Prediction of Gas Hydrate Forming Pressures by Using PR Equation of State and Different Mixing Rules

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Abstract
In this work, the ability of different mixing rules for the prediction of hydrate formation pressure are compared. For this purpose, by using Van der Waals–Plauteeuv model for solid hydrate phase and PR equation of state for calculation of fugacity of components in gas and liquid phases, the pressure of hydrate formation in different mixtures has been calculated by four different mixing rules: Van der Waals, Danesh, GNQ and Wong-Sandler, then by comparison of the calculated results with experimental data, the accuracy of the mixing rules were determined. Studied systems contain binary mixtures CH4, C2H6, C3H8, i-C4H10, CO2, and H2S with water in hydrate forming conditions. The interaction parameters in each mixture have been optimized by using two phase equilibrium data \( W(VL) \) and then the optimized parameters have been used for three phase equilibrium \( W(VLH) \) calculations. Comparison of the calculated pressure of hydrate forming with experimental pressure shows that for most mixtures in the studied temperature and pressure ranges, the GNQ mixing rule with an average percent of error 6% has more accuracy than the three other mixing rules: Van der Waals, Danesh and WS. According to the obtained results for methane equilibrium concentrations in liquid phase, it seems that Danesh mixing rule is more efficient for the prediction the mole concentrations of components. Since Danesh rule considers the polarity of the water molecule, it has greater precision in predicting the equilibrium fractions.

Keywords: Mixing Rules, Peng-Robinson, Equation of State, Gas Hydrate, Three Phase Equilibria

1- Introduction
Natural gas is one of the most important sources of energy in the world. One of the related problems to natural gas is gas hydrate formation. Gas hydrates are crystalline solids that form when gas or volatile liquid molecules suitable for hydrate formation are enclosed in a cage consisting of water molecules. Naturally occurring hydrates, containing mostly methane, exist in vast quantities and are being looked upon as a potential alternative energy source. Carbon dioxide hydrates are also important hydrates [1].

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Although hydrate formation is referred to as an advantage, this circumstance in gas transportation lines causes some problems like plugging of the lines and sometimes the explosion of pipes. Thus awareness of equilibrium conditions of hydrate formation is necessary for preventing this event.

In this work, equilibrium conditions in hydrate formation for six mixtures that contain binary systems have been studied. \((\text{CH}_4-\text{H}_2\text{O}), (\text{C}_2\text{H}_6-\text{H}_2\text{O}), (\text{C}_3\text{H}_8-\text{H}_2\text{O}), (\text{i-C}_4\text{H}_{10}-\text{H}_2\text{O}), (\text{CO}_2-\text{H}_2\text{O})\) and \((\text{H}_2\text{S}-\text{H}_2\text{O})\). The forming pressure in each system was calculated.

2- Modeling
At phase equilibrium, the fugacities or chemical potentials of species in the various phases must be equal. For three-phase hydrate–liquid water–vapor, \((\text{VLW})\) equilibrium, the basic equations for the equilibrium condition are:

\[
f_i^V = f_i^L = f_i^H \tag{1}
\]

Calculation of component fugacities in two phases, vapor and liquid, are based on the \((\phi - \varphi)\) and \((\gamma - \varphi)\) approach, and in this research the \((\phi - \varphi)\) model is used. In this method the fugacity of a component must be calculated using a suitable equation of state and mixing rules. In this study, Peng – Robinson equation of state was selected. The PR equation is [2]:

\[
P = \frac{RT}{v - b} - \frac{a}{v(v + b) + b(v - b)} \tag{2}
\]

\[
b = 0.07780 \frac{RT_c}{P_c} \tag{3}
\]

\[
a = 0.45724 \frac{RT_c^2}{P_c} \alpha(T_c) \tag{3}
\]

\[
\alpha(T_c) = \left[1 + m \left[1 - \left(\frac{T}{T_c}\right)^{0.5}\right]\right]^2 \tag{3}
\]

\[
m = 0.37464 + 1.5422 \omega - 0.26922 \omega^3 \tag{3}
\]

The coefficients \(a, b\) of Eq (2) were obtained for mixtures using the Van der Waals, Danesh, GNQ (general non quadratic) and WS (Wong-Sandler) mixing rules. The Van der Waals mixing rule is:

\[
a_{mix} = \sum_{i=1}^{NC} \sum_{j=1}^{NC} x_i x_j a_{ij} (1 - k_{ij}) \tag{4}
\]

\[
b_{mix} = \sum_{i=1}^{NC} x_i b_i \tag{4}
\]

Where \(k_{ij}\) is the binary interaction parameter and:

\[
a_{ij} = (a_{ai} a_j)^{0.5} \tag{5}
\]

In another applied mixing rule, the attraction parameter \(a\) has been separated into two parts, the Van der Waals classical mixing rule part \(a^C\) and the asymmetric contribution part \(a^A\) are as follows [3]:

\[
a = a^C + a^A \tag{6}
\]

\[
a^A = \sum_{p=1}^{NPOLAR} \sum_{i=1}^{NC} x_i a_{pi} l_{pi} \tag{7}
\]

\(p\) stands for polar component and \(l_{pi}\) is the binary interaction parameter between the polar component and the other components, which is a function of temperature,
calculated by the following expression [3]:
\[ I_{p1} = l_{p1}^0 - l_{p1}^1 (T - T_0) \]  
(8)

Where \( l_{p1}^0 \) and \( l_{p1}^1 \) are binary interaction parameters and \( T_0 \) is the ice point in K.

Another mixing rule used in this research is GNQ (general non quadratic) mixing rule. The general form in this rule for \( a_{mix} \) and \( b_{mix} \) parameters is the same as Van der Waals mixing rule, but the combining rule for \( a_y \) has the following form [4]:
\[ a_y = \sqrt{a_i a_j (1-k_y)} \quad , \quad k_y = \delta_i x_i + \delta_j x_j \]  
(9)

In the WS mixing rule, the molar excess Gibbs free energy at infinite pressure, calculated from an EOS, is equated to the same property calculated from the NRTL excess free energy model. The WS mixing rules are [5]:
\[ b_{mix} = \frac{Q}{1-D} \]  
(10)
\[ \frac{a_{mix}}{RT} = Q \times \frac{D}{1-D} = D \times b_{mix} \]  
(11)
\[ D = \sum x_i \frac{a_i}{b_i RT} + \frac{g^E}{C^* RT} \]  
(12)
\[ Q = \sum \sum x_i x_j (b - \frac{a}{RT})_{ij} \]  
(13)
\[ (b - \frac{a}{RT})_{ij} = \frac{1}{2} \left[ \left( b_i - \frac{a_i}{RT} \right) + \left( b_j - \frac{a_j}{RT} \right) \right] (1-k_{ij}) \]  
(14)

Where \( x_i \) is the mole fraction of component \( i \) in that phase and \( C^* \) is a constant depending on the EOS (where \( C^* = -0.802 \) for the PR EoS). The NRTL model was used for \( g^E \).

\[ (\frac{g^E}{RT})_{NRTL} = \sum x_i \sum x_j G_{ij} \]  
(15)
\[ \tau_{ji} = \frac{g_{ji} - g_{ii}}{RT} \]  
(16)
\[ G_{ji} = \exp(-\alpha_{ji} \tau_{ji}) \]  
(17)

The chemical potential of water in the hydrate phase is given by Van der Waals and Platteeuw [6]:
\[ \frac{\Delta \mu}{RT} = \int_{\mu_0}^\mu \frac{\Delta h_{ji}}{RT} dT + \int_{\mu_0}^\mu \frac{\Delta v_{ji}}{RT} dP - \mu \ln \left( \gamma_n \right) \]  
(18)
\[ = \sum_{m=1}^{\text{N_{cav}}} v_m \ln \left( 1 + \sum_{j=1}^{\text{N_{gas}}} C_m f_j \right) \]

Where, \( v_m \) is the number of cavities of type \( m \) per water molecule in the lattice, \( C_{jm} \) is the Langmuir Constant, and \( f_i \) is the fugacity of the gas component \( i \).

The Langmuir constants account for the gas-H2O interaction in the cavity. Using the Lennard-Jones-Devonshire cell theory, Van der Waals and Platteeuw showed that the Langmuir constant is [7]:
\[ C = \frac{4\pi \varepsilon^2}{kT} \exp \left( \frac{-w(r)}{KT} \right) r^2 dr \]  
(19)

Where \( T \) is the absolute temperature, \( k \) is Boltzmann's constant and \( w(r) \) is the...
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spherically symmetric cell potential which is a function of the cell radius, the coordination number and the nature of the gas-H₂O interaction. Usually the Kihara potential function with a spherical core for describing the interaction between the gas and water molecules in the cavity wall is used. Kihara parameters used in this work are given in Table (1) for the applied components.

Table 1. Kihara potential parameters [8]

<table>
<thead>
<tr>
<th>Component</th>
<th>a (Å)</th>
<th>σ (Å)</th>
<th>ε/k</th>
<th>(\sigma/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>0.295</td>
<td>3.2512</td>
<td>153.69</td>
<td></td>
</tr>
<tr>
<td>C2</td>
<td>0.488</td>
<td>3.4315</td>
<td>183.32</td>
<td></td>
</tr>
<tr>
<td>C3</td>
<td>0.730</td>
<td>3.4900</td>
<td>198.27</td>
<td></td>
</tr>
<tr>
<td>i-C4</td>
<td>0.798</td>
<td>3.6000</td>
<td>209.58</td>
<td></td>
</tr>
<tr>
<td>n-C4</td>
<td>1.029</td>
<td>3.4000</td>
<td>195.36</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>0.753</td>
<td>2.9040</td>
<td>171.97</td>
<td></td>
</tr>
<tr>
<td>H₂S</td>
<td>0.717</td>
<td>2.8770</td>
<td>210.50</td>
<td></td>
</tr>
</tbody>
</table>

3- Results and discussion
3.1- Results of optimization
For calculation pressure in equilibrium conditions using the \((\varphi - \varphi)\) model, first we must determine the interaction parameters in each mixing rule. These parameters are determined for each mixture by minimizing the following objective function:

\[
O.F = w_1 \sum_{i=1}^{NP} \frac{|p_i^{cal} - p_i^{exp}|}{p_i^{exp}} + w_2 \sum_{i=1}^{NP} \frac{|x_i^{cal} - x_i^{exp}|}{x_i^{exp}}
\]

(20)

Where \(w_1\) and \(w_2\) are the weight fraction in each term and \(w_1 = w_2 = 1\).

Binary interaction parameter in the Van der Waals mixing rule is \(k_{12}\), and this optimized value is given in Table (2). In the Danesh mixing rule, three parameters exist that contain \(k_{12}\), \(l_{21}^0\) and \(l_{21}^1\). The obtained parameters are presented in Table (3).

Tables (4) and (5) show the optimized values for GNQ and WS mixing rules respectively. In the GNQ mixing rule, \(\delta_1\) and \(\delta_2\), and in the WS mixing rule, \(g_{21} - g_{11}\), \(g_{12} - g_{22}\), \(\alpha_{12}\), \(k_{12}\) are interaction parameters for binary mixtures.

Table 2. Optimized parameters, \(k_{12}\), for Van der Waals mixing rule in PR EOS

<table>
<thead>
<tr>
<th>Mixture</th>
<th>CH₄-H₂O</th>
<th>C₂H₆-H₂O</th>
<th>C₃H₈-H₂O</th>
<th>C₄H₁₀-H₂O</th>
<th>CO₂-H₂O</th>
<th>H₂S-H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_{12})</td>
<td>-0.35022</td>
<td>-0.22093</td>
<td>-0.25718</td>
<td>-0.31265</td>
<td>-0.14304</td>
<td>-0.02670</td>
</tr>
</tbody>
</table>

Table 3. Optimized parameters, \(k_{ij}\) and \(l_{ij}\) for Danesh mixing rule in PR EOS

<table>
<thead>
<tr>
<th>Mixture</th>
<th>(k_{21})</th>
<th>(l_{21}^0)</th>
<th>(l_{21}^1) * 10⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄-H₂O</td>
<td>0.48960</td>
<td>1.74473</td>
<td>71.181</td>
</tr>
<tr>
<td>C₂H₆-H₂O</td>
<td>0.49209</td>
<td>1.45850</td>
<td>37.830</td>
</tr>
<tr>
<td>C₃H₈-H₂O</td>
<td>0.52681</td>
<td>1.56193</td>
<td>36.518</td>
</tr>
<tr>
<td>i- C₄H₁₀-H₂O</td>
<td>0.34199</td>
<td>1.31380</td>
<td>49.953</td>
</tr>
<tr>
<td>CO₂-H₂O</td>
<td>0.25023</td>
<td>0.83331</td>
<td>24.882</td>
</tr>
<tr>
<td>H₂S-H₂O</td>
<td>0.13137</td>
<td>0.36095</td>
<td>14.224</td>
</tr>
</tbody>
</table>
### Table 4. Optimized Parameters for GNQ Mixing Rule in PR EOS

<table>
<thead>
<tr>
<th>Mixture</th>
<th>$\delta_1$</th>
<th>$\delta_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$-H$_2$O</td>
<td>0.16875</td>
<td>0.07576</td>
</tr>
<tr>
<td>C$_2$H$_6$-H$_2$O</td>
<td>0.36333</td>
<td>0.06920</td>
</tr>
<tr>
<td>C$_3$H$_8$-H$_2$O</td>
<td>0.45046</td>
<td>0.092116</td>
</tr>
<tr>
<td>i-C$<em>4$H$</em>{10}$-H$_2$O</td>
<td>1.07940</td>
<td>0.11403</td>
</tr>
<tr>
<td>CO$_2$-H$_2$O</td>
<td>0.02552</td>
<td>0.05083</td>
</tr>
<tr>
<td>H$_2$S-H$_2$O</td>
<td>0.03256</td>
<td>0.01187</td>
</tr>
</tbody>
</table>

### Table 5. Optimized Parameters for WS Mixing Rule in PR EOS

<table>
<thead>
<tr>
<th>Mixture</th>
<th>$g_{21}-g_{11}$</th>
<th>$g_{12}-g_{22}$</th>
<th>$\alpha_{12}$</th>
<th>$k_{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$-H$_2$O</td>
<td>60.1736</td>
<td>23938.7640</td>
<td>0.70966</td>
<td>3.27553</td>
</tr>
<tr>
<td>C$_2$H$_6$-H$_2$O</td>
<td>-1010.2922</td>
<td>137.0329</td>
<td>0.62357</td>
<td>3.77522</td>
</tr>
<tr>
<td>C$_3$H$_8$-H$_2$O</td>
<td>293.4141</td>
<td>15766.5426</td>
<td>0.27138</td>
<td>3.29269</td>
</tr>
<tr>
<td>C$<em>4$H$</em>{10}$-H$_2$O</td>
<td>285.3414</td>
<td>5888.9290</td>
<td>0.27696</td>
<td>3.29248</td>
</tr>
<tr>
<td>CO$_2$-H$_2$O</td>
<td>318.1248</td>
<td>14875.8500</td>
<td>0.39698</td>
<td>1.52926</td>
</tr>
<tr>
<td>H$_2$S-H$_2$O</td>
<td>137.1430</td>
<td>30296.7154</td>
<td>-0.17181</td>
<td>1.16000</td>
</tr>
</tbody>
</table>

#### 3.2- Results of Equilibrium Calculation

Fig. 1 shows the equilibrium curve for the predicted methane hydrate formation pressure based on different mixing rules. Error of calculated pressure in the PR equation of state by using the Danesh mixing rule, Van der Waals, GNQ and WS respectively is 11.62%, 13.16%, 16.74% and 12.33%. So Danesh mixing has a minimum of error for methane hydrate in PR EOS. The reason for the high error in methane hydrate is high formation pressure. The error percent of the model increases at high pressures. As shown in Fig. 1, the obtained results of GNQ mixing rule has considerable deviation with the experimental data at high temperatures.

Model predictions of methane solubility in liquid water for temperatures between 262.4 and 320.1 K and for pressures between 17.9 and 3970 bar are presented in Fig. 2. Danesh mixing with 7.32% error has more accuracy than the three other mixing rules. Results of three phase equilibrium calculation ($VLH_n$) for other systems are given in Figs. 3 to 7. These figures show the predicted values of ethane, propane, carbon dioxide and hydrogen sulfide hydrates formation temperatures, respectively.
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Figure 1. Three phase equilibrium curve of methane hydrate based on four mixing rules by using PR equation of state.

Figure 2. Comparison of calculated methane solubility in liquid water by using PR EOS and four mixing rules, with experimental data.
Figure 3. Three phase equilibrium curve of ethane hydrate based on four mixing rules by using PR equation of state.

Figure 4. Three phase equilibrium curve of propane hydrate based on four mixing rules by using PR equation of state.
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Figure 5. Three phase equilibrium curve of i-butane hydrate based on four mixing rules by using PR equation of state.

Figure 6. Three phase equilibrium curve of carbon dioxide hydrate based on four mixing rules by using PR equation of state.
A summary of results and error percentage for the predicted pressure is given in Table 6 at all studied systems. As shown in this table, the GNQ mixing rule has the minimum error percent.

Table 6. Summary of three phase equilibrium calculation results (\( V_L W \), by using PR EOS and four mixing rules, in six binary mixtures in the considered range of temperature and pressure

<table>
<thead>
<tr>
<th>Mixture</th>
<th>T range (K)</th>
<th>P range (bar)</th>
<th>No. of Points</th>
<th>Danesh MR</th>
<th>Van der Waals MR</th>
<th>GNQ MR</th>
<th>WS MR</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄-H₂O</td>
<td>262.4-320.1</td>
<td>17.9-3970</td>
<td>38</td>
<td>11.62</td>
<td>13.16</td>
<td>16.74</td>
<td>12.33</td>
</tr>
<tr>
<td>C₂H₆-H₂O</td>
<td>273.7-286.5</td>
<td>5.1-27.30</td>
<td>16</td>
<td>15.78</td>
<td>15.84</td>
<td>5.27</td>
<td>15.89</td>
</tr>
<tr>
<td>C₃H₈-H₂O</td>
<td>273.2-278.4</td>
<td>1.65-5.62</td>
<td>16</td>
<td>4.68</td>
<td>4.76</td>
<td>3.31</td>
<td>4.65</td>
</tr>
<tr>
<td>iC₄H₁₀-H₂O</td>
<td>273.2-275</td>
<td>1.10-1.65</td>
<td>17</td>
<td>1.77</td>
<td>1.76</td>
<td>0.71</td>
<td>3.19</td>
</tr>
<tr>
<td>CO₂-H₂O</td>
<td>271.6-283.3</td>
<td>10.40-44.68</td>
<td>34</td>
<td>5.50</td>
<td>5.51</td>
<td>5.84</td>
<td>5.57</td>
</tr>
<tr>
<td>H₂S-H₂O</td>
<td>272.8-302.7</td>
<td>0.93-22.41</td>
<td>19</td>
<td>5.20</td>
<td>5.21</td>
<td>4.92</td>
<td>6.71</td>
</tr>
<tr>
<td></td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7.42%</td>
<td>7.70%</td>
<td>6.13%</td>
<td>8.05%</td>
</tr>
</tbody>
</table>
4- Conclusions
In all of the studied mixtures (except CH4 hydrate and CO2 hydrate), among the mixing rules (with VPT equation), GNQ mixing rule for predicting equilibrium pressure with an average percent of error 6%, is more suitable. It is considerable that the calculated pressure from the GNQ rule is highly dependent on optimized interaction parameters.

Obtained equilibrium pressure from Van der Waals mixing rule is closest to the results of the WS mixing rule. Although the WS mixing is based on Gibbs free energy and has more difficulty than other mixing rules, the results are not suggested, so using it is not recommended.

Calculated results for methane fraction in liquid phase shows that, the Danesh mixing rule for predicting concentrations of liquid is more suitable, because this rule considers the polarity components (H2O molecule).

References