



# Article A Predictive Model for Hydrate Formation Conditions in Alcohol-Containing Systems Based on the Cubic-Plus-Association State Equation

Yubin Wang<sup>1</sup>, Ziyuan Li<sup>2</sup>, Shujie Zhi<sup>1</sup>, Qi Yang<sup>1</sup>, Changjun Li<sup>2</sup> and Wenlong Jia<sup>2,\*</sup>

<sup>2</sup> School of Petroleum Engineering, Southwest Petroleum University, Chengdu 610500, China

\* Correspondence: jiawenlong08@126.com

**Abstract:** In alcohol-containing systems, the association of polar molecules significantly influences the calculation of water activity, leading to substantial deviations from ideal solution behavior. This makes it challenging for traditional hydrate formation condition models to accurately predict hydrate formation temperatures and pressures. To address this issue, we propose a novel unified thermodynamic framework based on the Parrish-Prausnitz (P-P) model and the Cubic-Plus-Association (CPA) equation of state (EoS) for calculating the hydrate formation condition in systems containing gas/water/alcohol, by using the advantages of the CPA EoS to characterize the association interaction of polar molecules. In addition, we utilize experimental data to model the molecular association in alcohol-containing systems and conduct regression analysis for binary interaction coefficients among alcohol, water, and gas. Multiple sets of experimental data on component fractions and hydrate formation conditions for methane-alcohol-water systems are used for validation. The proposed model shows an average relative error of 1.17–6.42% for predicting alcohol/methane component fractions in the liquid phase and 1.93–4.78% for predicting hydrate formation conditions in alcohol-containing systems.

Keywords: natural gas hydrate; alcohol-containing system; formation condition; thermodynamic model

# 1. Introduction

The thermodynamic model for natural gas hydrate formation conditions can be traced back to the van der Waals and Platteeuw (vdW-P) model, which was proposed based on classical adsorption theory by van der Waals and Platteeuw [1]. Subsequently, many efforts have been conducted for the improvement of the vdW-P model. Notably, Parrish and Prausnitz [2] made a significant contribution by introducing an empirical method to compute the Langmuir constant. This improvement gave rise to the classical P-P model, greatly simplifying the computation of the Langmuir constant and successfully extending the application of the vdW-P model to multi-component systems. However, in alcohol-containing systems, polar substances like water/alcohol can undergo complex self-association and cross-association interactions, affecting component fugacities, activities, and other thermophysical properties, resulting in dislocation of the gas hydrate formation conditions. Merely improving the thermodynamic model for hydrate formation may not yield the desired predictive accuracy. The traditional models attempt to address the impact of polar molecules by combining hydrate thermodynamic models, EoSs, and activity models [3,4]. However, this method complicates the modeling process and is inconvenient for application, making it challenging to accurately depict various molecular interactions and their impact on gas hydrate formation [5].

In the process of solving thermodynamic models for natural gas hydrate and multiphase equilibrium calculations, various phase equilibrium parameters such as fugacity and



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<sup>&</sup>lt;sup>1</sup> PipeChina Institute of Science and Technology, Langfang 065000, China

activity, as well as thermophysical parameters, including compressibility factor and enthalpy, are involved. EoS can calculate these parameters over a wide range of temperature and pressure, serving as the foundation of most thermodynamic models. In order to describe liquid phase non-ideality, many attempts have been made to improve EoS. Masoudi and Tohidi et al. [6] employed the modified Patel-Teja EoS to predict hydrate formation conditions in multi-component systems containing alcohols. The results showed higher predictive accuracy within the pressure range of 50 MPa. Delavar and Haghtalab et al. [7] utilized the Chen-Guo model, Soave-Redlich-Kwong (SRK) EoS, and Huron-Vidal (HV) mixing rules to describe the hydrate, gas, and aqueous phases in systems containing acidic gases, alcohols, and electrolytes. The predicted results were in good agreement with experimental data. Promisingly, there is potential to develop more reliable and widely applicable natural gas hydrate prediction models by enhancing equations of state or introducing correction factors.

Due to the incapacity of traditional EoS to represent hydrogen bonding interactions among polar substances like water and alcohols, significant deviation can arise in activity calculation. Kontogeorgis et al. [8] introduced an associating term within the SRK equation of state to describe hydrogen bonding interactions, resulting in the development of the CPA EoS. For associating fluids, the most critical aspect is the study of associating models. For the associating models of polar molecules like water and alcohols, the most widely applied are the 2B and 4C associating models proposed by Huang and Radosz in 1990 [9]. These models consider hydrogen and oxygen atoms individually as electron, proton donors or acceptors. In recent years, Kruger and Qvistgaard et al. [10,11] have proposed various associating models for ethylene glycol (MEG) and glycerol (TEG). These models consider the dipole sites formed by hydrogen and oxygen atoms on one side of the molecular structure, which exhibit a higher probability of association and provide a better description of the associating interactions among polar molecules. With the development of new associating models and bonding methods, further evaluation of the performance of these associating models is necessary. The application of CPA in predicting hydrate formation conditions in alcoholcontaining systems is subject to further research. Additionally, when CPA EoS introduces new associating models, it is imperative to adjust the binary interaction coefficients.

In conclusion, we have proposed a novel unified thermodynamic framework based on the P-P model and the CPA EoS for calculating the hydrate formation condition in multicomponent systems containing gas/water/alcohol. Within this framework, we have replaced the traditional activity model with the association term in the CPA EoS, effectively characterizing non-ideality in solution. Furthermore, various association models used for alcohol substances such as MEOH, MEG, DEG, and TEG are evaluated. Due to the consideration of multiple association models in our modeling process, it was necessary to adjust the existing binary interaction coefficients. Therefore, we collected a substantial amount of vapor-liquid phase equilibrium experimental data and conducted regression on these parameters. Finally, experimental data are used to validate the model.

#### 2. Thermodynamic Model

#### 2.1. P-P Hydrate Model

The P-P model used in this study is an improvement upon the classic vdW-P model by modifying the Langmuir constants. This model is based on statistical thermodynamics and the isothermal adsorption theory, leading to the chemical potential expressions for water in the hydrate phase and the water-rich phase, as shown in Equations (1) and (2).

$$\Delta \mu_{\rm W}^{\beta-{\rm H}} = \mu_{\rm W}^{\beta} - \mu_{\rm W}^{\rm H} = -RT \sum_{n=1}^{2} v_n \ln\left(1 + \sum_i C_{ni} f_i\right) = \Delta \mu_{\rm W}^{\beta-{\rm L}}$$
(1)

$$\frac{\Delta\mu_{W}^{\beta-L}}{RT} = \frac{\Delta\mu_{W}^{0}}{RT_{0}} - \int_{T_{0}}^{T} \frac{\Delta h_{w}^{\beta-L}}{RT^{2}} \mathrm{d}T + \int_{P_{0}}^{P} \frac{\Delta v_{w}^{\beta-L}}{RT} \mathrm{d}P + \ln a_{w}$$
(2)

where  $\Delta \mu_W^{\beta-H}$  is the difference in chemical potential between the empty hydrate lattice and the filled lattice phase, J/mol;  $\mu_W^{\beta}$  and  $\mu_W^{H}$  are the chemical potential of water in the fully empty and filled hydrate lattice phases, J/mol; *R* is the gas constant, J/(mol·K); *T* is the temperature, K;  $v_n$  is the number of type-*n* cages that each water molecule possesses;  $C_{ni}$  is the Langmuir constant;  $f_i$  is the fugacity of the gas component *i*, Pa;  $\Delta \mu_W^{\beta-L}$  is the difference in chemical potential between the empty hydrate lattice and the liquid phase, J/mol;  $\Delta \mu_W^0$  is the difference in chemical potential between water in the empty hydrate lattice and water in the pure liquid phase at a reference state, J/mol;  $\Delta h_w^{\beta-L}$  is the molar enthalpy difference between the  $\beta$  phase and the liquid phase, J/mol;  $a_w$  is the liquid phase activity coefficient.

The fundamental properties in the model, including the densities, heat capacities, enthalpies, and fugacities of solvents, hydrates, and gases, are calculated by EoS. Details on the calculation methods for the remaining parameters in this model can be found in reference [2].

#### 2.2. CPA EoS

In 1996, the Kontogeorgis team introduced the association term, capable of describing molecular association interactions, into the SRK EoS to form the CPA EoS, as shown in Equation (3) [8]:

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)} - \frac{1}{2}\frac{RT}{v}\left(1 - v\frac{\partial \ln g}{\partial v}\right)\sum_{i} x_{i}\sum_{A_{i}} (1 - X_{A_{i}})$$
(3)

where *g* is the radial distribution function, calculated by Equation (4);  $x_i$  is the mole fraction of component *i*;  $A_i$  the active binding sites A on molecule *i*;  $X_{A_i}$  the molar fraction of unbound active sites A in component *i*, calculated by Equation (5).

$$g = \frac{4v}{1 - 1.9b} \tag{4}$$

$$X_{A_{i}} = \frac{1}{1 + \rho \sum_{j} x_{j} \sum_{B_{j}} X_{B_{j}} \Delta^{A_{i}B_{j}}} i, j = 1, 2, \cdots, N_{CA}$$
(5)

where  $N_{CA}$  is the number of polar components;  $\rho$  is the molar density of the mixture, mol·m<sup>-3</sup>;  $\Delta^{A_i B_j}$  is the binding strength between binding site A of molecule *i* and binding site B of molecule *j*, calculated by Equation (6).

$$\Delta^{A_i B_j} = g \left[ \exp\left(\frac{\varepsilon^{A_i B_j}}{RT}\right) - 1 \right] b_{ij} \beta^{A_i B_j} \tag{6}$$

where  $\varepsilon^{A_i B_j}$  is the binding energy between active binding site  $A_i$  and  $B_j$ , kPa·m<sup>3</sup>·mol<sup>-1</sup>;  $\beta^{A_i B_j}$  is the binding volume between active binding site  $A_i$  and  $B_j$ .

Based on the structural characteristics of the CPA EoS, the compressibility factor can be expressed as the sum of the physical and association compressibility factors. The physical component's compressibility factor is the same as that of the SRK EoS, and the association component's compressibility factor is as described in Equation (7).

$$Z = -\frac{0.5Z}{Z - 0.475B} \sum_{i} x_{i} \sum_{A_{i}} \left( 1 - \frac{1}{1 + \frac{p}{ZRT} \sum_{j} x_{j} \sum_{B_{j}} X_{B_{j}} \Delta^{A_{i}B_{j}}} \right)$$
(7)

Therefore, the compressibility factor expression of the CPA EoS is as shown in Equation (8).

$$Z = \frac{Z}{Z-B} - \frac{A}{Z+B} - \frac{0.5Z}{Z-0.475B} \sum_{i} x_{i} \sum_{A_{i}} \left( 1 - \frac{1}{1 + \frac{p}{ZRT} \sum_{j} x_{j} \sum_{B_{j}} X_{B_{j}} \Delta^{A_{i}B_{j}}} \right)$$
(8)

Similar to the compressibility factor calculation method, the fugacity of the CPA EoS can also be obtained by adding the fugacity of the physical term to that of the association term. The fugacity of the physical term is as given in Equation (9), and the fugacity of the association term is as shown in Equation (10). The activity coefficients can be determined using Equation (11).

$$\ln\frac{f_i}{y_i p} = -\ln\left(\frac{Z-B}{Z}\right) + \frac{b_i}{b}(Z-1) + \frac{A}{B}\left(\frac{2\sum_i x_j a_{ij}}{a} - \frac{b_i}{b}\right)\ln\left(\frac{Z+B}{Z}\right)$$
(9)

$$\ln \frac{f_i}{y_i p} = \sum_{A_i} \ln X_{A_i} - \frac{1}{2} \sum_i n_i \sum_{A_i} \left( 1 - X_{A_i} \right) \frac{0.475B}{Z - 0.475B} \frac{b_i}{b}$$
(10)

$$a_i = f_i / f_i^{\Theta} \tag{11}$$

where  $a_i$  is the activity of component *i*;  $f_i$  is the fugacity of component *i*, MPa;  $f_i^{\Theta}$  is the fugacity of component *i* at standard conditions, MPa.

The CPA EoS employs a total of five parameters, including  $a_0$ , b,  $c_1$ ,  $\varepsilon^{A_i B_j}$ , and  $\beta^{A_i B_j}$ , to characterize each pure component. To calculate the properties of multi-component systems, in addition to establishing the physical and association parameters of each component within the CPA EoS, it is necessary to determine the mixing rules associated with these two types of parameters. For the physical parameters, the classical van der Waals single-fluid mixing rules are employed, as shown in Equations (12) and (13).

$$a = \sum_{i} \sum_{j} x_i x_j \sqrt{a_i a_j} \left( 1 - k_{ij} \right) \tag{12}$$

$$b = \sum_{i} x_i b_i \tag{13}$$

where  $k_{i,i}$  is the binary interaction coefficients.

For the association parameters, A and B can be determined through experimental data or mixing rules. However, the former is limited, while the latter remains the mainstream approach. For hydrogen-bonded fluids containing water and alcohols, Voutsas et al. [12] proposed CR-1 mixing rules to calculate A and B, as shown in Equations (14) and (15). In this study, the mixture association parameters for alcohol and water molecules are calculated using the CR-1 mixing rules.

$$\varepsilon^{A_i B_j} = \frac{\varepsilon^{A_i B_i} + \varepsilon^{A_j B_j}}{2} \tag{14}$$

$$\beta^{A_i B_j} = \sqrt{\beta^{A_i B_i} \beta^{A_j B_j}} \tag{15}$$

#### 2.3. Alcohol-Water Molecule Association Model

Molecular association primarily occurs between polar molecules, affecting component fractions, and consequently influencing the calculation of parameters like activity and fugacity. Ultimately, this affects the phase equilibrium conditions for hydrate formation. However, different association models employ distinct distributions of association sites, representing varying levels of association. In the CPA EoS, different association models

are characterized by distinct parameters  $\varepsilon^{A_i B_j}$  and  $\beta^{A_i B_j}$ , which directly affect the model's computational accuracy and correspond to different binary interaction coefficients. Therefore, the choice of an association model is particularly important for phase equilibrium predictions in systems containing polar molecules. The currently used association model is derived from Huang and Radosz [9], as shown in Table 1.

Substance	H <sub>2</sub> O	MEG	MeOH
Association model	4C	4C	2B
Schematic of association form	$\stackrel{\mathbb{B}}{{\underset{}{}{}{}{}{}$	$\begin{array}{c} \overset{A}{:} \overset{\bullet}{:} \overset{\bullet}{:} \overset{C}{\to} \overset{C}{:} \overset{C}{:} \overset{B}{:} \overset{B}{:}$	<sup>▲</sup> ••• • O — H <sup>B</sup>

 Table 1. Common water-alcohol molecule association models.

In recent years, there has been extensive research on modeling association models for alcohols. Kruger and Qvistgaard [10,11] proposed several association models for MEG and TEG (as shown in Tables 2 and 3). The association sites can be categorized into three fundamental types: positive electron acceptor sites, negative electron donor sites, and bipolar sites. Following this classification, positive sites form hydrogen bonds exclusively with negative and bipolar sites, while negative sites establish hydrogen bonds solely between positive and bipolar sites. Bipolar sites, on the other hand, engage in hydrogen bonding interactions with all types of sites. In traditional association models, only positive and negative sites are considered. For instance, the 4C association model incorporates two electron donor sites and two electron acceptor sites. In the new association models, there is a combination of positive and negative sites into a bipolar site. In terms of association levels, traditional association models usually have an equal probability of self-association and cross-association. In contrast, in the new models like 3C, 4E, and 4F, there is a higher probability of bond formation, with a greater likelihood of forming cross-association. This difference in bonding probabilities aligns more closely with the results obtained from molecular simulations. Therefore, the association models used for water and alcohol molecules in this study are presented in Table 4.

**Table 2.** Schematic of association form of MEG molecule.

Association Model	4C	3C	4E	<b>4</b> F
Schematic of association form	₩ C-C-C-Ö H *	©−c−c−ö H	* • • - c - c - <del>c</del>	

\*  $\langle \cdot \cdot \rangle$  is bipolar site;  $\langle \cdot \cdot \rangle$  is positive site;  $\langle \cdot \cdot \rangle$  is negative site.

Table 3. Schematic of association form of TEG molecule.

Association Model	4C	5C	6D
Schematic of association form	₽ <sup>0</sup> ~q~ <sup>0</sup> ~q <sup>i</sup> <sup>i</sup> ,	€ <sup>70</sup> ~0~ <sup>70</sup> √0 <sup>∰</sup> *	€ <sup>0</sup> ~0~0~0 <u>€</u>
Association model	$4\mathrm{F}$	5F	6F
Schematic of association form	H. and the *	H. On Othor	H.O. O. O. O. O.

\*  $\langle - - \rangle$  is bipolar site;  $\langle - - \rangle$  is positive site;  $\langle - - \rangle$  is negative site.

Substance	H <sub>2</sub> O	MeOH	MEG	DEG	TEG
Association model	4C	2B	4F	4C	4F

**Table 4.** Alcohol and water molecule association models in this study.

#### 3. Regression of Binary Interaction Coefficients for Alcohol-Water-Gas

The SRK EoS employs binary interaction coefficients ( $k_{ij}$ ) from the single-fluid mixing rules to describe intermolecular forces. The CPA EoS, upon introducing association terms, necessitates the adjustment of the pre-existing binary interaction coefficients. These coefficients directly affect the precision of phase equilibrium calculation [5,13]. This paper involves binary interaction coefficients between methane-solvent and solvent-solvent molecules. The Britt-Luecke algorithm is employed to regress vapor-liquid equilibrium experimental data [14]. The objective function used is shown in Equation (16).

$$Q = \sum_{i=1}^{m} \sum_{j=1}^{n} \left( z_{i,j}^{\exp} - z_{i,j}^{\operatorname{cal}} \right)^2 / \sigma_{i,j}^2$$
(16)

where  $z_{i,j}^{\text{cal}}$  is the calculated value;  $z_{i,j}^{\exp}$  is the experimental value;  $\sigma_{i,j}^2$  is the variance.

To evaluate the predictive accuracy of the model, the Average Relative Deviation (ARD) between the model predictions and experimental values is defined as shown in Equation (17).

$$ARD(x) = \frac{1}{N_{d}} \sum_{i}^{N_{d}} |x_{ca1,i} - x_{exp,i}| / x_{exp,i} \times 100\%$$
(17)

Many researchers believe that in gas molecule mixtures, the binary interaction coefficients depend to some extent on temperature [15]. When considering temperature, the form of the regression equation for binary interaction coefficients mainly depends on the actual relationship between the coefficients and temperature for different substances. We considered the distribution of experimental data and conducted a comparative analysis of various equation forms, such as linear equations and quadratic equations, among others. The linear equation was ultimately chosen because it best approximated the actual distribution of the experimental data, as shown in Equation (18).

$$k_{ij} = A + BT \tag{18}$$

where *A* and *B* are the Regression coefficients.

The regression yielded the binary interaction coefficients between methane and alcohol/water molecules, as shown in Tables 5 and 6. It should be noted that, for the purpose of comparing the predictive performance of the new and old association models, the superscript "a" in the table represents the use of the 4C association model for that component, while the superscript "b" indicates the use of the 4F model.

Table 5. The binary interaction coefficients between alcohol and water molecules.

		$k_{ij} = A + BT$			_ # _		N	
Substance 1	Substance 2 –	A	$B imes 10^4/\mathrm{k}^{-1}$	- 17K	P/kPa	AKD(P)%	N <sub>d</sub>	References
MeOH		-0.542	15	323.15~373.15	30~101.3	0.51	38	[16,17]
MEG a,*		-0.231	3.5	252 (4 410.05	E0 100	1.35	22	[10]
MEG <sup>b,*</sup>	H.O	-0.129	2.6	353.64~410.95	50~100	1.17	23	[10]
DEG	1120	-0.172	1.7	353.64~429.60	50~100	1.21	25	[18]
TEG <sup>a,*</sup>		-0.292	2.2	2EE (E 420 (4	E0 100	2.25	20	[10]
TEG <sup>b,*</sup>		-0.251	1.3	355.65~420.64	50~100	1.75	26	

\* <sup>a</sup> is 4C association model; <sup>b</sup> is 4F association model.

	Substance 2 –	$k_{ij} = A + BT$		<b>T</b> ( <b>1</b> /	D/I D		N	<b>D</b> (
Substance 1		A	$B imes 10^4/\mathrm{k}^{-1}$	– 1/K	Р/кРа	AKD(P)%	<sup>IN</sup> d	Keferences
MeOH		0.0487	1.8	283.15~373.15	3~105.1	0.79	33	[19,20]
MEG a,*		0.0498	3	<b>27</b> 0 1 <b>5</b> 200 1 <b>5</b>	0 0 00 (0	1.61		[01 00]
MEG <sup>b,*</sup>		0.0512	2.7	278.15~398.15	0.2~39.62	1.37	44	[21,22]
DEG	$CH_4$	0.1277	1.2	298.15~323.15	3.0~8.0	1.54	48	[23]
TEG a,*		0.1922	-0.9	000 1E 000 1E	0 1 11 11	1.88	•	
TEG <sup>b,*</sup>		0.1782	-0.6	2/3.15~398.15	0.1~41.41	1.57	39	[24,23]
H <sub>2</sub> O		0.5985	21	275.3~444.26	0.97~68.91	0.73	37	[26,27]

Table 6. The binary interaction coefficients between methane and alcohol/water molecules.

\* <sup>a</sup> is the 4C association model; <sup>b</sup> is the 4F association model.

## 4. Results and Discussion

In the previous section, the models for the association of alcohol and water molecules, the mixing rules, and the binary interaction coefficients for alcohol, water, and gas molecules were established. Subsequently, the CPA EoS will be combined with the P-P hydrate formation condition model, and a comparative analysis will be conducted using experimental data to assess the predictive performance of the model for hydrate formation conditions in alcohol-containing systems.

# 4.1. Prediction of Component Fractions in Methane-Alcohol-Water Systems

In the methane-alcohol-water system, there are both cross-association interactions between alcohol and water molecules and self-association interactions of alcohol and water molecules, which significantly affect the accuracy of EOS. Therefore, component fractions will be predicted separately in both the methane-alcohol/water binary system and the methane-alcohol-water ternary system to validate the predictive accuracy of CPA EoS and the applicability of the association model and mixing rules.

#### 4.1.1. Prediction of Component Fractions in Methane-Alcohol/Water Binary Systems

To validate the predictive capabilities of the proposed model for component fractions in the methane-alcohol/water binary system, binary phase equilibrium data for the methane-MeOH/MEG/DEG/TEG/H<sub>2</sub>O systems were collected. Within the temperature range of 273.15 to 444.26 K and pressure range of 0.1 to 106.6 MPa, methane mole fraction in the liquid phase was predicted using the CPA EoS in combination with single-fluid and CR-1 mixing rules. Prediction errors are shown in Table 7, and some computational results are presented in Figure 1. It can be seen that the average relative deviation of the mole fraction of methane in the liquid phase predicted by the proposed model in the methanealcohol/water system ranges from 3.16% to 6.42%. The reason for the significant error is the low solubility of methane in the liquid phase, especially at low pressures, where the deviation is more pronounced. For example, in the methane-MEG system, at a temperature of 398 K and a pressure of 0.33 MPa, the experimental value of methane's molar fraction in the liquid phase is 0.0005, while the predicted value is 0.0007, resulting in only a difference of 0.0002. However, this small difference leads to a relative deviation of 44%. Therefore, except for a few data points at low pressure, CPA EoS exhibits high accuracy in predicting the liquid phase composition for the methane-alcohol/water system. In the methanealcohol system, due to the presence of self-association of alcohol molecules, the suitability of the association model is more critical. For the methane-MEG/TEG systems, the 4F association model demonstrates superior predictive performance.

Multi-Component System	T/K	P/MPa	ARD( <i>x</i> <sub>1</sub> )/%	N <sub>d</sub>	References
$CII (1) M_{2}OII(2)$	298.15~373.15	5.45~106.6	4.27	28	[19]
$CH_4(1)$ -MeOH(2)	283.15~303.15	$5.05 \sim 40.05$	5.02	24	[20]
CII (1) MEC(2)	323.15~398.15	0.2~39.62	4.66 a,*/3.16 b,*	31	[21]
$CH_4(1)$ -MEG(2)	283.29~323.45	5~10.08	5.77 a,*/5.42 b,*	6	[22]
$CH_4(1)$ -DEG(2)	298.15~323.15	3~8	6.54	6	[23]
CII (1) TEC(0)	298.15~398.15	0.1~20.20	4.39 a,*/4.02 b,*	50	[24]
$CH_4(1)$ -1EG(2)	273.15~352.65	3.6~47.21	4.45 a,*/4.11 b,*	40	[25]
	298.15~444.26	2.22~68.91	5.57	73	[26]
$C\Pi_4(1) - \Pi_2O(2)$	275.11~313.11	0.973~18.00	6.42	16	[27]

Table 7. Methane-alcohol/water binary systems liquid phase component fraction prediction errors.

\* a is the deviation calculated using the 4C association model; b is the deviation calculated using the 4F association model.



**Figure 1.** Methane-alcohol system liquid phase component fractions prediction result. (**a**) CH<sub>4</sub>-MEG [21]; (**b**) CH<sub>4</sub>-TEG [25].

#### 4.1.2. Prediction of Component Fractions in Methane-Alcohol-Water Ternary Systems

To validate the predictive capabilities of the proposed model for component fractions in the methane-alcohol-water ternary system, ternary phase equilibrium data for the methane-MeOH/MEG/DEG/TEG-H<sub>2</sub>O systems were collected. Methane molar fractions in the liquid phase were predicted in the temperature range of 278.15 to 342.69 K and pressure range of 0.1 to 46.92 MPa. Prediction errors are shown in Table 8, and some computational results are presented in Figure 2. In the methane-alcohol-water ternary system, the average relative deviation of the model's predictions for methane molar fractions in the liquid phase ranged from 4.14% to 5.25%. This indicates that the model exhibits a high level of accuracy in predicting gas-liquid phase equilibrium in the methane-alcohol-water system. Furthermore, for the gas-liquid phase equilibrium predictions in the methane-MEG/TEG-water ternary systems, the performance of the 4F association model remains superior to the 4C association model.

Multi-Component System	T/K	P/MPa	<b>ARD</b> ( <i>x</i> <sub>1</sub> )/%	N <sub>d</sub>	References
CU(1) M(OU)	298.15~373.15	5.45~106.6	4.27	28	[19]
$CH_4(1)$ -MeOH(2)	283.15~303.15	$5.05 \sim 40.05$	5.02	24	[20]
CII (1) MEC(0)	323.15~398.15	0.2~39.62	4.66 a,*/3.16 b,*	31	[21]
$CH_4(1)$ -MEG(2)	283.29~323.45	5~10.08	5.77 a,*/5.42 b,*	6	[22]
$CH_{4}(1)-DEG(2)$	298.15~323.15	3~8	6.54	6	[23]
CII (1) TEC(0)	298.15~398.15	0.1~20.20	4.39 a,*/4.02 b,*	50	[24]
$CH_4(1)$ -TEG(2)	273.15~352.65	3.6~47.21	4.45 a,*/4.11 b,*	40	[25]
CII (1) II O(2)	298.15~444.26	2.22~68.91	5.57	73	[26]
$CH_4(1)-H_2O(2)$	275.11~313.11	0.973~18.00	6.42	16	[27]

Table 8. Methane-alcohol-water ternary systems liquid phase component fraction prediction errors.

\* a is the deviation calculated using the 4C association model; b is the deviation calculated using the 4F association model.



**Figure 2.** Methane-alcohol-water system liquid phase component fractions prediction result. (a) CH<sub>4</sub>-MeOH-H<sub>2</sub>O [20], (b) CH<sub>4</sub>-TEG-H<sub>2</sub>O [25].

## 4.2. Prediction of Gas-Hydrate Formation Conditions in Gas-Alcohol-Water Systems

Based on the analysis in Section 4.1, it is evident that the combination of CPA EoS with association models and mixing rules provides an effective description of intermolecular interactions in alcohol-containing systems, demonstrating high predictive accuracy for CH<sub>4</sub> component fractions. In this section, we will combine the P-P hydrate formation condition model to evaluate the applicability of the proposed model for predicting hydrate formation conditions in various systems. Furthermore, to comprehensively evaluate the advantages of this model, traditional Peng-Robinson (PR) EoS and SRK EoS will be introduced for comparative analysis. For polar systems, in order to provide more compelling comparative results, the HV mixing rules were introduced into the PR and SRK EoS to replace the van der Waals mixing rules.

#### 4.2.1. Prediction of Gas-Hydrate Formation Conditions in Gas-Water Binary Systems

In the gas-water binary system, a comparative analysis is conducted to assess the predictive accuracy of the PR-HV, SRK-HV, and CPA EOS combined with the P-P model for hydrate formation conditions. We primarily focus on  $CH_4/CO_2$  hydrates and use the hydrate formation condition data measured by Nakano [28], Dyadin [29], and Takenouchi [30] as reference values. Within the pressure range of 13 to 186 MPa, we employed three models to predict the  $CH_4/CO_2$  hydrate formation temperatures. The error analysis is presented in Table 9 and comparison between predicted values and experimental data is depicted in Figure 3. As shown in Table 9, the CPA EOS, which considers molecular

association, exhibits a lower deviation between predicted and experimental values compared to the PR-HV/SRK-HV EOS combined with the P-P model. Due to methane being an inert gas and not participating in molecular association, the primary interaction in the methane-water system is the self-association of water molecules. In Figure 3a, it can be observed that the combination of the PR-HV EOS with the P-P model overestimates the hydrate formation pressure, while the combination of the CPA/SRK-HV EOS with the P-P model both performs well. In Figure 3b, the combination of the PR-HV/SRK-HV state equations with the P-P model exhibits a larger predictive deviation. This indicates that in the  $CO_2$ -H<sub>2</sub>O system, the cross-association between carbon dioxide and water amplifies the computational deviation of these two models. In contrast, the method proposed in this work demonstrates high predictive accuracy in both CH<sub>4</sub>-H<sub>2</sub>O and CO<sub>2</sub>-H<sub>2</sub>O systems.

Table 9. Gas-water binary system hydrate formation condition prediction errors.

Stratom		D/A (D	λŢ		ARD(P)%	D (	
System	17K	P/MPa	IN <sub>d</sub>	SRK-HV	СРА	PR-HV	<ul> <li>References</li> </ul>
CH <sub>4</sub> -H <sub>2</sub> O	296.6~311.6	37~178	12	1.4	1.3	17	[28,29]
CO <sub>2</sub> -H <sub>2</sub> O	284.2~292.7	13~186	13	8.65	5.33	8.82	[30]



**Figure 3.** Comparison between experimental and calculated gas-water binary system hydrate formation conditions. (a) CH<sub>4</sub>-H<sub>2</sub>O [28,29], (b) CO<sub>2</sub>-H<sub>2</sub>O [30].

4.2.2. Prediction of Gas-Hydrate Formation Conditions in Gas-Alcohol-Water Ternary Systems

To comprehensively compare the predictive abilities of the three models for hydrate formation conditions in the "methane-alcohol-water" ternary system, we collected multiple sets of hydrate formation experimental data. The data included four types of alcohol solutions: MeOH, MEG, DEG, and TEG, with alcohol concentrations ranging from 6 to 65 wt%. The comparison between the calculated values and the experimental values is shown in Figure 4, and the calculation errors are presented in Table 10.



**Figure 4.** Comparison between experimental and calculated methane-alcohol-water ternary system hydrate formation conditions. (a) CH<sub>4</sub>-MeOH-H<sub>2</sub>O [31–33], (b) CH<sub>4</sub>-MEG-H<sub>2</sub>O [34–36], (c) CH<sub>4</sub>-DEG-H<sub>2</sub>O [35,37,38], (d) CH<sub>4</sub>-TEG-H<sub>2</sub>O [35,39].

Table 10. Gas-alcohol-water	ternary systems l	nydrate formation	condition prediction errors.
	5 5		*

Alashal True			D/1 (D	N	ARD(P)%			D (
Alconol Type	Concentration/w	rt% 1/K	P/MPa	Nd	SRK-HV	CPA	PR-HV	References
MeOH	6-65	234.5-287.05	2.59-33.92	34	9.34	4.78	9.80	[31–33]
MEG	10-65	247.4-287.1	2.42-16.38	32	3.90	1.93	5.49	[34-36]
DEG	6.6-50	265-283.2	2.35 - 14.50	34	5.16	2.91	4.31	[35,37,38]
TEG	10-50	266.3-293.0	3.17-39.87	32	4.16	1.96	5.62	[35,39]

From Table 10, it can be observed that, even though the HV mixing rules account for the interactions of polar molecules, the average relative deviations of PR-HV and SRK-HV still range from 4.32% to 9.80% and 3.9% to 9.34%, respectively. However, the average relative deviations of the CPA EoS predictions are 1.93% to 4.78%, indicating a significant improvement in accuracy. From Figure 4, it can be observed that the three models generally exhibit consistent predictive trends. The main deviations occur under conditions of high alcohol concentration or elevated pressure. Taking the prediction results of methanemethanol-water system hydrate formation conditions in Figure 4a as an example, at a methanol mass concentration of 65 wt%, all three models have overestimated the hydrate formation pressure. For example, at a temperature of 240.3 K, the experimental hydrate

formation pressure is 10.31 MPa, while the predicted values for the three models, CPA EoS, PR-HV, SRK-HV combined with the P-P model, are 15.16 MPa, 16.41 MPa, and 16.06 MPa. However, in Figure 3b, the prediction errors remain within a normal range, with no sudden significant increase in errors. Furthermore, we examined the sources of the experimental data and found that these data were obtained from different references. Therefore, we believe that the significant prediction errors in Figure 3a may be attributed to experimental errors inherent in the data source. From an overall perspective, the CPA EoS, due to its consideration of molecular association, exhibits better predictive performance.

# 5. Conclusions

This paper introduces a hydrate formation condition prediction model for alcoholcontaining systems, which can be calculated within a unified thermodynamic framework. This model is well-suited for alcohol-containing systems and demonstrates high predictive accuracy in various hydrate inhibitor environments such as MEOH, TEG, and DEG.

- 1. This new model takes into account the impact of molecular association on the vaporliquid equilibrium and hydrate phase equilibrium and successfully describes the influence of molecular association on hydrate formation conditions;
- 2. The proposed model is validated using experimental data in multi-component systems, including alcohol-water, methane-alcohol/water, and methane-alcohol-water, within a temperature range of 273.15 to 444.26 K and a pressure range of 0.1 to 106.6 MPa. With an average relative error ranging from 1.17% to 6.42%, this indicates that the model exhibits high precision in predicting the methane component's mole fraction in the liquid phase. Furthermore, the 4F association model for MEG and TEG exhibits higher prediction accuracy;
- 3. In alcohol-containing systems, the SRK-HV and PR-HV models exhibit an average relative deviation in predicting hydrate formation conditions ranging from 4.32% to 9.80% and 3.9% to 9.34%. In contrast, the proposed model demonstrates a noticeable enhancement in accuracy, with an average relative deviation of 1.93% to 4.78%, which can effectively predict the hydrate formation conditions in alcohol-containing systems;
- 4. In alcohol-containing systems, the proposed model demonstrates superior computational performance under most conditions. However, for conditions with high alcohol concentrations or pressure, significant errors persist. Enhancing the model's applicability in these conditions will be a primary focus of our future work. In addition, comparing the computational times of the various different models may be more beneficial for readers to balance accuracy and computational speed. In future studies, if we encounter more complex models or larger-scale computations, we will certainly include a comparison of computational times to provide a more comprehensive perspective.

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