

New insight into prediction of phase behavior of natural gas hydrate by different cubic equations of state coupled with various mixing rules

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Abstract Progress in hydrate thermodynamic study necessitates robust and fast models to be incorporated in reservoir simulation softwares. However, numerous models presented in the literature makes selection of the best, proper predictive model a cumbersome task. It is of industrial interest to make use of cubic equations of state (EOS) for modeling hydrate equilibria. In this regard, this study focuses on evaluation of three common EOSs including Peng–Robinson, Soave–Redlich–Kwong and Valderrama–Patel–Teja coupled with van der Waals and Platteeuw theory to predict hydrate P – T equilibrium of a real natural gas sample. Each EOS was accompanied with three mixing rules, including van der Waals (vdW), Avlonitis non-density dependent (ANDD) and general non-quadratic (GNQ). The prediction of cubic EOSs was in sufficient agreement with experimental data and with overall AARD% of less than unity. In addition, PR plus ANDD proved to be the most accurate model in this study for prediction of hydrate equilibria with AARD% of 0.166. It was observed that the accuracy of cubic EOSs studied in this paper depends on mixing rule coupled with them, especially at high-pressure conditions. Lastly, the present study does not include any adjustable parameter to be correlated with hydrate phase equilibrium data.

Keywords Gas Hydrate · Cubic equation of state · Mixing rule · Thermodynamic modeling

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1 Introduction

1.1 Significance of cubic equations of state (EOS) for modeling hydrate equilibria

Thermodynamic of clathrate hydrates has been one of the most intriguing subjects of research in the current and past century (Peng et al. 2010). Generally speaking, hydrate is a snow-like solid, forming spontaneously at high pressure and low temperature by contact of low molecular weight gas species and water molecules (Chen et al. 2009). Although main research works on hydrate have been commenced after observing blockage of gas flow lines by Hammerschmidt (1934), however, fast growth of publications implies interest of scientists in this subject (Shahnazar and Hasan 2014; Dehaghani and Badizad 2016a; Shadman et al. 2016). On the one hand, petroleum industry has been suffered from economic and technical issues associated with hydrate formation during natural gas transmission, and on the other hand, broad advantages such as gas storage and separation show promising side of hydrates (Lucia et al. 2014; Dehaghani and Badizad 2016b). As a beneficial aspect, geologists estimated huge source of natural gas trapped in hydrate form at deep oceans and permafrost. Exploitation of such reserves could mitigate energy crisis in near future (Badizad et al. 2016; Dehaghani and Badizad 2016c). Also, hydrate is a safe form of gas storage, particularly for environmentally hazardous gases such as CO₂ (Pearson et al. 1983).

Depending on thermodynamic conditions, gas species form different clathrate structures, namely sI, sII and sH; each includes cages of varying shape and size (Shahnazar and Hasan 2014). To achieve advantages of hydrate or control its formation, an engineer primarily needs an

accurate knowledge of hydrate formation conditions. In this way, thermodynamic provides a realistic understanding of equilibrium behavior of gas hydrate. Thus, having a robust predictive model is mandatory to control hydrate-related processes.

Although primary research works conducted by Katz's group provide empirical correlations for P – T equilibrium diagrams of hydrate systems (Sloan and Koh 2007), however, existence of natural gas with various compositions and also distinct operational conditions at gas processing units demands an exact and reliable thermodynamic framework. It was not the case, until van der Waals and Platteeuw laid foundation of hydrate equilibria calculation based on statistical mechanic (van der Waals and Platteeuw 1959). As stated by Sloan and Koh, their work is probably the first sensible application of statistical thermodynamic in industry (Sloan and Koh 2007).

After seminal work of van der Waals and Platteeuw (shortly vdW– P), numerous works have been carried out to evaluate vdW– P coupled with different equations of state (EOS). By a glance at the literature, immediately a question would arise: What is the proper EOS to be accompanied with vdW– P theory in order to present the best prediction for hydrate formation condition? That is to say, too many publications would confuse an engineer to select the proper EOS. In particular, most papers claim to present the best model. Regardless of how close an EOS could predict hydrate equilibria, from an engineering point of view, it should be simple enough so that could be implemented in a commercial simulator (Sloan 1998). Despite the fact that most chemical processing packages such as CSMGem and AspenPlus are able to run fast and accurate models for batch calculation of hydrate equilibrium, however, a reservoir engineer might need a simpler model that could carry out repetitive, tedious flash calculations in huge number of grids representing an underground reservoir (Hemmingsen et al. 2011).

As production of natural gas from underground hydrate resource would be the chief task of petroleum engineering in near future, thus, software developing companies would implement compositional simulation of hydrate production as a novel module in their packages. In this way, as most reservoir simulators apply cubic EOSs (CEOS) to perform flash calculation for running a compositional simulation, it is most practical to supply hydrate modeling option to those software such that it makes use of the same CEOS. Analogously, this idea was also emphasized by Riazi and Moshfeghian (2009) for modeling the microemulsion phase behavior.

1.2 Literature survey

Despite sporadic investigations carried out to evaluate prediction of hydrate equilibrium behavior by cubic equations of state (CEOS), however, none of them presents a thorough analysis for natural gas mixture. Additionally, most authors have narrowly focused on investigating new and in turn complicated EOS. To highlight this neglected point, in this section, we revisit most important works which have ever been carried out on this subject.

Mohammadi and Richon (2007) applied Valderrama–Patel–Teja EOS (VPT-EOS) in combination with non-density dependent (ANDD for short) mixing rule proposed by Avlonitis et al. (1994) to predict the phase equilibrium boundaries of hydrate system containing methane and ethylene glycol. In their work, P – T diagram of hydrate equilibria was accurately predicted up to ethylene glycol of 50 wt%. Karamoddin and Varaminian (2011) examined capability of Peng–Robinson EOS (PR-EOS) coupled with different mixing rules such as van der Waals (vdW), ANDD and general non-quadratic (GNQ) for predicting hydrate formation pressure of pure species CH_4 , C_2H_6 , C_3H_8 , $i\text{-C}_4\text{H}_{10}$, N_2 , CO_2 and H_2S . It is noteworthy that, in contrast to their work, the present research dealt with hydrate formation of gas mixture. Later, they extended their previous work by applying Soave–Redlich–Kwong (SRK) and VPT-EOS (Karamoddin and Varaminian 2013b). In another study, Karamoddin and Varaminian 2013a applied SRK- and VPT-EOS coupled with ANDD mixing rule to model hydrate dissociation condition of HCFC22, HFC134a and HFC152a refrigerants. They compared prediction of SRK- and VPT-EOS with cubic plus association equation of state (CPA) and pointed out close prediction of all models. Their work implies capability of CEOSs to represent hydrate equilibria as accurate as sophisticated models such as CPA.

Hemmingsen et al. (2011) used SRK- and PR-EOS with vdW mixing rule to model depression of hydrate formation temperature once adding mono-ethylene glycol (MEG) into a mixture of methane + propane + water. Surprisingly, they pointed out accurate prediction of SRK- and PR-EOS for MEG concentrations up to 60 wt%. Based on their work, one could infer concealed ability of CEOSs for predicting hydrate equilibria even in the presence of large amounts of inhibitors. In a recent study, El Meragawi et al. (2015) compared performance of PR-EOS and Perturbed Chain Statistical Associating Fluid Theory (PC-SAFT) for predicting equilibrium condition of hydrate + vapor + liquid water (H–V– L_w) system of species including CH_4 , C_2H_6 , C_3H_8 , $i\text{-C}_4\text{H}_{10}$, CO_2 , N_2 , Ar, O_2 and H_2S . Their work demonstrates better prediction of PR-EOS than PC-SAFT to represent hydrate equilibria of foregoing species. It should be emphasized that PC-SAFT is a molecular-

based EOS, particularly suitable for polar and associating compounds (Abolala et al. 2014). Despite sophisticated form of PC-SAFT, it predicts hydrate dissociation pressure of natural gas constituents as good as PR-EOS (El Mera-gawi et al. 2015).

Based on the literature discussed above, it seems more practical to model hydrate of natural gas by simple CEOS with accuracy close to CPA and PC-SAFT equations. In other words, cubic EOSs are more reliable than thought before. Hence, it is worthwhile exploring concealed advantageous of different CEOSs for representing equilibrium behavior of natural gas hydrates. With the best of author's knowledge, no one has conducted such investigation, yet. Moreover, selection of the best mixing rule to be accompanied by a CEOS has not been respected in the hydrate literature, yet.

This study aims to evaluate accuracy and range of applicability of three most common CEOSs, namely SRK, PR and VPT (a modified form of Patel–Teja EOS) for prediction of hydrate equilibrium temperature of a natural gas sample. To do so, each EOS was coupled with a mixing rule including vdW, ANDD and GNQ. To achieve more realistic representation of hydrate formation phenomenon, our modeling approach takes the effect of asymmetry of enclathrated guest molecules and interaction with water molecules beyond the first shell of a cage into account. In the remainder of this paper, a brief introduction to our thermodynamic framework is presented, and afterward, performance of each modeling approach is discussed thoroughly.

2 Thermodynamic approach

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

By the aid of statistical mechanics, van der Waals and Platteeuw (1959) derived the following expression for chemical potential of water component in hydrate phase:

$$\Delta\mu_w^{\beta-H} = \mu_w^\beta - \mu_w^H = -RT \left[\sum_{i=1}^{N_{\text{cavity}}} v_i \ln \left(1 - \sum_{j=1}^{N_{\text{species}}} \theta_{ij} \right) \right] \quad (1)$$

where superscripts β and H stand for hypothetical empty and occupied hydrate lattice, respectively. v_i denotes number of i type cavities per number of water molecules. θ_{ij} represents fractional occupancy of cage i by guest species of type j . Analogous to classical Langmuir adsorption isotherm, fractional occupancy is related to fugacity of equilibrium phases by the following expression (Sloan 1998):

$$\theta_{ij} = \frac{C_{ij}f_j}{1 + \sum_{k=1}^N C_{ik}f_k} \quad (2)$$

where

$$f_j = y_j\phi_jP \quad (3)$$

where ϕ_j denotes fugacity coefficient of component j , obtained by following exact thermodynamic expression (Dehaghani and Badizad 2017):

$$\ln \phi_j = \ln \left(\frac{f_j}{y_jP} \right) = \frac{1}{RT} \int_0^p \left(v_j - \frac{RT}{P} \right) dP \quad (4)$$

Adsorption coefficient, C_{ij} appeared in Eq. (2), accounts for all interactions, particularly gas–water, which maintain stability of clathrate. Having a mathematical expression for potential function of such interactions, simply, Langmuir constants will be acquired as (Sloan and Koh 2007):

$$C = \frac{4\pi}{kT} \int_0^{R-a} e^{-\frac{w(r)}{kT}} r^2 dr \quad (5)$$

where k denotes Boltzmann constant and $w(r)$ stands for a smoothed cell radial potential function, which could be of various forms depending on type of interaction.

Thus far, it has been an unsolved problem to exactly represent all interactions in hydrate equilibria via a closed-form analytical formula for $w(r)$. Although molecular simulation could do similar task, they are time-consuming and just suitable for academic purposes. However, the problem is not as so bad as it seems. Originally, van der Waals and Platteeuw (1959) considered London interaction between gas and water in hydrate using Lenard-Jones potential function. In this line, McKoy and Sinanoglu (1963) pointed out spherical core Kihara potential function more accurately accounts for interactions in hydrate clathrate, that is,

$$w(r) = 2z\epsilon_k \left[\frac{\sigma_k^{12}}{R^{11}r} \left(\delta^{10} + \frac{a_r}{R} \delta^{11} \right) - \frac{\sigma_k^6}{R^5r} \left(\delta^4 + \frac{a_r}{R} \delta^5 \right) \right] \quad (6)$$

$$\delta^N = \frac{1}{N} \left[\left(1 - \frac{r}{R} - \frac{a_r}{R} \right)^{-N} - \left(1 + \frac{r}{R} - \frac{a_r}{R} \right)^{-N} \right] \quad (7)$$

where N takes values of 4, 5, 10 and 11 as seen in Eq. (6). z means coordination number, i.e., number of oxygen atoms at the periphery of a cavity. Kihara parameters are obtained by the following mixing rules (Sloan and Koh 2007):

$$\sigma = \frac{\sigma_w + \sigma_g}{2} \quad (8a)$$

$$\epsilon = \sqrt{\epsilon_w \epsilon_g} \quad (8b)$$

$$a_r = \frac{a_{r,w} + a_{r,g}}{2} \tag{8c}$$

where σ , ε and a_r stand for collision diameter, energy parameter and hard core radius, respectively. Subscripts w and g mean water and guest molecules, respectively. Table 1 summarizes the Kihara parameters used in this study.

As stated by many authors (Tee et al. 1966; Avlonitis 1994; Sloan and Koh 2007; John et al. 1985), there is marked discrepancy between Kihara parameters obtained by second virial or viscosity data, and those acquired through regression of hydrate phase equilibrium data. That is to say, as Kihara potential is not sufficient for representing interactions in hydrate system, hence, models derived only based on this potential serve to be rather correlative tools. In fact, early researchers enforced a not totally realistic model to fit P - T equilibrium data of hydrate systems. John et al. (1985) addressed this issue by using the Kihara parameters which were obtained by second virial or viscosity data. In turn, they emphasized on eliminating the basic assumptions of original vdW-theory; most importantly, they neglected distortion of clathrate upon intrusion of guest molecules (Dyadin et al. 1987). This assumption poses limitation on predictive ability of vdW-P theory. To achieve realistic prediction, John et al. proposed an expression accounting for distortion of hydrate lattice and interaction of encapsulated species with far water molecules beyond the first shell of cage, given by:

$$C = Q^* C^* \tag{9}$$

where C^* is the original (uncorrected) Langmuir constant expressed by Eq. (5). However, John et al. (1985) suggested an extended form as:

$$C^* = \frac{4\pi}{kT} \int_0^{R-a} \exp\left(-\left[\frac{w_1(r) + w_2(r) + w_3(r)}{kT}\right]\right) r^2 dr \tag{10}$$

where $w_1(r)$, $w_2(r)$ and $w_3(r)$ represent interaction potentials between guest and water molecules at first, second and third shell of cavity, respectively. Table 2 summarizes parameters of respective potentials.

In Eq. (9), Q^* is the correction coefficient due to non-idealities in hydrate phase caused by restricted motion of guest molecules in cages and corresponding distortion of

cavities. To extend original vdW-P theory, John et al. (1985) proposed the following empirical expression for Q^* :

$$Q^* = \exp\left(-a_0 \left[\omega \left(\frac{\sigma}{R-a}\right) \left(\frac{\varepsilon}{kT_0}\right)\right]^n\right) \tag{11}$$

where a_0 and n are cavity-dependent adjustable parameters. Their values are reported in the literature (John et al. 1985). ω denotes acentric factor representing asphericity of a given guest species.

2.2 Cubic equations of state (CEOS)

As stated in the introductory section, evaluating capability of cubic EOSs for predicting hydrate equilibria is the main objective of the present study. In what follows, a brief account of three most celebrated CEOSs is presented.

2.2.1 Soave-Redlich-Kwong equation of state (SRK-EOS)

Since proposal of the groundbreaking equation of state by van der Waals (Schmidt and Wenzel 1980), numerous modified equations have been suggested which occupy a massive portion of phase equilibria literature (Valderrama 2003). Among them, the Redlich-Kwong (RK) proposal was a marked contribution into reviving the interest in vdW-type EOS. Soave (1972) modified original RK equation by including the acentric factor (ω) into attraction part of that EOS and derived the following expressions:

$$P = \frac{RT}{V-b} - \frac{a_c \alpha(T_r, \omega)}{V(V+b)} \tag{12a}$$

$$a_c = 0.427 \frac{R^2 T_c^2}{P_c} \tag{12b}$$

$$b = 0.086 \frac{RT_c}{P_c} \tag{12c}$$

$$\alpha(T_r, \omega) = [1 + m(1 - T_r^{0.5})]^2 \tag{12d}$$

$$m = 0.480 + 1.574 - 0.176\omega^2 \tag{12e}$$

where T_c and P_c represent critical temperature and pressure, respectively.

2.2.2 Peng-Robinson equation of state (PR-EOS)

PR is a modification to SRK-EOS in both temperature and volume dependency of attraction term, proposed as follows (Peng and Robinson 1976):

$$P = \frac{RT}{v-b} - \frac{a_c \alpha(T_r, \omega)}{v(v+b) + b(v-b)} \tag{13a}$$

$$a_c = 0.45724 \frac{R^2 T_c^2}{P_c} \tag{13b}$$

Table 1 Kihara parameters used for calculating Langmuir adsorption coefficient

	a_r , Å	ε , K	σ , Å
C ₁	0.3834	3.165	154.54
C ₂	0.5651	3.2641	176.41
C ₃	0.6502	3.0394	203.31
N ₂	0.3526	3.0124	125.15
CO ₂	0.6805	3.9818	168.77

Table 2 Characteristic of water shells (radius R , coordination number Z) used in cell potential function (John et al. 1985)

Hydrate structure	Cage	First shell		Second shell		Third shell	
		$R \times 10, \text{ nm}$	Z	$R \times 10, \text{ nm}$	Z	$R \times 10, \text{ nm}$	Z
sI	5^{12}	387.5	20	659.3	20	805.6	50
	$5^{12}6^2$	415.2	21	770.8	24	828.5	50
sII	5^{12}	378.0	20	666.7	20	807.9	50
	$5^{12}6^4$	470.3	28	746.4	28	878.2	50

$$b = 0.07780 \frac{RT_c}{P_c} \tag{13c}$$

$$\alpha(T_r, \omega) = [1 + m(1 - T_r^{0.5})]^2 \tag{13d}$$

$$m = 0.37464 - 1.54226\omega - 0.2699\omega^2. \tag{13e}$$

2.2.3 Valderrama–Patel–Teja Equation of State (VPT-EOS)

Despite successful outcomes of PR and SRK-EOSs, scientists focused on an unsolved shortcoming of those expressions. All of them give fixed critical compressibility factor (Z_c) considerably higher than experimental values. To tackle this drawback, Patel and Teja (1982) put forward a three-parameter CEOS, known as PT-EOS, which includes adjustable Z_c by introducing a third parameter into EOS. Apart from varying Z_c , PT-EOS was an effort to extent applicability of CEOSs for polar substances such as water and alcohols. Although PT-EOS was a major improvement in area of CEOSs, nevertheless, unlike SRK or PR, it involves more complexity, that is, solving an additional three-degree polynomial to calculate Z_c .

To reduce complexity of original PT-EOS while maintaining its advantages, Valderrama (1990) proposed a generalized expression by considering the experimental values of Z_c , given by:

$$P = \frac{RT}{v - b} - \frac{a_c \alpha(T_r)}{v(v + b) + c(v - b)} \tag{14a}$$

$$a_c = \Omega_a \frac{R^2 T_c^2}{P_c} \tag{14b}$$

$$b = \Omega_b \frac{RT_c}{P_c} \tag{14c}$$

$$c = \Omega_c \frac{RT_c}{P_c} \tag{14d}$$

$$\Omega_a = 0.66121 - 0.76105Z_c \tag{14e}$$

$$\Omega_b = 0.02207 - 0.20868Z_c \tag{14f}$$

$$\Omega_c = 0.57765 - 1.8708Z_c \tag{14g}$$

$$a(T_r) = [1 + F(1 - T_r^\psi)]^2 \tag{14h}$$

$$F = 0.46283 + 3.5823(\omega Z_c) + 8.19417(\omega Z_c)^2 \tag{14i}$$

As seen above, VPT includes Z_c as a substance-dependent parameter in its attraction term.

2.3 Mixing rules

Historically, cubic EOSs were originally developed to represent phase behavior of pure fluids (Valderrama 2003). Despite this fact, to extend their applicability for mixtures, it is necessary to invoke a suitable mixing rule. To this end, a mixing rule is expected to give realistic average of co-volume and energy parameters for species constituting a homogeneous mixture. At this point, immediately, one question would arise: What is the best mixing rule? Or, regarding our study, is there any criterion for choosing the proper mixing rule to be coupled with a given CEOS in order to attain the best prediction for hydrate phase equilibria? In fact, no paper has ever respected this point. As a starting point, this study attempts to answer this question by evaluating three well-established mixing rules. In the next section, a brief discussion for these mixing rules is presented.

2.3.1 van der Waals (vdW) mixing rule

van der Waals mixing rule is regarded as the classical mixing rule which has been widely incorporated in commercial reservoir simulators, e.g., CMG and Eclipse, that is (Knapp et al. 1998):

$$a_{\text{mix}} = \sum_i^{N_c} \sum_j^{N_c} x_i x_j a_{ij} (1 - K_{ij}) \tag{15a}$$

$$a_{ij} = \sqrt{a_i a_j} \tag{15b}$$

$$b_{\text{mix}} = \sum_i^{N_c} x_i b_i \tag{15c}$$

where summation runs over all components present in mixture. K_{ij} represent binary interaction parameter (BIP) for dissimilar components i and j , acquired through regression of phase behavior data. For BIPs of interest in this study, refer to the literature (Karamoddin and Varaminian 2013b).

This rule takes pairwise interaction of adjacent species into account, neglecting multi-component interactions like those treated in local composition approach (Karamoddin and Varaminian 2013b). Therefore, vdW mixing rule is particularly suitable for mixtures of identical species, such as reservoir hydrocarbons. Nevertheless, hydrate formation deals with water as a polar and asymmetric component. In this case, effect of asymmetry is substantial, necessitating modern mixing rules.

2.3.2 Avlonitis non-density dependent (ANDD) mixing rule

Valderrama (2003) reported an exhaustive review, in which he listed numerous mixing rules and asserted these expressions are mostly of empirical basis upon weak theoretical support. In this fact, those mixing rule based on stronger theoretical reasoning could be reliable and deserve more investigation. As mentioned in preceding section, vdW rule is restricted to nonpolar mixtures. In an effort to accounting polar mixtures, Avlonitis et al. (1994) proposed a novel mixing rule for mixtures containing polar (asymmetric) components as follows:

$$a = a^C + a^A \tag{16}$$

where superscripts C and A stand for classical (nonpolar) and asymmetric contribution of attractive term. a^C takes an expression just like vdW mixing rule, Eq. (15a).

To derive an expression for a^A , Avlonitis et al. (1994) supposed that increasing temperature alleviates asymmetric interactions. Additionally, at higher temperatures, mixture of mostly same components will behave similar to symmetric one. Simply put, if a mixture is totally composed of polar and asymmetric species, a^A will be zero. Based on these hypotheses, Avlonitis et al. (1994) suggested the following expression:

$$a^A = \sum_p x_p^2 \sum_i x_i a_{pi} l_{pi} \tag{17}$$

Here first summation goes over polar components. a_{pi} is the geometric average of a_p and a_i , that is, $a_{ip} = \sqrt{a_p a_i}$. l_{pi} denotes a special binary interaction coefficient which was proposed to be a linear function of temperature:

$$l_{pi} = l_{pi}^0 - l_{pi}^1 (T - T_0) \tag{18}$$

where l_{pi}^0 and l_{pi}^1 are positive adjustable constants reported in the literature (Karamoddin and Varaminian 2013b) for components of interest in this study. T_0 denotes ice point in Kelvin.

2.3.3 General non-quadratic (GNQ) mixing rule

As an extension to vdW-type mixing rules, non-quadratic expressions were introduced. These mixing rules offer concentration-dependent formula for binary interaction coefficients (Valderrama 2003). In this way, different expressions have been proposed (Panagiotopoulos and Reid 1985; Adachi and Sugie 1986), which could be summarized as (Valderrama 2003):

$$K_{ij} = \delta_i x_i + \delta_j x_j \tag{19}$$

where δ_i and δ_j are adjustable parameters, particularly to a given i, j pair of species. The parameters of interest in this work were adopted from the literature (Karamoddin and Varaminian 2013b).

Unlike vdW, non-quadratic mixing rules do not allow symmetry of interaction coefficients, i.e., $k_{ij} \neq k_{ji}$.

3 Results and discussion

In the preceding section, a brief introduction of three most popular CEOSs and mixing rules was presented. At this stage, we are going to model phase behavior of liquid water + hydrate + vapor (L_w -H-V) system using foregoing EOSs in combination with mixing rules. To this end, a natural gas sample from a gas processing unit located in Gachsaran field, Iran, was analyzed in PVT laboratory of Iranian Central Oil Fields Company (ICOFC) and its hydrate P-T equilibrium data were employed for modeling purpose in this study. Table 3 presents composition of natural gas sample investigated in the present study.

Formation temperature of gas hydrate was predicted using an EOS in set of PR, SRK and PTV coupled with a mixing rule including vdW, ANDD and GNQ. Figure 1 sketches the calculation procedure through a flow chart. As a criterion for prediction accuracy, average absolute relative deviation percent (AARD%) was defined as follows:

$$AARD\% = \frac{1}{N_p} \sum_{i=1}^{N_p} \frac{|T_i^{cal.} - T_i^{exp.}|}{T_i^{exp.}} \times 100 \tag{20}$$

where N_p denotes number of data points. Superscripts cal. and exp. stand for calculated and experimental values, respectively.

Table 3 Composition of natural gas sample

Component	Mole fraction
C ₁	0.82
C ₂	0.11
C ₃	0.04
CO ₂	0.02
N ₂	0.01

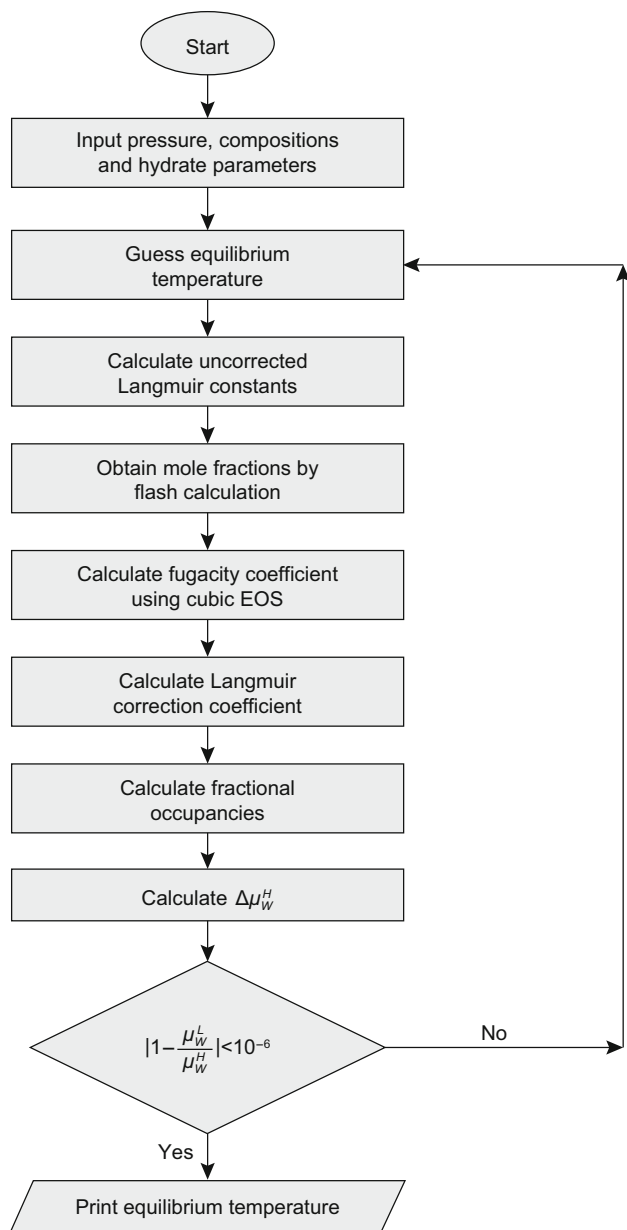


Fig. 1 Sketch of flowchart used to calculate hydrate formation temperature

Figures 2, 3 and 4 show P - T for hydrate equilibrium system, scatter plot and error analysis diagram belonging to PR-, SRK- and VPT-EOSs, respectively. Note that Figs. 2, 3 and 4 cover a broad range of P - T range including I-H-V, L_w -H-V and L_H - L_w -H equilibrium. Hence, there are two quadruple points (marked by arrow) in equilibrium diagram, which feature sharp kicks. Also, Table 4 presents overall AARD% of each CEOS versus coupled mixing rule.

As shown in Fig. 2a, PR-EOS sufficiently emulates the general trend of P - T diagram except at high pressures (upper than 753 psi) where PR tends to overestimate

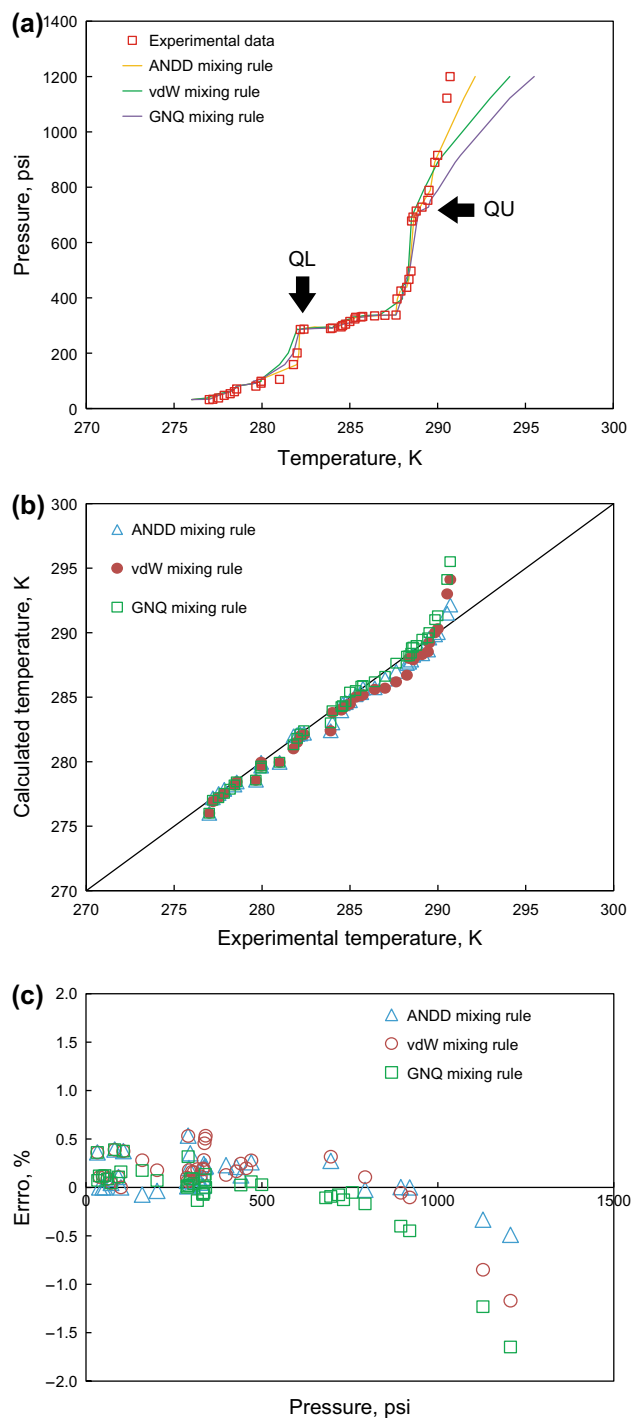


Fig. 2 Analysis of hydrate temperature predicted by PR-EOS coupled with different mixing rules: (a) P - T equilibrium diagram of L_w -H-V system; (b) scatter plot of predicted temperatures versus experimental values; and (c) error% ($100 \times \frac{\rho_{exp} - \rho_{cal.}}{\rho_{exp.}}$) of predicted hydrate temperature in varying pressures. Arrows indicate lower (QL) and upper (QU) quadruple points

hydrate formation temperature. Regarding mixing rules combined with PR, one could notice better performance for PR while coupling with ANDD. As shown in Fig. 2b, data

cloud of ANDD is of densely distributed around the 45° straight line which implies close agreement between PR–ANDD prediction and experimental data. For further analysis, Fig. 2c demonstrates better prediction for GNQ in comparison with vdW mixing rule up to 753 psi (incipient of high-pressure region). Although prediction of hydrate equilibrium temperature by PR + GNQ is associated with appreciate inaccuracy at high pressures, however, one could notice the parallel trend of PR + GNQ prediction and *P–T* equilibrium curve of experimental data.

Apart from visual analysis, all three mixing rules give predictions with nearly equal AARD% over whole pressure range (32.4–1200) psi, as summarized in Table 4. As a result, PR-EOS is able to give accurate predictions for hydrate formation temperature over wide range of pressures. For this purpose, ANDD is the best mixing rule to be coupled with PR.

Figure 3a depicts hydrate temperature predicted by SRK with different mixing rules. Despite fair agreement with experimental data, but, SRK is associated with higher overall AARD% of 0.207 than PR, as reported in Table 4. Interestingly, mixing rules led to identical trend of SRK and PR prediction. This could be ascribed to the fact that PR is the improved form of SRK and both models stem from same philosophy. This argument supports better overall performance of PR in comparison with SRK.

As shown in Fig. 3a, ANDD renders SRK consistent follow of experimental *P–T* curve in whole pressure range. Both vdW and GNQ bring about departure of SRK prediction at high pressures corresponding to error% of –1.3 at 1200 psi. However, as shown in Fig. 3b, c, GNQ gives prediction with the lowest deviation up to 753 psi. In general, SRK prediction is in agreement with experimental hydrate *P–T* diagram. Based on the present investigation, ANDD is the best mixing rule to be coupled with SRK to represent hydrate phase equilibria.

Now, we proceed to evaluate VPT-EOS capability for predicting hydrate formation temperature. Interestingly, VPT-EOS gives prediction fairly different from PR and SRK. As shown in Fig. 4, it would be difficult to distinct the preferred mixing rule for coupling with VPT. Up to 335 psi, all mixing rules render VPT similar predictions. However, from 335 to 890 psi, ANDD gives rise to underestimation of equilibrium temperature. From 890 to 1200 psi, vdW and ANDD give identical predictions closer to experimental data than GNQ. Generally, unlike PR and SRK, mixing rules coupled with VPT-EOS do not follow a consistent trend of prediction. Figure 4c supports this observation through erratic distribution of error% in varying pressures. This could be attributed to different origin of VPT which is a modified form of three-parameter PT-EOS (Valderrama 1990). Therefore, one could not expect similar trend between predictions of PR/SRK and VPT. As

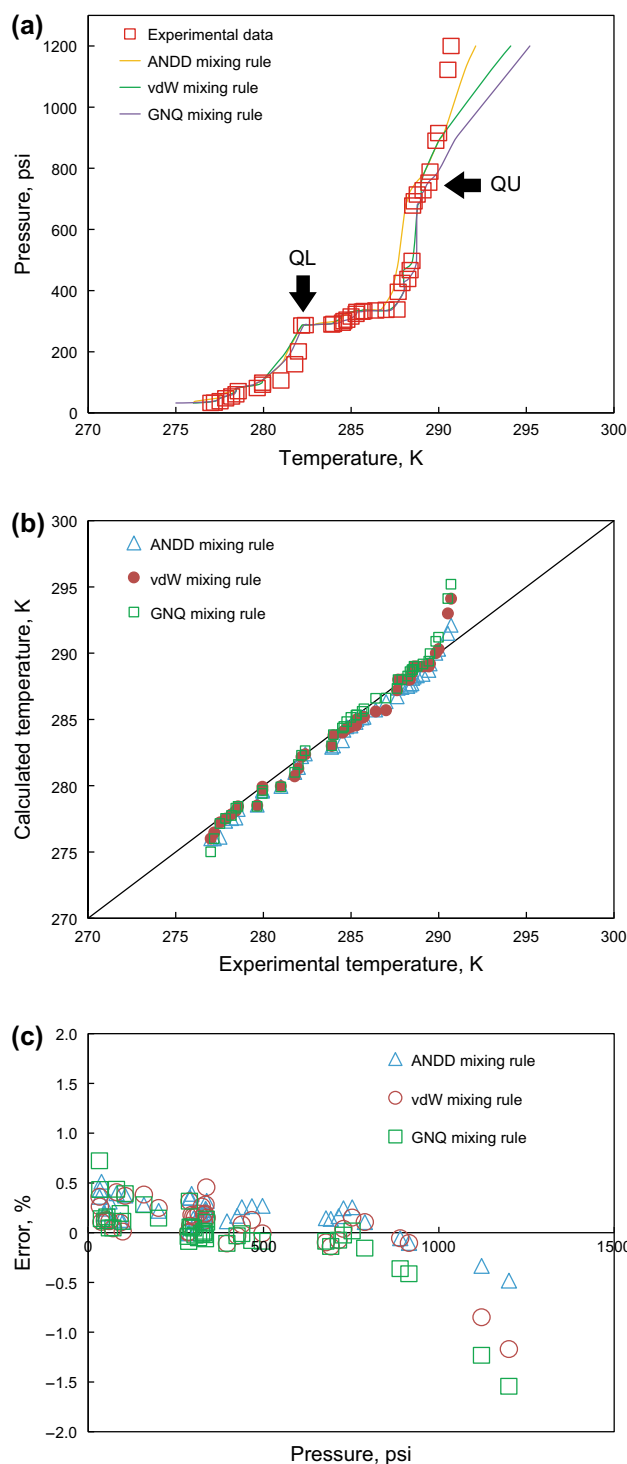


Fig. 3 Analysis of hydrate temperature predicted by SRK-EOS coupled with different mixing rules: (a) *P–T* equilibrium diagram of *L_w–H–V* system; (b) scatter plot of predicted temperature versus experimental values; and (c) error% ($100 \times \frac{\rho_{exp} - \rho_{cal.}}{\rho_{exp.}}$) of predicted hydrate temperature in varying pressures. Arrows indicate lower (QL) and upper (QU) quadruple points

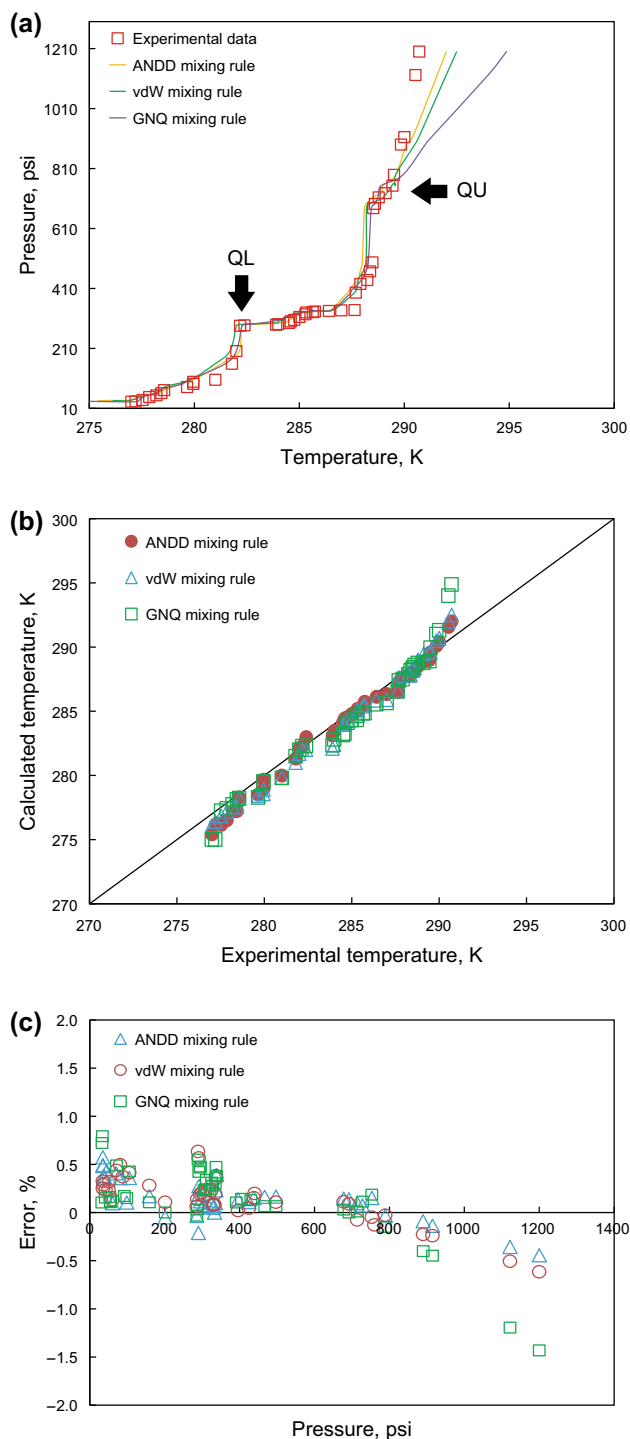


Fig. 4 Analysis of hydrate temperature predicted by VPT-EOS coupled with different mixing rules: (a) P - T equilibrium diagram of L_w -H-V system; (b) scatter plot of predicted temperature versus experimental values; and (c) error% ($100 \times \frac{\rho_{exp} - \rho_{cal}}{\rho_{exp}}$) of predicted hydrate temperature in varying pressures. Arrows indicate lower (QL) and upper (QU) quadruple points

summarized in Table 4, PR, SRK and VPT give prediction for hydrate formation temperature with overall AARD% of 0.194, 0.207 and 0.226, respectively, regardless of mixing rule.

Generally speaking, all discussed cubic EOSs are of overall equal performance in representing the hydrate phase equilibria. However, based on our analysis, PR is the most appropriate EOS for this task. Note that PR is a widely used formula in all reservoir simulation packages to carry out flash calculations. With respect to our analysis, software developing companies could implement “*exploitation of hydrate resources*” as a new module in their commercial packages without invoking a new EOS to obtain hydrate equilibrium conditions. However, as observed in Figs. 2, 3 and 4, cubic EOSs tend to depart from true behavior of hydrate system unless a proper mixing rule was coupled with it. In other words, mixing rule is of significant contribution, especially at high-pressure conditions. In this respect, one could infer ANDD to be the best mixing rule for generalizing a cubic EOS to predict formation condition of natural gas hydrate. As mentioned earlier, ANDD takes effect of asymmetric interactions into account. Albeit simple form of ANDD, it attempts to account for polar interactions in hydrate system, which reinforce a CEOS to give more realistic predictions at high pressures. In this respect, Avlonitis et al. (1994) made similar observation. They pointed out effectiveness of ANDD for modeling phase behavior of hydrocarbon systems in the presence of methanol and water.

It should be emphasized that vdW and GNQ mixing rules originally were developed for mixtures merely containing nonpolar species. However, we made predictions for hydrate system containing water as a polar component up to high pressures as much as 1200 psi. Such high pressure would only occur at hostile conditions of underground reservoirs. Despite this fact, the total AARD% of prediction by PR–vdW and PR–GNQ is sufficient to have an accurate representation for hydrate phase behavior of our natural gas sample. From practical point of view, applying the vdW mixing rule is associated with less calculations in comparison with GNQ and is of higher preference for complex simulations.

As stated by Valderrama, GNQ is appropriate to represent phase behavior of binary mixtures including a supercritical component (Valderrama 2003). Also, Karamoddin and Varaminian (2011) pointed out suitability of GNQ for prediction of hydrate equilibria of binary gas mixtures. Therefore, with the best of author’s knowledge, it is the first time that capability of GNQ for representing interactions in hydrate system of a gas mixture has been investigated. It should be emphasized that parameters reported by Karamoddin and Varaminian (2011) were obtained by correlation of vapor/liquid equilibrium data of binary

Table 4 AARD% of hydrate formation temperature predicted by different cubic EOS + mixing rules

Equation of state	AARD%			
	vdW	ANDD	GNQ	Overall
PR	0.224	0.166	0.198	0.194
SRK	0.241	0.214	0.223	0.207
VPT	0.225	0.217	0.254	0.226

species, not LHV. Therefore, those parameters could be invoked universally irrespective of kinds of species forming hydrate structure.

The mixing rules, employed in this work, ignore the impact of pressure on molecular interactions, which would be of quite importance in harsh conditions. The presence of multi-liquid phases complicates the flash calculation, which could not be handled by conventional cubic EOS. However, this observation does not go against worth of our study because, as shown in Figs. 2, 3 and 4, all models, in particular those treated by ANDD mixing rule, are of acceptable accuracy in whole range of pressures. On the other hand, L_w -H-V and to lesser extent I-H-V are the main interest of industrial and academic studies, which have been nicely predicted by cubic EOS in this work.

Last but not least, most thermodynamic frameworks suggested for modeling hydrate equilibria require adjustment of a few parameters such as Kihara parameters. However, in contrast to traditional practice, the modeling approach applied in this study does not include any adjustable parameter to be regressed with hydrate equilibrium data and it could be used directly as a predictive tool.

4 Conclusions

This study is an effort to explore neglected ability of cubic equations of state for predicting phase behavior of natural gas hydrate. To this end, hydrate formation temperature of a real natural gas sample was predicted using three common cubic EOSs (PR, SRK and VPT) coupled with three mixing rules (vdW, ANDD and GNQ). The equilibrium calculation was conducted over a broad pressure range of 32.4–1200 psi for L_w -H-V system. It was observed that prediction of cubic EOSs was in close agreement with experimental data with AARD% of less than 1. In addition, we concluded that PR + ANDD is the most accurate model for prediction of hydrate equilibria with AARD% of 0.166, because ANDD takes the polar and asymmetric interactions into account which are dominate interactions in hydrate system. In general, the accuracy of cubic EOSs

studied in this paper depends on mixing rule coupled with them, especially at high-pressure conditions.

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