecules (such as CO_2, N_2, CH_4, H_2S, etc.) at low temperature and high pressure, in which the guest molecules are wrapped in cage-shaped holes through hydrogen bonding between water molecules, and the guest molecules play a role in stabilizing the lattice [8]. The structure of hydrate formation also differs with the size of the guest molecules. At present, gas hydrate mainly has the following three structures: type I, type II, and type H. The degree of difficulty of hydrate formation, as well as the thermodynamic stability, is different for different gas molecules. The current research on gas hydrate is mainly based on three aspects: energy, flow assurance, and gas separation

and storage. In terms of energy, the exploration and development of natural gas hydrate is the main focus [9], while flow assurance is mainly studied on the prevention and treatment of hydrate formation and blockage in pipelines [10–13]. Hydrate-based separation and storage technologies include low-boiling-point gas separation, seawater desalination, solid state storage and transportation of natural gas, CO_2 capture and storage, and so on [14–16].

High pressure and low wellhead temperature in winter, combined with the throttling effect on the production fluid at the surface, provide ideal temperature and pressure conditions for hydrate formation [17]. Therefore, hydrate blockages in CO_2 flooding production fluid pipelines occur frequently, severely affecting normal production activities and causing significant economic losses. It is of great significance to conduct research on relevant prevention and control technologies for hydrate blockages in CO_2 flooding production fluid for the safe and efficient development of oil and gas resources and for assuring the flow of pipeline transportation. Traditional hydrate prevention and control technologies mainly include system dehydration, pipeline heating, pressure control, and injection of thermodynamic inhibitors (alcohols), which change the thermodynamic conditions of the system to prevent hydrate formation [18–20]. Therefore, it is crucial to understand the phase equilibrium conditions for hydrate formation in production fluids.

Due to the high CO_2 mole fraction in the associated gas of CO_2 flooding and the presence of small hydrocarbon gases such as CH_4, the hydrate formation conditions differ significantly from those of natural gas hydrates. Although there have been many studies on hydrate blockages in natural gas pipelines, there are fewer studies on hydrate blockages caused by high CO_2 mole fraction in gas. Additionally, as the production process progresses, the composition of the produced gas changes gradually, requiring the establishment of phase equilibrium conditions for hydrate formation under a wide range of CO_2 mole fractions to address the issue of hydrate blockages in CO_2 flooding production fluids. The phase equilibrium conditions of hydrates can be obtained through a combination of experiments and modeling. There have been numerous reports on the phase equilibrium conditions of CO_2-containing gases, especially CO_2-CH_4 mixed gases, both domestically and internationally [21–23]. Adisasmito et al. studied the phase equilibrium conditions of CO_2-CH_4 mixed gas hydrate formation under temperature conditions of 273–288 K and pressure conditions of 1.2–11.0 MPa [24]. Based on experimental data, they have also proposed a multi-parameter empirical model, which has shown good predictive accuracy. Belandria et al. reported experimental data on the phase equilibrium conditions of CO_2-CH_4 mixed gas hydrate formation under temperature conditions of 279.1–289.9 K and pressure conditions of 2.96–13.06 MPa [25].

Sadeq et al. measured the hydrate dissociation equilibrium conditions for CO_2-CH_4 with water, N_2-CH_4 with water, and CO_2-N_2 with water using a cryogenic sapphire cell. The involved temperature and pressure ranges were from 275.75 to 293.95 K and from 5 MPa to 25 MPa, respectively [26]. Yasuda et al. investigated the phase equilibrium for hydrates formed with CO_2 and CH_4 at temperatures below the freezing point of water [27]. This is of significant importance for the prevention and treatment of hydrates under low-temperature conditions, as well as for the development of natural gas hydrates in frozen soil regions. The experimentally measured phase equilibrium data are mainly used for the regression of key parameters in phase equilibrium models. Currently, there are three main types of hydrate phase equilibrium prediction models: the Van der Waals–Platteeuw (vdW–P) model, the Klauda–Sandler (K–S) model, and the Chen–Guo model [28]. Among them, the Chen–Guo model has good prediction accuracy in predicting phase equilibrium conditions in complex systems (multicomponent, porous media, oil–water emulsion) [29]. However, existing theoretical models require complex gas–liquid–solid phase equilibrium calculations, making direct on-site application difficult.

In this study, the phase equilibrium conditions of CO_2-CH_4 mixed gas hydrate formation under different CO_2 mole fractions were first calculated based on the Chen–Guo model. Then, a multi-parameter empirical prediction model was established by polynomial fitting

based on the calculated phase equilibrium data, and the enthalpy of mixed gas hydrate dissociation was calculated.

2. Theoretical

2.1. Chen–Guo Model for CO_2-CH_4 Hydrate Formation

The Chen–Guo theoretical model is a thermodynamic model for hydrate phase equilibrium [29]. This model introduces the concepts of local stability, quasi-uniform occupation theory, and a two-step mechanism for hydrate formation. For a mixed gas system, the gas–hydrate phase equilibrium conditions can be expressed as:

$$f_i = f_i^H = x_i f_i^0 \left(1 - \sum_j \theta_j\right)^{\alpha} \quad (1)$$

$$f_i^0 = \exp\left(\frac{-\sum_j A_{ij}\theta_j}{T}\right) \times \mathrm{a}_i \exp\left(\frac{\mathrm{b}_i}{T - \mathrm{c}_i}\right) \times \exp\left(\frac{\beta P}{T}\right) \times a_w{}^{\frac{1}{\lambda_2}} \quad (2)$$

$$f_i^0 = \exp\left(\frac{\mathrm{D}(T - 273.15)}{T}\right) \times \mathrm{a}_i \exp\left(\frac{\mathrm{b}_i}{T - \mathrm{c}_i}\right) \times \exp\left(\frac{\beta P}{T}\right) \times a_w{}^{\frac{1}{\lambda_2}} \quad (3)$$

$$\theta_j = \frac{C_j f_j}{1 + \sum_i C_i f_i} \quad (4)$$

$$C = X \exp\left(\frac{\mathrm{Y}}{T - \mathrm{Z}}\right) \quad (5)$$

In Equation (1), f_i represents the fugacity of component i in the gas phase, in MPa; f^H represents the fugacity of component i in the hydrate phase, in MPa; x_i represents the mole fraction of component i in the base hydrate; α is the structural parameter, which is 3/23 for CO_2-CH_4 mixed gas hydrates; f_i^0 is the fugacity of component i in the basical hydrate above the freezing point, calculated by Equation (2); by introducing a correction factor D, the degree of freedom below the freezing point is calculated by Equation (3); and θ_j represents the occupancy of component j in the cages, calculated using Equation (4), where C_j is the Langmuir adsorption constant, calculated by Equation (5). The constants related to CO_2-CH_4 gas hydrates in the above equations can be found in Table 1. When solving the above model, a certain temperature or pressure needs to be assumed, and a series of trial calculations are performed to satisfy Equation (1) and determine the final values.

Table 1. Constants in Chen–Guo theoretical model.

Gas	$X \times 10^5$/MPa^{-1}	Y/K	Z/K	a $\times 10^{-9}$/MPa	b/K	c/K	β/(K/MPa)	D
CO_2	1.6464	2799.66	15.9	963.72	−6444.50	36.67	4.242	−22.5
CH_4	2.3048	2752.29	23.01	1584.4	−6591.43	27.04		

2.2. Multi-Parameter Empirical Model for CO_2-CH_4 Hydrate Formation

Although the theoretical models (Chen–Guo model, vdW–P model) can accurately predict the formation conditions of CO_2-CH_4 mixed gas hydrates, it requires a series of complex thermodynamic equilibrium calculations. In this study, reliable phase equilibrium data obtained from these theoretical models were processed through regression analysis. Using temperature and CO_2 mole fraction as variables and hydrate equilibrium pressure as the objective function, a simplified empirical model for predicting the phase equilibrium conditions of CO_2-CH_4 hydrates was established.

Firstly, temperature T (in °C) was taken as the variable and ln P (in MPa) as the objective function, and linear equations were fitted for different CO_2 mole fraction (y) (Equation (6)). Next, the two coefficients B and C in Equation (6) were separately fitted as functions of the CO_2 molar fraction (y), as shown in Equation (7). To ensure calculation accuracy, a fourth polynomial was used for fitting, and the values of the five parameters a, b, c, d, and e could be obtained. In some cases, a linear or quadratic polynomial

regression was also used to fit the parameters under certain conditions. Thus, a multi-parameter empirical model for predicting the phase equilibrium conditions of CO_2-CH_4 gas hydrates can be established. The input parameters of this model are only CO_2 mole fraction and temperature, and the corresponding hydrate formation pressure values can be obtained through simple mathematical calculations, avoiding the complex thermodynamic equilibrium trial-and-error iterative calculations in the phase equilibrium models.

$$\ln P = BT + C \tag{6}$$

$$f = ay^4 + by^3 + cy^2 + dy + e \tag{7}$$

2.3. Clausius–Clapeyron Equation for the Dissociation Enthalpy of CO_2-CH_4 Hydrates

In order to investigate the thermodynamic stability of hydrates formed under different CO_2 mole fractions, this study used the Clausius–Clapeyron equation (Equation (8)) combined with the established multi-parameter empirical model to calculate the dissociation enthalpy (ΔH_d) of CO_2-CH_4 hydrates. ln P and 1/T always exhibit a clear linear relationship under different CO_2 mole fractions, and the slope can be obtained through linear regression, which can then be used to calculate the dissociation enthalpy of CO_2-CH_4 hydrates.

$$\frac{d\ln P}{d(1/T)} = -\frac{\Delta H_d}{ZR} \tag{8}$$

where P represents the equilibrium pressure, in MPa; T represents the equilibrium temperature, in K; ΔH_d represents the enthalpy of hydrate dissociation, in kJ/mol; Z represents the compressibility factor of the CO_2-CH_4 mixed gas, calculated by the BWRS equation [30]; and R represents the universal gas constant, in $J \cdot mol^{-1} \cdot K^{-1}$.

3. Results and Discussions

3.1. Prediction Results of the Chen–Guo Theoretical Model

This work uses the Chen–Guo theoretical model to calculate the phase equilibrium conditions of CO_2-CH_4 gas hydrates under certain gas compositions below and above the freezing point of water. The calculated results are compared with experimental data in the CO_2 mole fraction range of 0–1, the temperature range of −10.55–17.7 °C, and the pressure range 0.75–15 MPa [24,27]. In these reported studies, hydrate dissociation conditions were measured by employing a temperature search in a high-pressure apparatus. A comparison was also made with the results of the vdW–P theoretical model [8], the empirical model proposed by Adisasmito et al. [24]. Figures 1 and 2 shows the comparison between the experimental values (P_{exp}) and the models' predicted values (P_{cal}) of hydrate formation pressure at different temperatures for different gas compositions below and above the freezing point, respectively.

From Figure 1, it can be seen that the Chen–Guo theoretical model shows slightly better agreement with the experimental values compared to the vdW–P theoretical model above the freezing point. As listed in Table 2, the average absolute relative deviation (AARD) of the pressure values calculated by the Chen–Guo model is about 3.05% (compared to 3.07% for the vdW–P model). However, as shown in Figure 2 and Table 2, the accuracy of the Chen–Guo model's predictions (AARD is 6.44%) below the freezing point is significantly lower than that of the vdW model (AARD is 3.23%). The overall AARDs of the Chen–Guo and vdW–P models are 3.10% and 3.62%, respectively. Adisasmito's model was derived from a regression of experimental data above the freezing point of water. Although it has high predictive accuracy, as shown in Table 2, its range of application is narrow (1.2–11 MPa, 0–15 °C). In order to obtain more accurate phase equilibrium data, this work combined the two theoretical models, namely, the formation conditions of mixed gas hydrates below the freezing point were calculated by the vdW–P model, while the data above the freezing point were provided by the Chen–Guo model.

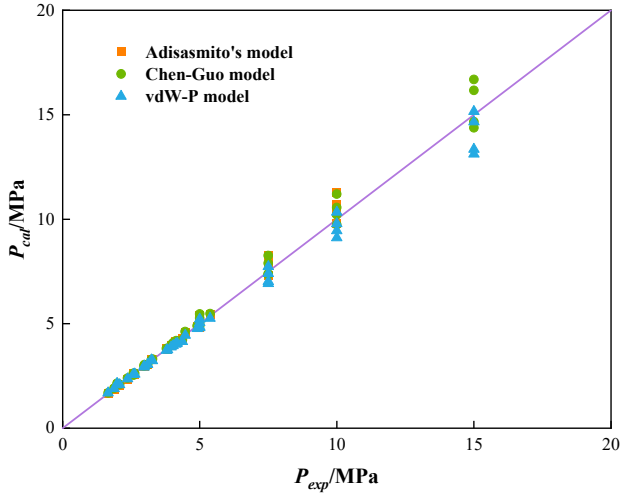


Figure 1. Comparison of calculated results of Chen–Guo hydrate model with experimental data above the freezing point of water.

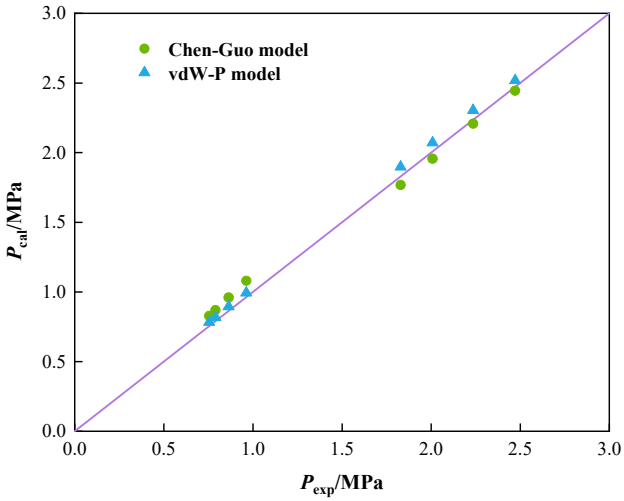


Figure 2. Comparison of calculated results of Chen–Guo hydrate model with experimental data below the freezing point of water.

Table 2. The average absolute relative deviation (AARD) of the pressure values predicted by different models.

Models	Below Ice Point	Above Ice Point	Overall
vdW–P	3.23%	3.07%	3.10%
Chen–Guo	6.44%	3.05%	3.62%
Adisasmito	-	2.82%	-
This work	3.22%	3.07%	3.09%

Typically, the pressure in gas pipelines is lower than 10 MPa, and the pressure at the outlet of oil and gas wells is generally far lower than 20 MPa. Therefore, this study used the theoretical models to calculate the formation pressure of CO_2-CH_4 hydrates under the conditions of CO_2 molar fraction ranging from 0% to 100%, temperature ranging from −11.5 to 20.85 °C, and pressure ranging from 0.81 MPa to 28.1 MPa, which can better meet the requirements of field applications. This temperature and pressure range essentially covers the temperature and pressure that may be involved in the transportation process of oil and gas from the wellhead to the pipeline, meeting the requirements for hydrate prevention during the oil and gas transportation process. Furthermore, from the perspective of hydrate

extraction, it also covers the temperature and pressure conditions for the formation of onshore permafrost and offshore natural gas hydrates, and it can be used for applications related to CO_2 replacement for natural gas hydrate exploitation [15].

Figure 3 shows the formation pressure of CO_2-CH_4 hydrates at different temperatures and CO_2 molar fractions (in logarithmic form). In order to check whether the mixed gas is liquefied, we also plotted the dew point lines of the mixed gas at CO_2 molar fractions of 0.6, 0.8, 0.9, and 1.0 in Figure 3.

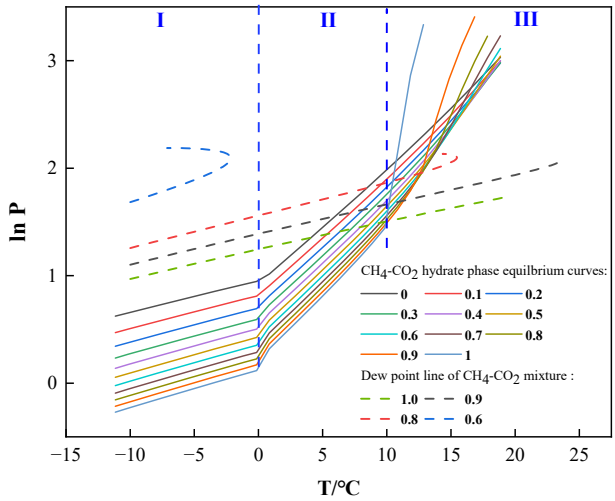


Figure 3. Equilibrium conditions of CO_2-CH_4 gas hydrate under different CO_2 mole fraction.

From the figure, it can be observed that temperature significantly affects the formation pressure of CO_2-CH_4 hydrates, with lower temperatures resulting in lower hydrate formation pressures. The trend of curve changes can be divided into three regions based on temperature: below freezing point (I), regions with a freezing point up to 10 °C (II), and above 10 °C (II). In the first two regions, the formation pressure of hydrates increases with the increase of temperature, and the higher the content of carbon dioxide in the mixed gas, the lower the formation pressure of hydrates. It is worth noting that within the freezing point region (I), the rate of increase in hydrate formation pressure with increasing temperature is significantly lower than in the region above the freezing point. Taking a gas mixture with a CO_2 mole fraction of 0.4 as an example, due to the large temperature difference between day and night in the cold region, the outdoor temperature in winter can even be below 0 °C. Under conditions of approximately 2 MPa, hydrates can quickly form.

Furthermore, the calculation results also indicate that in region (I) and (II), as the CO_2 mole fraction increases, the formation pressure of hydrates gradually decreases, indicating that the presence of CO_2 makes hydrate formation easier, which poses greater challenges for the prevention and control of hydrates. Therefore, attention should be paid to wellhead thermal insulation and pressure regulation to keep the conditions in the wellbore under the hydrate equilibrium condition. In addition, the pressure of produced fluids needs to be reduced in the process of external transport, so there will be throttling effect. The pressure before and after throttling should be controlled based on the hydrate phase equilibrium condition to prevent the formation of hydrates in the throttling process.

In the third region (temperature above 10 °C), when the CO_2 mole fraction is very high, as the temperature increases, the phase equilibrium line of the mixed gas intersects with the dew point line. After the intersection point, as the temperature rises, the mixed gas partially liquefies, and at this time, the pressure for hydrate formation increases sharply. Moreover, the higher the carbon dioxide content, the greater the increase in pressure. This is opposite to the first two regions. We call this intersection a critical point here. As the CO_2 mole fraction in the gas phase decreases and the methane content increases, the difficulty of liquefying the mixed gas increases. As shown in Figure 3, at the same temperature, the

liquefaction pressure of the mixed gas increases with the increase in methane content. For pure CO_2, when the temperature is 12.85 °C, the formation pressure of hydrates reaches 28.1 MPa. However, when the CO_2 mole fraction decreases to 0.8 and the temperature is around 18 °C, the formation pressure of hydrates reaches 28.1 MPa. This indicates that above the critical point, the higher the CO_2 mole fraction, the more difficult it is to form hydrates. Obviously, such stringent formation conditions are difficult to achieve in normal oil and gas production processes, and under such conditions, hydrates can be considered almost non-existent.

3.2. Prediction Results of the Multi-Parameter Empirical Model

Due to the different characteristics of the equilibrium lines of mixed gas hydrate in different temperature ranges, this study conducted fitting for the three regions in Figure 3 respectively to obtain more accurate empirical models. In Figure 3, it was found that ln *P* exhibited a clear linear relationship with *T* in region (I), (II), and (III), and the slope of the straight lines in the three regions also gradually increases as the temperature increases.

For regions (I), (II), and (III), the coefficients B and C in Equation (6) fitted for different CO_2 mole fraction are shown in Figure 4a–c. The variation of the coefficients B and C with CO_2 mole fraction indicates a strong correlation. Among them, B and C exhibit a monotonic increasing and decreasing trend with increasing CO_2 mole fraction, respectively. Specially, in region (III), when the CO_2 mole fraction exceeds 0.8, the C value drops sharply. To accurately describe this trend of change, we fitted the relationship between C and CO_2 mole fraction in two stages, namely 0–0.9 and 0.9–1. As shown in Figure 4, the fitted curves match the data points well, and the values of the fitted five parameters a–e in Equation (7) are listed in Table 3. Thus, a multi-parameter empirical model for predicting the phase equilibrium conditions of CO_2-CH_4 gas hydrates was established.

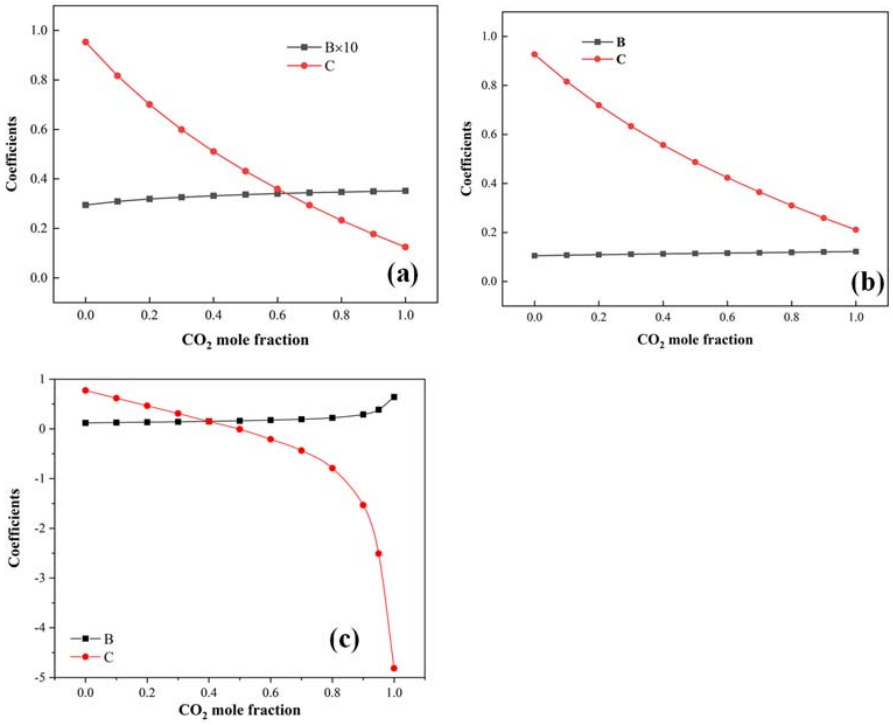


Figure 4. Variation of the fitted coefficients B and C with CO_2 mole fraction: (**a**) below the freezing point, (**b**) temperature range of 0–10 °C, (**c**) temperature range of 10–20.85 °C.

Table 3. Fitted polynomial coefficients a, b, c, d, and e in Equation (6) for region (I), (II), and (III).

Temperature Range	Fitted Polynomial Coefficients	B	C
−11.5–0 °C	a	0	0
	b	0	0
	c	−0.00538	0.43031
	d	0.01063	−1.23640
	e	0.02975	0.93997
0–10 °C	a	0	0
	b	0	0
	c	−0.00305	0.32563
	d	0.01967	−1.02598
	e	0.10539	0.91792
10–20.85 °C (y_{CO2}: 0–0.9)	a	1.0743	−4.255
	b	−1.42982	4.279
	c	0.64437	−1.3745
	d	−0.01906	−1.4117
	e	0.12073	0.7711
10–20.85 °C (y_{CO2}: 0.9–1)	a	0	0
	b	0	0
	c	31.92	−265.96
	d	−57.146	472.52
	e	25.866	−211.37

To verify the accuracy of our empirical model, this study compared its predicted values with experimental data, the Chen–Guo model, and the vdW–P model, as shown in Figure 5, and the AARDs of this work were listed in Table 2. From Figure 5, it can be observed that the proposed empirical model has a good prediction accuracy, with an AARD of 3.09% for the whole temperature and pressure ranges. It is slightly better than the results of the two theoretical models. Compared to the Chen–Guo model, there is a significant improvement in prediction accuracy of pressures below freezing point. The proposed multi-parameter empirical model is simpler to use and has high accuracy and wide temperature and pressure ranges, making it suitable for on-site applications. It can provide guidance for the optimization or development of CO_2 hydrate prevention and control technologies.

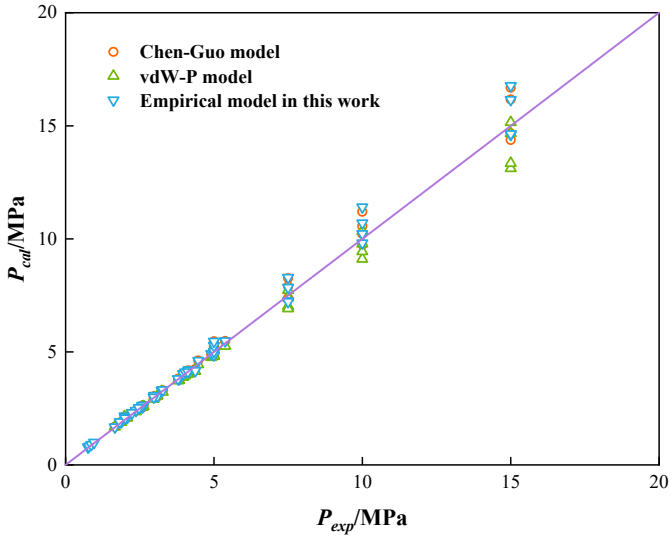


Figure 5. Comparison of multi-parameter empirical model with the experimental data and theoretical models.

3.3. Dissociation Enthalpy of CO_2-CH_4 Gas Hydrate

The magnitude of dissociation enthalpy can reflect the thermodynamic stability of hydrates. Due to the difficulty of forming hydrates with mixed gases above the critical point, the calculation of enthalpy values in this section is only applicable to CO_2-CH_4 hydrates below the freezing point and within the temperature range of 0–10 °C. Figure 6 shows the relationship between the natural logarithm (ln P) of the equilibrium pressure of CO_2-CH_4 hydrates under different CO_2 mole fractions (y_{CO2}) and the reciprocal ($1/T$) of the corresponding equilibrium temperature. From the figure, it can be seen that there is a clear linear relationship between ln P and $1/T$ under different CO_2 mole fractions. The slope can be obtained through linear regression, and then the decomposition enthalpy of CO_2-CH_4 mixed gas hydrates under different compositions can be calculated. Moreover, the slope of the fitted line is different under conditions below and above the freezing point.

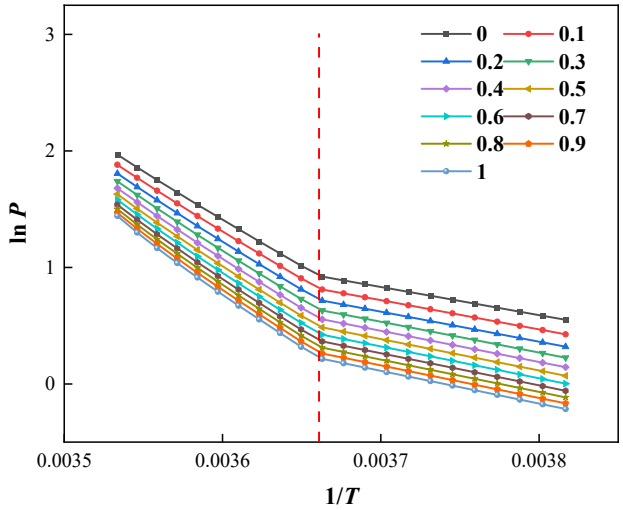


Figure 6. Clausius–Clapeyron relationship of CO_2-CH_4 hydrates under different CO_2 mole fraction.

Figure 7 shows the change in dissociation enthalpy of CO_2-CH_4 gas hydrate with different CO_2 mole fractions above the freezing point of water. As shown in the figure, it can be seen that as the CO_2 mole fraction increases, the dissociation enthalpy of CO_2-CH_4 gas hydrates increases rapidly in the range of y = 0 to 0.4, increases slowly in the range of y = 0.4 to 0.8, and decreases slowly in the range of y = 0.8 to 1.0. Overall, there is a trend of increasing followed by decreasing. When y_{CO2} increases from 0 (pure methane hydrate) to 0.8, the dissociation enthalpy of CO_2-CH_4 gas hydrates gradually increases from 62.22 kJ/mol to 64.67 kJ/mol, and the increasing trend gradually slows down. This result indicates that within a certain range of CO_2 mole fraction, the presence of CO_2 increases the thermodynamic stability of mixed gas hydrates, making their dissociation more difficult. The energy consumption required to remove hydrate blockages using heating methods is also higher, which is one of the challenges in preventing and controlling hydrates in production fluids with high CO_2 mole fraction. Additionally, when CO_2 mole fraction increases from 0.8 to 1 (pure CO_2 hydrate), the dissociation enthalpy of hydrates slightly decreases from 64.67 kJ/mol to 64.53 kJ/mol, indicating that the thermodynamic stability of pure CO_2 hydrates is slightly weaker than that of hydrates formed by high CO_2 mixed gases.

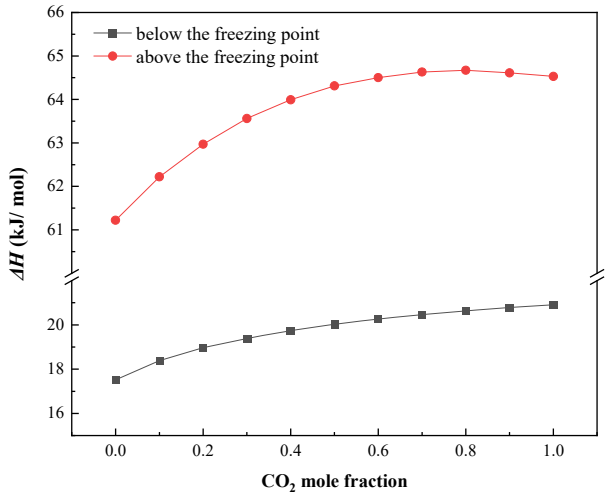


Figure 7. Dissociation enthalpy of CO_2-CH_4 hydrates under different CO_2 mole fraction in gas phase.

The cause of the above phenomenon is related to the sizes of CO_2 and CH_4 molecules and the occupation of hydrate cages. Since CO_2 molecules are larger than methane molecules, the size of CO_2 matches better with the large cages in the structure I hydrates, while the size of methane matches better with the small cages. As the CO_2 mole fraction in the gas increases, CO_2 molecules tend to occupy the large cages of the structure I hydrate, while methane molecules tend to occupy the small cages. The combined effect of these two factors makes the structure of hydrates more stable, resulting in an increase in the dissociation enthalpy of hydrates with increasing CO_2 mole fraction in the gas. However, when the CO_2 mole fraction in the gas further increases, the small cages in the hydrates are gradually occupied by the larger CO_2 molecules, leading to a decrease in the stability of the hydrate structure. Therefore, when the CO_2 mole fraction in the gas reaches a certain value, the dissociation enthalpy of hydrates gradually decreases.

Figure 7 also shows the dissociation enthalpy of mixed gas hydrates below the freezing point. From the figure, it can be observed that the dissociation enthalpy of mixed gas hydrates increases with the increase in carbon dioxide molar fraction, but the rate of increase gradually diminishes. Unlike the situation above the freezing point, there is no decrease in enthalpy values. In addition, the enthalpy range of mixed gas hydrates below the freezing point is 17.52–20.92 kJ/mol, significantly lower than the values above the freezing point. In order to eliminate hydrate blockage below freezing point, in addition to stimulating the dissociation and release of gas from the hydrate, it is also necessary to heat the ice into water, which consumes a significant amount of energy. In addition, due to the lower formation temperature of hydrates below the freezing point, it is easy to cause the formation of secondary hydrates, making blockage more severe.

At present, natural gas hydrate is the main research object, but there are few reports on the technology of carbon dioxide hydrate control. Due to the mild conditions for the formation of carbon dioxide hydrate, CO_2 hydrates are more stable than methane hydrates. Compared with the control of methane hydrate, the thermodynamic inhibition method needs to add a higher concentration of thermodynamic inhibitors. In the kinetic inhibition method, the kinetic inhibitor for CO_2 hydrate must bear a higher degree of undercooling [11–13]. In addition, since CO_2 is an acidic gas, the effectiveness of current kinetic inhibitors for natural gas systems needs to be further evaluated. In short, the prevention and control of hydrates in the production fluids of CO_2 flooding is a significant challenge.

4. Conclusions

Due to the high CO_2 mole fraction in the associated gas of CO_2 flooding, it is prone to the formation of hydrate blockages in pipelines. Accurately understanding the critical conditions for the hydrates' formation in production fluids of CO_2 flooding is crucial for

preventing and controlling hydrate formation. In this study, a predictive model for the phase equilibrium conditions of CO_2-CH_4 mixed gas hydrate formation was developed, and the following conclusions were drawn:

(1) The Chen–Guo theoretical model can accurately predict the conditions for the formation of CO_2-CH_4 mixed gas hydrates above the freezing point of water, with an absolute average relative error of 3.05%. However, the prediction error of the model below the freezing point is large.

(2) Based on the phase equilibrium data obtained from the Chen–Guo and vdW–P theoretical model, a multi-parameter empirical predictive model was established using polynomial fitting. The absolute average relative deviation of the phase equilibrium pressure calculation results of this model is 3.09%, slightly better than the theoretical models. This model has the advantages of simplicity, stability, high accuracy, and applicability to a wide range of CO_2 mole fractions, temperatures, and pressure. It can effectively guide the development of hydrate prevention and control technologies for CO_2-driven production fluids.

(3) Below the critical point, as the CO_2 mole fraction in gas phase increases, the formation pressure of mixed gas hydrates decreases, making hydrate formation easier. Within a certain concentration range, an increase in CO_2 mole fraction also leads to an increase in the dissociation enthalpy of mixed gas hydrates, resulting in a stronger thermodynamic stability of the hydrates. This poses a significant challenge for the prevention and control of hydrates in production fluids of CO_2 flooding. However, above the critical point, the higher the CO_2 mole fraction, the greater the pressure for hydrate formation.

(4) As CO_2 and CH_4 coexist in gas phase, CO_2 molecules tend to occupy the large cages of the structure I hydrate, while CH_4 molecules tend to occupy the small cages, demonstrating a certain synergistic effect. The combined effect of these two factors makes the structure of hydrates more stable. In view of the prevention and control of hydrates in fluids with high CO_2 mole fraction, the existing prevention and control methods of natural gas hydrates need to be re-evaluated.

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