



Modeling phase equilibrium with a modified Wong-Sandler mixing rule for natural gas hydrates: Experimental validation



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HIGHLIGHTS

- Phase equilibrium models are developed for natural gas hydrates.
- A modification is proposed in Wong-Sandler (mWS) mixing rule.
- Proposed models are validated with experimental data.
- Patel-Teja model with mWS shows the best performance.

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ABSTRACT

As natural gas hydrate forms at low temperature and high pressure (i.e., near critical region), vapor phase fugacity calculation becomes crucial in this region due to the intermolecular interactions. This work introduces the modified form of the Wong-Sandler mixing rule in the Peng-Robinson (PR) and Patel-Teja (PT) equation of state (EoS) models to revamp the fugacity calculation of vapor phase. This mixing rule which is based on the excess Gibbs free energy leads to precisely capture the polar and asymmetric properties of mixture components. The modified Wong-Sandler mixing rule is formulated by representing its correction factors for energy and co-volume parameters in terms of temperature and gas-phase composition. Here, the hydrate phase fugacity is determined by the Chen-Guo model that is coupled with an EoS model for hydrate equilibrium analysis. On the other hand, the liquid phase nonideality is estimated by using the Wilson activity-coefficient model. The proposed modified Wong-Sandler based phase equilibrium models are shown to be better than the existing phase rule based models with the three example natural gas hydrate systems ($\text{CH}_4 + \text{N}_2$, $\text{CH}_4 + \text{C}_2\text{H}_6$, $\text{CH}_4 + \text{C}_2\text{H}_4$) using tetrahydrofuran as a thermodynamic promoter. Validating these models with real time data sets, it is further investigated that the PT based model shows a better performance compared to the PR equation of state. This apart, these two models show their superiority over the existing PT-van der Waals (PT-vdW) model, for which, a new parameter set is proposed for the said three systems for their improved performance.

1. Introduction

The world is prone to the shortage of energy urging an enormous amount of fuel in upcoming decades. It is expected that the conventional fuels will continue to supply 80% of the fuel demand that could be liable to another major issue concerning global warming [1,2]. As a bridge fuel between conventional and green energy sources, the natural gas hydrates (NGH) could provide a promising solution for these mutually associated problems of fuel demand and global warming [3,4]. This could be achieved by replacing the methane (CH_4) encaged in the hydrates at sea-floor with the greenhouse gases like carbon dioxide (CO_2) [5,6]. Besides, the technique of entrapment of huge amount of

gases into a compact form in the hydrates have a major application in the field of gas storage and transportation [7]; separation [8], desalination of water [9], CO_2 sequestration [10], refrigeration [11] and so forth. The gas hydrates are first discovered in 1811 as an inclusion compound in which the water molecules form a known ice-like crystalline structure. This tricky solid solution makes itself thermodynamically stable by encapsulating the small gas molecules into the cavities formed by water molecules [1,6]. The nature of guest-gas molecules decides the structure of gas hydrate that are termed as structure I (sI), structure II (sII) and structure H (sH). The details about structure of gas hydrate and mechanism of hydrate formation are well known [4].

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In general, the formation pressures of fuel gas hydrates are very high and it is not desirable in concern with the safety and economy of the fuel gas storage and transportation system. Some organic compounds such as tetrahydrofuran (THF), cyclopentane, aldehydes, ketones, and so on, lead to form the gas hydrate at atmospheric pressure and moderate temperature range [12,13]. These compounds dramatically lower down the gas hydrate formation pressure when added to the liquid phase and hence, are termed as thermodynamic promoters. Among the various categories of promoters, the THF solution is reported to have highest stabilization effect [12]. Pahlavanzadeh et al. [13] have demonstrated the effect of different promoters for methane gas hydrates and found the tremendous reduction in hydrate formation pressure with THF over other promoters. On the other hand, there are some organic and inorganic compounds that lead to elevate the gas hydrate formation pressure when present in the system and hence, termed as inhibitors [14]. For instance, the salt content in sea water inhibits the hydrate formation [15]. A large category of promoters and inhibitors are utilized in the actual application of the gas hydrate technique to fairly tune up the gas hydrate formation or dissociation conditions [16].

As the natural gas is relatively clean-burning fuel, the researchers have paid much attention towards developing a model for NGH energy generation unit [2–6,16]. The aim is to develop a model for bulk phase prior to the real system that can further accommodate the inherent properties of saline and sediment environments [17,18]. There are certain challenges associated with the efficient operation and automation of the NGH energy generation system, storage and transportation of fuel gases. In order to overcome these challenges, the time-independent (thermodynamic) hydrate quantification is focused [4]. However, the advancements in thermodynamic models for accurate prediction of the formation condition of gas hydrates are lacking in the literature as compared to the abundant experimental data for phase equilibrium of natural gas hydrates.

The basic thermodynamic model is proposed by van der Waals and Platteeuw, which uses statistical thermodynamics to derive the hydrate phase model [19]. However, the thermodynamic predictions are crucial in case of gas mixtures due to the hydrate structure transition [20,21]. The modern spectroscopy enabled more accurate predictions for gas mixtures through the bridge of statistical thermodynamics. Uchida et al. [22] have examined the methane and ethane hydrate properties using Raman spectroscopy, X-ray diffraction and gas chromatography to divulge the mechanism of structure transitions and the cage occupancy through Gibbs free energy calculation. Chen and Guo [23] have proposed a more realistic approach to thermodynamic modeling of gas hydrate. The local stability is considered in their model with a better estimation of coordination number. Meanwhile, Klauda and Sandler [24] have derived a fugacity-based model replacing the reference energy parameter calculation and thus reducing the empirical relations. However, the Chen-Guo model has better fascinated the researchers with the simplified calculation of chemical potential and Langmuir constants [23]. The phase equilibrium conditions are obtained by equating the hydrate phase fugacity calculated in the Chen-Guo model to the vapor phase fugacity. Since the hydrate formation occurs above the critical point, the ϕ – ϕ approach (i.e., equation of state (EoS)) is common for predicting the vapor-liquid equilibria (VLE) and frequently used in vapor phase fugacity calculation. Among various equations of state, the Peng-Robinson (PR) [13,25] and the Patel-Teja (PT) [26,27] models are extensively adopted. The PR equation of state assumes fixed value of critical compressibility factor that results in deviation of predicted values of densities of the saturated liquid and critical volumes from their experimental values [26]. In order to address these issues, Patel and Teja [26] have incorporated two additional parameters along with critical temperature and pressure to ensure that the energy parameter approaches a zero value ($a \rightarrow 0$) at high temperatures. In addition, they gave critical compressibility factor as an empirical dependency on the acentric factor. The PR-EoS and PT-EoS both have

wide application in pure and mixture gas hydrate systems [13,25–29].

Modeling phase equilibrium for mixture-gas hydrates requires the appropriate mixing rule to determine the mixture parameters that are dependent on the individual component property. The most common mixing rule which has been used for gas hydrate systems is the van der Waals one-fluid type mixing rule [29]. This is widely applicable for non-polar mixtures but it fails to determine the properties of polar and asymmetric component mixtures [30]. The other category of mixing rules, which are made to capture the polar mixture properties, are based on excess Gibbs free energy (G^E) and commonly known as G^E -type mixing rules. They include the Huran-Vidal [31], Kurihara [32], modified Huran-Vidal [33], linear combination of Vidal and Michelson (LCVM) [34] and the Wong-Sandler [30] mixing rules. Amongst, the Wong-Sandler (WS) mixing rule has gained much attention for its accuracy in prediction of phase equilibrium for strongly nonideal mixtures. The Helmholtz free energy considered in the WS mixing rule ensures the quadratic dependence of second virial coefficient on the composition of gas components as required by statistical thermodynamics [30]. Also, the Helmholtz free energy at infinite pressure is approximated as Gibbs free energy at zero pressure [30]. It is worth noticing that the G^E -type mixing rules are immensely used in VLE calculation [35,36] but not in a common practice for predicting gas hydrate formation conditions [37].

As a brief look into the literature for predictions of the NGH formation conditions, the thermodynamic models have undergone successive modifications over the basic models [38]. Chen and Guo [23] have presented the new approach to model the phase equilibrium of gas hydrates using the concepts reported in their previous work [23]. They have illustrated their model for natural gas hydrate having hydrocarbons of different chain length. The predictions for hydrate formation temperature are found in a good competence with the prediction made by Barken and Shenin [23]. Subsequently, Klauda and Sandler [24] have proposed a fugacity based model using the basic of van der Waals and Platteeuw (vdW-P) model and identified the parameters for natural gas hydrates in the THF solution [39]. They have reported the improved predictions with their model over the classical vdW-P model [39]. The extension of the Chen-Guo model for ternary system of sour natural gas hydrate is presented by Sun et al. [40]. Further as a modification in mixing rule for vapor phase fugacity calculation, Ma et al. [32] have configured the Chen-Guo model with the PT equation of state that was complied with Kurihara mixing rule. The model is illustrated with different inhibitor containing systems showing better prediction of gas solubility over the model using the van der Waals mixing rule [32]. It should be noted that the more accurate G^E -type Wong-Sandler (WS) mixing rule is rarely applied to the prediction of gas hydrate formation conditions. Djavidnia et al. [37] have demonstrated the WS mixing rule with the PR-EoS for $\text{CH}_4/\text{CO}_2/\text{CH}_3\text{OH}$ system. However, based on our knowledge, there is no work published concerning the use of the WS mixing rule in THF based hydrates. Furthermore, the WS mixing rule with the three-parameter PT-EoS has not been formulated so far for any gas hydrate system. In this context, we introduce a modification in the classical Wong-Sandler mixing rule. The proposed approach concerns the formulation of second virial coefficient as it is vital for calculating the mixture parameters introducing correction factors, namely k_{ij} and l_{ij} , for the mean-value approximation of the mixture parameters, namely energy (a) and co-volume (b) parameter respectively. Those factors are expressed as a linear function of temperature and vapor phase composition. This modified WS mixing rule is then compiled with the PR and PT equation of state models and proposed to use in the Chen-Guo model for phase equilibrium analysis of the gas hydrates. To validate these models, we use experimental data sets of the $\text{CH}_4/\text{N}_2/\text{THF}$ (System I) [27], $\text{CH}_4/\text{C}_2\text{H}_6/\text{THF}$ (System II) [28], and $\text{CH}_4/\text{C}_2\text{H}_4/\text{THF}$ (System III) [41]. Showing the superiority of the proposed modified (mWS) mixing rule over the existing WS and classical vdW in terms of average absolute relative deviation (AARD), it is investigated that the mWS based PT and PR equation of state models outperform the

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