An insight into the role of the association equations of states in gas hydrate modeling: a review

Feridun Esmaeilzadeh1 · Nazanin Hamedi1 · Dornaz Karimipourfard1 · Ali Rasoolzadeh1

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Abstract
Encouraged by the wide spectrum of novel applications of gas hydrates, e.g., energy recovery, gas separation, gas storage, gas transportation, water desalination, and hydrogen hydrate as a green energy resource, as well as CO₂ capturing, many scientists have focused their attention on investigating this important phenomenon. Of course, from an engineering viewpoint, the mathematical modeling of gas hydrates is of paramount importance, as anticipation of gas hydrate stability conditions is effective in the design and control of industrial processes. Overall, the thermodynamic modeling of gas hydrate can be tackled as an equilibration of three phases, i.e., liquid, gas, and solid hydrate. The inseparable component in all hydrate systems, water, is highly polar and non-ideal, necessitating the use of more advanced equation of states (EoSs) that take into account more intermolecular forces for thermodynamic modeling of these systems. Motivated by the ever-increasing number of publications on this topic, this study aims to review the application of associating EoSs for the thermodynamic modeling of gas hydrates. Three most important hydrate-based models available in the literature including the van der Waals–Platteeuw (vdW–P) model, Chen–Guo model, and Klauda–Sandler model coupled with CPA and SAFT EoSs were investigated and compared with cubic EoSs. It was concluded that the CPA and SAFT EoSs gave very accurate results for hydrate systems as they take into account the association interactions, which are very crucial in gas hydrate systems in which water, methanol, glycols, and other types of associating compounds are available. Moreover, it was concluded that the CPA EoS is easier to use than the SAFT-type EoSs and our suggestion for the gas hydrate systems is the CPA EoS.

Keywords Hydrate · Mathematical modeling · Equation of state · SAFT · CPA · Association EoS

Abbreviations
PR Peng–Robinson
PT Patel–Teja
ANNs Artificial neural networks
ANFIS Adaptive neuro-fuzzy inference system
vdW–P Van der Waals and Platteeuw
PRSV2 Stryjek and Vera modification of Peng–Robinson
BiMSA Binding mean spherical approximation
NRTL Non-random two-liquid

List of symbols
\[ A_{id} \] Free energy of an ideal gas
\[ A_{hs} \] Free energy of a hard-sphere fluid relative to the ideal gas
\[ A_{chain} \] Free energy when chains are formed from hard spheres
\[ A_{disp} \] Contributions to the free energy of dispersion
\[ A_{assoc} \] Contributions to the free energy of association
\[ \rho_n \] Total number density of molecules in solution
\[ d_{ii} \] Hard sphere diameter of segment \( i \)
\[ \sigma_{ii} \] Soft sphere diameter of segment \( i \)
\[ \epsilon_{ii} \] Energy parameter
\[ \sigma_{ij} \] Cross parameter between different segments
\[ \epsilon_{ij} \] Cross parameter between different segments
\[ M_i \] Number of associating sites
\[ X_i^{\alpha} \] Mole fraction of molecule \( i \), not bonded at site \( \alpha \)
\[ \sum_{\alpha} \] Summation over all sites on molecule \( \alpha \)
\[ \sum_j \] Summation over all components

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Feridun Esmaeilzadeh
esmaeil@shirazu.ac.ir

1 Department of Chemical Engineering, School of Chemical and Petroleum Engineering, Shiraz University, Shiraz 71345, Iran
1 Introduction

1.1 Gas hydrates

The framework of water molecules formed by hydrogen bonds may cause the formation of vacant cavities or cages in which small molecules (< 0.9 nm) like small paraffin, CO₂, H₂S, etc. can be hold (“trapped”) and creates crystalline compounds resemble ice named as gas hydrates (Sarshar et al. 2010c; Esmaeilzadeh 2006; Sun et al. 2005). To date, more than 130 gas molecules are known to form hydrate. Indeed, the stabilization of the gas hydrate depends on the van der Waals intermolecular forces between the gas and water molecules. Despite the ice, gas hydrates can be stable at temperatures higher than 273.15 K (Talaghat et al. 2009b; Kvenvolden 1998; Milkov 2004; Taylor and Kwan 2004). Originally, the word “clathrate” stems from the Greek word “Khlatron” which means barrier (Chatti et al. 2005).

Based on previous publications, to compare hydrate stability regions for a variety of hydrate formers, as shown in Fig. 1 the optimum conditions for hydrate formation are investigated. As can be seen, the formation of hydrate is more likely to occur at high pressures and low temperatures. Actually, the left side of each line in Fig. 1 presents the conditions in which the hydrate can be formed, an area with high pressure and/or low temperature (Sloan 2003; Lee et al. 2012).

Figure 1 demonstrates that methane needs extremely higher pressures to form hydrate with respect to propane. Therefore, it can be concluded that according to the type (size) of guest molecules, the nature of the guest molecules, the pressure–temperature conditions, and the number of water molecules involved in the cavities, three different structures of gas hydrate are considered: structure I (sI), structure II (sII), and structure H (sH) (Pauling and Marsh 1952; Claussen 1951; Ripmeester et al. 1987; Talaghat et al. 2009a). The detailed explanations of these structures can be found in previous studies (Sloan 2003; Sloan 2005; Sloan and Koh 2007).

1.2 Effect of inhibitors and promoters

Some problems are arising by hydrate formation, such as obstacles in pipelines, waste of money, safety risks in oil and gas production, transportation, and processing (Afzal...
et al. 2007; Mohammadi et al. 2009b, 2010; Sarshar et al. 2008, 2010c). Therefore, there is a considerable need in the industry to prevent hydrate formation. Alongside various hydrate inhibition methods like heating, pressure reduction (Esmaeilzadeh et al. 2011), and water removal, one of the most useful and applicable ways is to apply gas hydrate inhibitors (Sarshar et al. 2010a). Gas hydrate inhibitors (GHI)s are classified into two big categories: thermodynamic hydrate inhibitors (THIs) and low-dosage hydrate inhibitors (LDHIs). THIs prevent hydrate formation by reducing the activity of water in the aqueous system through intermolecular interactions with water molecules (Mech et al. 2015; Esmaeilzadeh and Fathikalajahi 2009). Some common THIs are sodium chloride, magnesium chloride, methanol, ethylene glycol, etc. (Mohammadi et al. 2009b; Mohammadi and Richon 2010). While THIs affect the thermodynamic conditions of hydrate formation (e.g., temperature and pressure) and make the hydrate stability region smaller, LDHIs influence the induction and nucleation stages by decreasing the hydrate nucleation and growth rate through increasing the gas hydrate formation induction time. Induction time is the time interval between reaching the hydrate formation condition and the formation of the hydrate. As a result, they delay hydrate crystal agglomeration (Bakhtyari et al. 2018; Moeini et al. 2017). During the past years, many polymer chemicals like polyvinylpyrrolidone (PVP) and polyvinylcaprolactam (PVCap) have been investigated, among which biodegradable and environmentally friendly ones are of great importance (Daraboina et al. 2011; Kelland 2006; Ohno et al. 2010; Al-Adel et al. 2008).

On the other hand, hydrate can be taken into account as a useful phase in many applications (Sarshar et al. 2010b). Indeed, it can be used in gas storage (Sun et al. 2003b; Khokhar et al. 1998; Gudmundsson et al. 1994; Ohgaki et al. 1996; Sun et al. 2003a; Lee et al. 2005; Veluswamy and Linga 2013; Aliabadi et al. 2015), transmission (Sun et al. 1996; Sun et al. 2003a; Lee et al. 2005; Veluswamy and Linga 2013; Aliabadi et al. 2015), separation technology (Eslamimanesh et al. 2012b; Kamata et al. 2004; Arjmandi et al. 2007; Nagata et al. 2009; Shiojiri et al. 2004; Tang et al. 2013), energy resource (Collett 2002; Kvenvolden 1993; Makogon et al. 2007; Collett 2004; Chong et al. 2016), CO2 capturing (Kang and Lee 2000; Zhong et al. 2016; Spencer and Currier 2002; Duc et al. 2007; Dickens 2003; Ma et al. 2016; Babu et al. 2016; Zhong et al. 2015; Yang et al. 2015; Sarshar et al. 2009), and solving geohazard problems (Maslin et al. 2010; Kvenvolden 1999; Milkov et al. 2000; Ruppel et al. 2008; Yamamoto et al. 2015). As mentioned, the conditions of hydrate formation are difficult (high pressure and low temperature), and in practical applications, the conditions need to be moderated (Eslamimanesh et al. 2012a). Therefore, promoters appear to be significantly useful chemicals moderating the formation conditions of hydrates (Papadimitriou et al. 2011; Illbeigi et al. 2011; Sloan Jr and Koh 2007; Partoon and Javanmardi 2013; Shahnazar and Hasan 2014; Sabil et al. 2010a; Aliabadi et al. 2015). Overall, one can classify promoters into two essential classifications: thermodynamic and kinetic promoters. As the names suggest, thermodynamic promoters affect the equilibrium conditions of liquid water, hydrate, and vapor (Lw–H–V) and shift it to a higher temperature and lower pressure like tetrahydrofuran (THF), dimethyl cyclohexane, and cyclopentane; however, kinetic promoters cause the hydrate formation to become faster through accelerating the nucleation and growth steps like biosurfactants (Sloan Jr and Koh 2007; Partoon and Javanmardi 2013).

### 1.3 Equation of states for associating fluids

Simple molecules, either organic (e.g., toluene, methyl chloride) or inorganic (O2, CO, N2, N2O, etc.), have a long history of being thermodynamically modeled by many commonly used EoSs, namely Peng–Robinson (PR) (Peng and Robinson 1976), Soave–Redlich–Kwong (SRK) (Soave 1972), and Esmaeilzadeh–Roshanfekr (ER) (Esmaeilzadeh and Roshanfekr 2006). These EoSs only take into account the van der Waals attractions as well as weak electrostatic forces, resulting from dipoles, quadrupoles, etc. The aforementioned cubic EoSs have two parts: the attraction intermolecular force and the repulsion intermolecular force.

On the other hand, many real-world fluids have Columbic, strong polar forces, along with forces together with chain flexibility, induction forces, acid–base interactions, electrolyte solutions, etc. To deal with the associating compounds, the term “chemical theory” has been coined, which means the associating complexes are acted as unique new chemical species. Taking into account the chemical equilibria between the initial components and these complexes leads to new EoSs, reflecting the effect of non-ideal structures of associating fluids (Müller and Gubbins 2001). This idea is the foundation of the development of several molecular-based EoSs from statistical thermodynamics such as different versions of statistical associating fluid theory (SAFT) (Gil-Villegas et al. 1997; Tan et al. 2008; Economou 2002) and cubic plus association (CPA) (Kontogeorgis et al. 1999, 2006a, b). The inevitable existence of water or alcohol-based hydrate inhibitors in any hydrate system is a significant challenge to model these systems using conventional EoSs, which neglect any association interactions. Therefore, the application of newly developed statistical EoSs has been becoming more and more substantial for the thermodynamic modeling of hydrate systems, which is the focus of this study to propose a suitable thermodynamic package for modeling of gas hydrate equilibrium conditions.
1.4 Objective

Whether as a negative phenomenon or a useful application in chemical processes, the thermodynamic modeling and phase behavior of gas hydrate are a vital engineering necessity. Indeed, the prediction of dissociation conditions of the hydrate phase plays a major role in the design of industrial applications regarding gas hydrate. This study aims to address the statistical EoS application for the thermodynamic modeling of gas hydrates and come to a conclusion about the advantages and shortcomings of each approach. Since a variety of models were presented to compute the chemical potential of components in the solid and fluid phases, adequate knowledge on the advantages and shortcomings of each model is of interest and significance. The water vapor pressures at the hydrate equilibrium temperatures (below 350 K) are much lower than the pure or mixed gas vapor pressures. Therefore, the vapor phase primarily consists of gas molecules. Hence, the fugacity of the vapor phase can be simply computed using common cubic EoS and mixing rules. However, the bottleneck of the hydrate equilibrium conditions modeling is to computing the chemical potential or fugacity of the solid and liquid phases. The objective of this work is to introduce several popular novel models that are used for hydrate modeling of systems containing associating compounds. Three important models are reviewed for the hydrate phase, while for the fluid phases the SAFT and CPA EoS along with the cubic EoSs are discussed.

2 Thermodynamic modeling of gas hydrate

The basic deterministic idea to enhance a reliable thermodynamic model anticipating gas hydrate dissociation conditions is the equality of the chemical potential of the components in the three involved phases (i.e., hydrate, gas, and fluid phases). Reviewing the previous publications, the thermodynamic approaches of hydrate systems modeling are categorized into three sections. The equality of the chemical potential and the fugacity, as well as the type of the component (water or other components), are the basis of categorization. More details of the different approaches for gas hydrate modeling can be found in the following subsections.

2.1 The van der Waals and Platteeuw (vdW–P) solid solution theory

The most common and well-known model to calculate the behavior of the hydrate phase is the van der Waals and Platteeuw (vdW–P) (Van der Waals and Platteeuw 2007; Platteeuw and Van der Waals 1959). This statistically based, thermodynamic model is the starting point for many further types of research regarding the hydrate thermodynamic model. In the original work, the equalization of the water chemical potential in all the coexisting phases is considered:

\[ \mu_w^H(T, P) = \mu_w^{liq}(T, P) = \mu_w^V(T, P) \]  

(1)

Since the vapor pressures of water in the hydrate formation temperature ranges are very low, the contribution of water in the vapor phase is neglected. The chemical potential of water in the hydrate phase is calculated as follows:

\[ \mu_w^H = \mu_w^g + RT \sum_{m=1}^{\text{No of cavities}} \theta_m \ln \left( 1 - \sum_{i=1}^{nc} \theta_{mi} \right) \]  

(2)

where \( \theta_m \) and \( \theta_{mi} \), respectively, denote the number of cages of type “m” per water molecules in a hydrate unit cell and the fractional occupancy of the hydrate cavity type “m” by the guest molecule of type “i”. The latter is specified as follows (Sloan Jr and Koh 2007; Van der Waals and Platteeuw 2007):

\[ \theta_{mi} = \frac{C_{mi}f_i}{1 + C_{mi}f_i} \]  

(3)

where \( f_i \) stands for the fugacity of the guest component “i”.

The parameter \( C_{mi} \) represents the Langmuir constant of component “i” and simulates the occupation of the cavity by the guest molecule like the ideal adsorption of gas molecules on the solid surfaces and is formulated as follows:

\[ C_{mi}(T) = \frac{4\pi}{k_BT} \int_0^{R-a} \exp \left( \frac{-W(r)}{k_BT} \right) r^2 dr \]  

(4)

where \( R \) is the radius of the spherical cavity and \( W(r) \) specifies the appropriate potential function for calculation of the intermolecular forces between the gas and water molecules. McKoy and Sinanoğlu (1963) used the three-parameter Kihara potential function and developed the formula for calculation of \( W(r) \) to take into account all the interactions between the gas molecule on the cavity and all the water molecules on the cavity wall, which can be seen in the following equation:

\[ W(r) = 2Ze \left[ \frac{\sigma R^{12}}{R^{11}r} \left( \delta^{10} + \frac{a}{R} \delta^{11} \right) - \frac{\sigma R^6}{R^5r} \left( \delta^4 + \frac{a}{R} \delta^5 \right) \right] \]  

(5)

where

\[ \delta^N = \frac{1}{N} \left( 1 - \frac{r}{R} - \frac{a}{R} \right)^{-N} - \left( 1 + \frac{r}{R} - \frac{a}{R} \right)^{-N} \]  

(6)

Apart from the aforementioned equations, Parrish and Prausnitz (1972) developed an empirical correlation for \( C_{mi} \) calculation. Their equation, which made the process of
calculation much easier, is valid for temperatures between 260 and 300 K. This equation can be shown by the following equation:

$$C_{mi} = \frac{A_{mi}}{T} \exp \left( \frac{B_{mi}}{T} \right)$$  \hspace{1cm} (7)

In Eq. (7), $A_{mi}$ and $B_{mi}$ are optimized constants, which can be found in Parrish and Prausnitz (1972). They also improved the vdW–P model by applying the fugacity of hydrate former instead of its partial pressure to take into account the non-ideality of the vapor phase. It is worth mentioning that the constants were found for most of the components ranging from hydrocarbons to noble gases. Moreover, they introduced a procedure to calculate the hydrate equilibrium conditions for the gas mixtures.

Apart from the aforementioned equation, the water chemical potential difference between the liquid/ice phase and vacant lattice, $\Delta \mu_w^{\beta-L/I}$, is calculated based on the following equation:

$$\frac{\Delta \mu_w^{\beta-L/I}}{RT_0} = \frac{\Delta \mu_w^0}{RT_0} - \int_0^T \frac{\Delta h_w^{\beta-L/I}}{RT^2} dT + \int_0^P \frac{\Delta v_w^{\beta-L/I}}{RT} dP - \ln \left( x_w T w \right)$$  \hspace{1cm} (8)

In Eq. (8), $\Delta \mu_w^{\beta-L/I}$ denotes the chemical potential difference between the vacant lattice and liquid water or ice at reference condition ($101.325$ kPa, $T_0$). $\Delta h_w^{\beta-L/I}$ and $\Delta v_w^{\beta-L/I}$, respectively, represent the volume and enthalpy difference between vacant lattice and liquid water or ice. $P$ is pressure, and the term $x_w T w$ represents the activity coefficient of water in the aqueous solution. Also, $T_0$ represents the temperature at which ice appears and depends on the guest molecules. $\Delta h_w^{\beta-L/I}$ can be measured using the following equation:

$$\Delta h_w^{\beta-L/I} = \Delta h_w^0 + \int_0^T \left( -38.12 + 0.141 \left( T - T_0 \right) \right) dT$$  \hspace{1cm} (9)

Table 1 presents the previous studies on the gas hydrate equilibrium modeling using the vdW–P model.

### 2.2 The Chen–Guo hydrate model

The Chen–Guo hydrate model is in accordance with a two-stage mechanism: first, the formation of hydrate empty cages via a quasi-chemical reaction and second, the adsorption of some gases (with relatively small dimensions) into the cavities, accounting for the non-stoichiometric hydrate properties. As opposed to the vdW–P thermodynamic model, which considers the equality of water in the hydrate and fluid phases, the Chen–Guo hydrate model balances the hydrate former fugacity in the fluid phase and that in hydrate phase as follows (Chen and Guo 1996):

$$f_i^H = f_i^s = f_i^L$$  \hspace{1cm} (10)

$$f_i = f_i^H = x_i f_i^0 \left( 1 - \sum_{j=1}^c \theta_j \right)^\alpha$$  \hspace{1cm} (11)

$$\sum_i x_i = 1$$  \hspace{1cm} (12)

$$\alpha = \frac{\lambda_1}{\lambda_2}$$  \hspace{1cm} (13)

In Eq. (13), $\lambda_1$ and $\lambda_2$ denote the number of small cavities per water molecule and the number of hydrate formers (salt molecules) encaged in the basic hydrate (large cavities) per water molecule, respectively. $f_i$ stands for the fugacity of hydrate former “$i$” in the gas/liquid phase computed by an equation of state, and $x_i$ stands for the mole fraction of gas component “$i$” in the large cavities. $\theta_j$ represents the fraction of small voids occupied by the gas component. It is formulated as:

$$\theta_j = \frac{C_{i,j}}{1 + \sum_k C_{i,k}}$$  \hspace{1cm} (14)

$C_k$ stands for the Langmuir constant, which represents the interactions between the guest and host molecules, and in the Chen–Guo hydrate model, the Antonie-type equation was considered for it:

$$C_k = X_k \exp \left( \frac{Y_k}{T - Z_k} \right)$$  \hspace{1cm} (15)

Here, $X_k$, $Y_k$, and $Z_k$ represent the constants of component “$k$,” which is optimized using the gas hydrate equilibrium data and the values of them have been given in the literature (Chen and Guo 1998).

The symbol $f_i^{0H}$ in Eq. (11) denotes the hydrate former fugacity in an equilibrium state with the unfilled pure basic hydrate “$i$,” manipulated as:

$$f_i^{0H} = f_i^0 \exp \left( \frac{\beta P}{T} \right) a_w^2$$  \hspace{1cm} (16)

$$\beta = \frac{\Delta V}{\lambda_c R}$$  \hspace{1cm} (17)

In Eq. (16), $a_w$ is the activity of water that can be calculated using an appropriate relation for water activity coefficient. It is worth mentioning that, in most cases without a thermodynamic inhibitor or promoter in water, the activity of water is assumed to be equal to unity and for the hydrate inhibitors has the value less than unity.
Table 1 Review of the works using vdW–P model

| Guest component | Fluid phase | Temperature, K | Pressure, MPa | Fugacity of the gas phase | Thermodynamic model description | Fluid-phase thermodynamic model | References |
|------------------|-------------|----------------|---------------|--------------------------|---------------------------------|--------------------------------|------------|
| Pure and mixtures of C₁–C₄ | Aqueous imidazolium ionic liquid solutions | 298.15–333.5 | 10–24 | SAFT2 EoS | Heterosegmented SAFT EOS | Jiang and Adidharma (2013) |
| Pure and mixtures of C₁–C₄ | Water | 244.2–300.15 | 0.041–54.53 | SAFT2 EoS | Equation 13 (ideal fluid, \( a_w = 1 \)) | Jiang and Adidharma (2011) |
| Pure and mixtures of CFC13, HCFC22, HFC23, HFC32, HFC125, HFC141b, HFC152a, HFC143a, and R744 | Water | 271.80–338.19 | 0.056–4.020 | Simplified PC-SAFT | Simplified PC-SAFT | Abolala et al. (2014) |
| Mixtures of noble gases (argon, krypton and xenon) and light hydrocarbons (C₁–C₃) | Water | 90–624 | ~0.01–60.0 | Simplified PC-SAFT | Simplified PC-SAFT | Abolala and Varaminian (2015) |
| Pure and mixtures of CH₄, C₂H₆, C₃H₈, iC₄H₁₀, CO₂, N₂, Ar, O₂ and H₂S | Water | 269.15–320.10 | 0.010–39.700 | PC-SAFT and PR | PC-SAFT and PR | El Meragawi et al. (2015) |
| CO₂, tetrahydrofuran, cyclopentane | Water, tetrahydrofuran, cyclopentane | ~280–294 | 0–4 | CPA | CPA | Herslund et al. (2014a) |
| CO₂, N₂, Cyclopentane | Water | 260–460 | ~0–30 | CPA | CPA | Herslund et al. (2014b) |
| CO₂, N₂, Tetrahydrofuran | Water, tetrahydrofuran | 272.9–285.4 | 1–48 | CPA | CPA | Herslund et al. (2014c) |
| CO₂, N₂ | Water | ~275–283 | ~0–50 | CPA | CPA | Herslund et al. (2012) |
| C₁–C₃ | Water, methanol, glycerol, ethylene glycol, and triethylene glycol | 233.1–293 | 0.18–39.87 | SAFT | SAFT | Li et al. (2006) |
| Methane, ethane, propane, isobutane, carbon dioxide, and hydrogen sulfide | Water, methanol, ethanol, glycerol, NaCl, KCl, CaCl₂, and MgCl₂ | 239.4–315.1 | 0.093–328.8 | PC-SAFT | UNIQUAC | Kondori et al. (2018) |
| Methane, ethane, propane, carbon dioxide, argon, ethene, nitrogen, oxygen, hydrogen sulfide, isobutane, ethyne | Water | 273.15–344.26 | ~0–240 | SAFT-VR Mie | SAFT-VR Mie | Waseem and Alsafi (2018) |
| CH₄, CO₂ | Water | 273.15–299.15 | 1.3–70.0 | SAFT2 | SAFT2 | Hejrati Lahijani and Xiao (2017) |
In Eq. (17), $A_{ij}$ is the binary interaction parameters expressing the interaction between the guest molecules in the small voids and in the large voids; $A'_{i}$, $B'_{i}$, and $C'_{i}$ are the constants of component “i.” The values of them can be optimized or found in the literature (Chen and Guo 1998). Table 2 presents a review of the studies that used Chen–Guo model for modeling of hydrate equilibrium conditions.

2.3 The equalization of water fugacity in the hydrate and fluid phases

Another common approach in hydrate modeling is the equality of the water fugacities in all of the phases. Usually, three phases, i.e., hydrate, hydrocarbon (either gas or liquid), and liquid water, are considered, at the same temperature and pressure. This thermodynamic problem can be formulized as follows (Klauda and Sandler 2000):

$$f^i_w = f^j_w$$  \hspace{1cm} (19)

where the subscript “$w$” represents the water.

As stated, the vdW–P model assumes the equality of the chemical potential of water in the hydrate and fluid phases. Using the vdW–P expression of chemical potential, the fugacity of water in the hydrate phase is calculated as follows:

$$f_w^H = f_w^\theta \exp \left[ \frac{(\mu_w^H - \mu_w^\theta)}{RT} \right]$$  \hspace{1cm} (20)

In Eq. (20), $f_w^\theta$ is the fugacity of empty hydrate lattice. The fugacity of water in the gas and liquid phases is computed using the EoS.

Based on phase equilibrium and by using different methods predicting fugacities, many more-or-less complex modeling approaches have been developed (Table 3).

3 Results

Chocked up pipelines by hydrate were the main reasons for starting researches about hydrate formation. Afterward, its applications, such as gas storage and CO$_2$ capturing, were discovered, and researchers became more interested in investigating the hydrate formation and dissociation conditions. Indeed, in some cases hydrate formation is very beneficial, whereas sometimes it has disadvantages; either way, this research topic is of great importance (Shahnazar and Hasan 2014; Chen and Guo 1996; Parrish and Prausnitz 1972). Inspired by Sloan (2005), Fig. 2 shows the increasing rate
of the number of publications in the twentieth century. As can be seen, the number of publications each year had an increasing manner until 2010, when it started to oscillate.

As mentioned, thermodynamic modeling of gas hydrates is one of the most important engineering topics, with lots of applications in oil, gas, and chemical industries. The first statistical EoS used to model these systems was the SAFT EoS. Li et al. (2006) suggested the SAFT in conjunction with the vdW–P to predict the behavior of single hydrates (C1–C3, and CO2) in the presence of methanol and glycercyl as hydrate inhibitors. However, CPA application for the vapor–liquid equilibria (VLE) (Folas et al. 2006) and liquid–liquid equilibria (LLE) (Oliveira et al. 2007) of natural gas hydrate composition has been investigated before 2007; Kontogeorgis et al. (2007) were the first ones to combine CPA EoS with the vdW–P model and suggested reliable models for the phase behavior of water, alcohols, and natural gas components.

Tavasoli et al. (2016) investigated the influence of cyclic hydrocarbons (i.e., benzene and cyclohexane) on the methane and CO2 hydrates. They implemented the fugacity-based model, in which Valderrama–Patel–Teja (VPT) EoS [with non-density-dependent (NDD) mixing rule] (Valderrama 1990) and Statistical Associating Fluid Theory EoS presented by Huang and Radosz (SAFT-HR) (Huang and Radosz 1990, 1991) were compared. They investigated the four systems of methane + benzene + water, methane + cyclohexane + water, CO2 + benzene + water, and CO2 + cyclohexane + water and, respectively, reported the error of 8.09, 8.42, 6.18, and 13.25 for the SAFT-HR EoS, corresponding to 9.37, 6.95, 3.99, and 15.35 for VPT EoS. Their obtained outcomes are shown in Fig. 3. As can be seen, the two EoSs generally led to almost the same results; however, the SAFT-HR superiority at high pressures is quite visible. It is worth mentioning that due to the consideration of associating term in SAFT-HR, it is expected to result in more reliable predictions; nonetheless, in some cases, VPT EoS even provided more accurate results. This can be attributed to the fact that the introduction of the fitting parameters in the mixing rule (non-density-dependent) of VPT EoS compensated its weaknesses.

In order to compare the error of the SAFT EoS with that of some non-associating EoSs, the value of errors corresponding to various EoSs for systems of pure natural gas hydrates (C1–C3, CO2, H2S), their combination with alcohols and electrolytes are tabulated in Table 4. As can be seen, for the pure gas system, the SAFT EoS is not the most accurate one. However, it results in a lower error in the cases of the existence of alcohols and electrolytes.

Several factors influence the hydrate equilibrium calculations including: the hydrate model selection, the appropriate EoS selection, type of hydrate former, existence of inhibitors

| System components | Fluid phase | Temperature, K | Pressure, MPa | Gas-phase fugacity | Fluid phase | References |
|-------------------|-------------|----------------|---------------|-------------------|-------------|------------|
| CH4               | Water       | 275.5–299.7    | 0.5–4.6       | CPA               | CPA         | ZareNezhad and Ziaee (2013) |
| CH4, CO2, H2S     | Water       | ~250–295       | 0.10–100.1    | CPA               | CPA and UNIFAC for activity | Sinehbaghizadeh et al. (2019) |
| Methane, ethane, propane, carbon dioxide, hydrogen sulfide, nitrogen, hydrogen, krypton, xenon, and methyl fluoride | Water       | 274–292        | 2–20           | CPA (Patel–Teja for physical term) | CPA (Patel–Teja for physical term) | Ma et al. (2013) |
Table 3  Review of the works using equality of fugacity approach

| Guest component | Fluid phase | Temperature, K | Pressure, MPa | Fugacity of water in hydrate phase | Thermodynamic model description | References |
|-----------------|-------------|----------------|---------------|-----------------------------------|----------------------------------|------------|
| CH$_4$, CO$_2$, and H$_2$S | Water | 273–300 | 0.1–1.6 | vdW–P | Improved CPA | Li et al. (2016) |
| C$_1$–C$_4$ CO$_2$ | Water | 233.1–293 | 0.18–39.87 | vdW–P | SAFT | Li et al. (2006) |
| Binary mixtures of CO$_2$, H$_2$, H$_2$S, N$_2$, and C$_1$–C$_4$ | Water | 273.4–295.2 | 0.2068–34.33 | vdW–P | SAFT for the gas and liquid phases | Li et al. (2007) |
| C$_1$–C$_4$ N$_2$ CO$_2$ | Water | 250.55–288.55 | 5–40 | vdW–P | CPA for the gas and liquid phases | Chapoy et al. (2010) |
| Methane | Water | 239.45–290.2 | 2.021–36.343 | vdW–P | CPA for the gas and liquid phases | Haghighi et al. (2009a) |
| Natural gas (mixture of C$_1$–C$_5$, CO$_2$, N$_2$) | Methanol | 258.85–293.95 | 1.855–37.448 | vdW–P | CPA for the gas and liquid phases | Haghighi et al. (2009b) |
| Methane | Ethylene glycol | 253.15–283.15 | 5.0–40.0 | vdW–P | Both VPT and CPA for the gas and liquid phases | Rod Burgass et al. (2011) |
| Three mixtures of methane, ethane, and CO$_2$ | Water | 254.5–294.4 | 0.149–1.385 | vdW–P | CPA | Ngema et al. (2019a) |
| Fluorinated refrigerant | (NaCl or CaCl$_2$ or MgCl$_2$) + cyclopentane | 261.1–287.2 | 0.813–3.239 | vdW–P | CPA | Ngema et al. (2019b) |
| CO$_2$ | Water | 270.71–573.15 | 0.1–55 | vdW–P | CPA | Chapoy et al. (2013) |
| CH$_4$ C$_2$H$_6$ C$_3$H$_6$ C$_3$H$_8$ | MEG–H$_2$O–NaCl, MEG–H$_2$O–CaCl$_2$, MEG–H$_2$O–MgCl$_2$, MEG–H$_2$O–KCl and MEG–H$_2$O–NaBr | 248.25–313.15 | 3.42–24.74 | vdW–P | CPA and Debye–Hückel activity coefficient | Chapoy et al. (2012b) |
| Natural gas (C$_1$–C$_5$, CO$_2$, and N$_2$) | Water | 273.6–281.7 | 2.032–17.628 | vdW–P | CPA | Mahabadian et al. (2016) |
| Chlorodifluoromethane and 1,1,1,2-tetrafluoroethane | Water | 278–290 | 0.2–0.8 | vdW–P | CPA, (SRK and are also considered) | Karamoddin and Varaminian (2013) |
| Natural gas (C$_1$–C$_5$, CO$_2$) | Water | 200–285 | Up to 40 | vdW–P | PC-SAFT | Fouad et al. (2015) |
| CH$_4$, CO$_2$ | Water | 273.97–291.58 | 0.684–9.486 | vdW–P | VPT + NDD and SAFT-HR EOSs | Tavasoli and Feyzi (2016) |
| C$_1$–C$_5$, CO$_2$, N$_2$ | Water, monoethylene glycol (MEG), sodium bromide, sodium chloride | ~260–310 | Up to 150 | vdW–P | SRK, CPA-modified Debye–Hückel electrostatic term | Burgass et al. (2018) |
| System conditions                        | Guest component                          | Fluid phase | Temperature, K | Pressure, MPa | Fugacity of water in hydrate phase | Thermodynamic model description | References                  |
|-----------------------------------------|------------------------------------------|-------------|----------------|---------------|-----------------------------------|---------------------------------|-----------------------------|
|                                         | CO₂ + (N₂ or CH₄ or O₂ or Ar or CO)      | Water       | 264.1–288.55   | 1.72–55.11    | vdW–P                             | CPA                             | Chapoy et al. (2015)         |
|                                         | H₂                                       | Water, methyl tert-butyl ether methyl cyclohexane | 269–280       | 60–100        | vdW–P                             | CPA                             | Martín and Peters (2009)     |
|                                         | C₁–C₆, H₂S, CO₂                           | Water, MEG  | 258.15–298.15  | 2.0–40.0      | vdW–P                             | SRK, CPA                        | Boesen et al. (2017)         |
|                                         | C₁–C₆, CO₂, N₂                           | Water       | 273.15–238.15  | 3.45–13.79    | vdW–P                             | CPA                             | Zhang et al. (2011)          |
|                                         | C₁–C₃, CO₂                               | Water       | 272.8–280.2    | 1.3–7         | vdW–P                             | CPA                             | Youssef et al. (2009)        |
|                                         | CH₄                                      | Water, NaCl, KCl, and MgCl₂ | 268.55–287.38 | 3.93–24.78   | vdW–P                             | CPA                             | Haghighi (2009)              |
|                                         | Methane, ethane, propane, isobutane, carbon dioxide, nitrogen, and hydrogen sulfide | Water, methanol, ethanol, monoethylene glycol, calcium chloride, sodium chloride, and potassium chloride | 250.5–320.5   | ~0–150        | vdW–P                             | CPA                             | Sirino et al. (2018)         |
|                                         | CO₂                                      | Water       | 253.15–277.15  | 13.9          | vdW–P                             | CPA, Valdenara–Patel–Teja, and SRK | Chapoy et al. (2012a)         |
|                                         | CO₂–N₂ and CO₂–CH₄                       | Water       | 278.1–285.3    | 3.24–29.92    | vdW–P                             | CPA                             | Sfaxi et al. (2012)          |
|                                         | R-134a, R-141b, and R-152a               | Water       | ~273–288       | ~0–0.450      | vdW–P                             | CPA                             | Nikbakht et al. (2012)       |
|                                         | CO₂, C₁–C₃, N₂                           | Water       | ~245–294       | ~3–25         | vdW–P                             | CPA                             | Karakatsani and Kontogeorgis (2013) |
Fig. 2 Number of publications related to hydrate from 2000 until 2019

Fig. 3 Comparison of the experimental data (Sun et al. 2002; Tohidi et al. 1996; Tavasoli and Feyzi 2016; Danesh et al. 1993; Mohammadi et al. 2009a; Tavasoli and Feyzi 2016; Mooijer-van den Heuvel et al. 2001) and the predictions of SAFT-HR and VPT EoSs (Tavasoli and Feyzi 2016) for the effect of cyclic hydrocarbons on the methane and CO₂ gas hydrates
and promoters in the system, and choosing the proper statistical or empirical relations for calculation of the Langmuir constants. In the thermodynamic modeling of hydrate equilibrium conditions, two approaches are used in the literature. The first approach is the chemical potential-based approach introduced with the van der Waals-Platteeuw (vdW–P) model, and the other one is the fugacity-based approach proposed by Klauda–Sandler and Chen–Guo. There is also a significant difference between the fugacity-based model proposed by Klauda and Sandler and that obtained by Chen–Guo. The basis of the Klauda–Sandler model is the equality of water chemical potential in all coexisting phases, while the basis of the Chen–Guo model is the equality of the hydrate formers fugacities in all phases. Moreover, the vdW–P ignores the contribution of water in the vapor phase because of its low vapor pressures at the hydrate formation temperature range. Therefore, several models with various assumptions are available and the sensitivity analysis can be applied for one model, for example, the vdW–P model. In Table 5, as a case study, we compared the average absolute relative deviation in calculated pressures of the PC-SAFT EoS and the PR EoS for the same gases, the same hydrate model (vdW–P), and the same Kihara parameters (Sloan Jr and Koh 2007).

### Table 4 Comparison of the error resulting from different EoSs for natural gas hydrate, with and without alcohols and electrolytes

| Study | AADP, %<sup>a</sup> |
|-------|----------------------|
| Pure gases (C<sub>1</sub>–C<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>S) | |
| vdW–P model: fugacities and activity were, respectively, calculated using SAFT EoS, and UNIQAC (Kondori et al. 2018) | 2.1748 |
| Chen-G model: fugacities and activity were, respectively, calculated using SRK EoS, and UNIQAC (Delavar and Haghtalab 2014) | 1.521 |
| Fugacity-based model: using henry law and modified UNIFAC, respectively, to calculate gases solubility and aqueous-phase activity (Klauda and Sandler 2003) | 5.65 |
| vdW–P model: using Peng–Robinson for fugacity calculation (Zhang et al. 2006) | 2.88 |
| Fugacity-based model: using the Stryjek and Vera modification of Peng–Robinson EoS to calculate fugacities (Khosravani et al. 2012) | 2.66 |

| Study | AADT, %<sup>b</sup> |
|-------|----------------------|
| Pure gases (C<sub>1</sub>–C<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>S) & alcohols (methanol, ethanol, glycerol) | |
| vdW–P model: fugacities and activity were, respectively, calculated using SAFT EoS, and UNIQAC (Kondori et al. 2018) | 0.183 |
| vdW–P model: using Peng–Robinson and Aasberg-Petersen model, respectively, for fugacity and water activity calculation (Javanmardi et al. 2001) | 0.478 |
| Using modified Patel–Teja EoS for simplified Holder-John multi-shell hydrate model (Zuo et al. 1996) | 0.865 |
| Pure gases (C<sub>1</sub>–C<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>S) and electrolytes (NaCl, KCl, CaCl<sub>2</sub>, and MgCl<sub>2</sub>) | |
| vdW–P model: fugacities and activity were, respectively, calculated using SAFT EoS, and UNIQAC (Kondori et al. 2018) | 0.1 |
| Fugacity-based model: using the Stryjek and Vera modification of Peng–Robinson EoS and COSMO-SAC activity coefficient to describe the fluid phases and vdW–P to describe the hydrate phase (Hsieh et al. 2012) | 0.18 |
| Fugacity-based model: using the Stryjek and Vera modification of Peng–Robinson EoS and COSMO-SAC activity coefficient to describe the fluid phases and vdW–P to describe the hydrate phase (Chin et al. 2013) | 0.16 |

<sup>a</sup>Average absolute deviation in pressure (AADP)

<sup>b</sup>Average absolute deviation in temperature (AADT)

### Table 5 Comparison between the average absolute relative deviation of calculated pressures for the PC-SAFT EoS and the PR EoS (El Meragawi et al. 2015)

| Hydrate former | PC-SAFT | Peng–Robinson |
|----------------|---------|---------------|
| Methane        | 11.12   | 6.86          |
| Ethane         | 19.97   | 20.05         |
| Propane        | 4.97    | 4.90          |
| Isobutane      | 1.04    | 1.17          |
| O<sub>2</sub>   | 57.68   | 64.25         |
| N<sub>2</sub>   | 2.64    | 6.61          |
| H<sub>2</sub>S  | 3.46    | 5.49          |
| Average        | 14.35   | 15.63         |
| Methane + propane | 9.69   | 13.40         |
| Methane + N<sub>2</sub> | 11.10  | 8.61          |
| Methane + H<sub>2</sub>S | 8.38   | 8.35          |
| Propane + N<sub>2</sub> | 13.96  | 15.55         |
| Average        | 14.58   | 11.28         |
| Methane + N<sub>2</sub> + CO<sub>2</sub> | 1.52   | 3.82          |
| Methane + H<sub>2</sub>S + CO<sub>2</sub> | 26.03  | 14.85         |
| Methane + ethane + propane | 13.62 | 6.46          |
| Methane + ethane + N<sub>2</sub> | 21.85  | 15.39         |
| Methane + propane + isobutane | 7.21   | 7.97          |
| Average        | 14.05   | 9.70          |

To verify the inhibition effect of monoethylene glycol,
Boesen et al. (2017) suggested a fugacity-based model for C1, CO2, and H2S hydrate systems. They compared the results of CPA and SRK EoSs and reached almost the same results. Moreover, chapoy et al. (Chapoy et al. 2012a) conducted an experimental and modeling assessment to investigate the phase behavior of CO2 + water system. Considering the fugacity-based model, they compared the performance of CPA, SRK [with Huron–Vidal (HV) (Huron and Vidal 1979) mixing rules], and VPT [with NDD (Valderrama 1990; Avlonitis et al. 1994; Wong and Sandler 1992) mixing rule]. They came to the conclusion that VPT + NDD model resulted in the highest accuracy, followed by CPA, and SRK + HV models. Implementing the fugacity-based model, Karamoddin and Varaminian (Karamoddin and Varaminian 2013) addressed the capability of three EoSs, namely SRK, VPT, and CPA, for the prediction of refrigerants hydrate dissociation condition. Figure 4 provides a visual comparison of the performance of these three EoSs for HCFC22 hydrate. As can be seen, the three approaches led to acceptable errors. Indeed, the average error of SRK, VPT, and CPA was reported to be 2.8, 3.2, and 3.0 percent, respectively. This implies that the associating term of CPA was not able to provide the most accurate results.

In order to compare the popularity of the CPA and SAFT EoSs, Fig. 5 is depicted. In general, the number of studies related to CPA is higher. As can be seen, in some of the years (e.i. 2009, 2010, and 2012) the SAFT was not the case of study at all. Moreover, the highest number of publications about CPA was published in 2019, whereas the SAFT EoS was not considered in any publication in 2019. One can consider the complexity of the SAFT EoS for this observation. To fully investigate the reason for this, we need to assess the type of gas hydrates along with the chemical formula of the promoters and inhibitors. Thus, Fig. 6 is plotted.

As Fig. 6 exhibits, most of the applications of statistical EoSs are related to natural gas hydrate. It is worth mentioning that usually a mixture of C1–C5, CO2, N2, Ar, H2S, O2, CO is considered as a synthetic natural gas. Figure 6b demonstrates the number of publications using the CPA and SAFT EoSs for different types of components including ILs, electrolytes, surfactants, alcohols, and other hydrocarbons. The number of publications implementing CPA is more significant in almost all of the cases, even for electrolyte mixtures. Kontogeorgis et al. (2007) stated that CPA and SAFT result in similar predictions for mixtures of water and alcohols (methanol, MEG, and TEG). Also, using the CPA EoS leads to negligible errors for electrolyte mixtures (Chapoy et al. 2012b; Ngema et al. 2019a, b).

4 Conclusions

In this study, different approaches using statistical EoSs for predicting hydrate dissociation conditions have been reviewed. According to the fact that hydrate has many novel, promising applications, its modeling has gained much attention. Indeed, as the models get developed, they are more sophisticated in order to more accurately predict the phase behavior of hydrates. Moreover, because of the existence of water along with promoters, inhibitors, or even impurities in the system, applying statistical thermodynamic equations of states is of great importance. According to the previous publications, CPA is more popular than SAFT. This can be attributed to the fact that it is more facile and yet completely
reliable. In addition, this study reveals that even though using a complex associating EoS, such as SAFT or CPA, contributes to slightly better results (e.g., for systems containing alcohols or electrolytes), it does not necessarily guarantee more accurate predictions in all of the cases. Indeed, the introduction of adjustable parameters in the mixing rule of non-associating EoSs overcomes their weaknesses, making them proper options for thermodynamically model such polar systems.

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