Evaluation of PC-SAFT on the Saturation Pressure Prediction of Different Mixture System at High Temperatures and Pressures

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Abstract. Perturbed-chain statistical associating fluid theory (PC-SAFT) equation of state (EOS) has been used to predict saturation pressure of five different mixing systems which are n-alkane mixture, CH4-CO2-H2O mixture, CO2-dimethyl carbonate (DMC), C3H8-pentafluoroethane (PFE) and methanol-methyl propionate (MTP) under high temperatures and pressures conditions. The data for those five types of mixing systems are cited from previous research. For the n-alkane mixture, PC-SAFT prediction is compared with experimental data. The mixture composition is 30%-70% CH4-C6H14, 50%-50% CH4-C6H14 and 70%-30% CH4-C6H14, respectively. The average absolute relative deviation (AARD) for each mixture is 1.51%, 2.68% and 4.87%. As for 20%-80% CO2-H2O and 4%-16%-80% CH4-CO2-H2O mixture, the AARD is 1.27% and 4.14%, respectively. The AARDs of PC-SAFT prediction on different CO2-DMC mixture are 0.78%, 0.72% and 0.91%, and the overall AARDs between PC-SAFT prediction and experimental data for C3H8-PFE and methanol-MTP mixtures are 6.76% and 5.5%, respectively. Compared with Peng-Robinson (PR) EOS used in original work, PC-SAFT EOS successfully predict the bubble point pressure for common substances used in chemical industry.

1. Introduction

CO2 is the major greenhouse gas of which is mainly caused by fossil fuel combustion. As a result, the capture and sequestration of CO2 has always attracted significant attention from scientists and engineers [1]. The most widely accepted approach to sequester CO2 is the injection of CO2 as an enhancer for the recovery of oil (EOR) into reservoir [2]. This type of EOR process has a common factor, which is the continuous appearance of mixtures of CO2 with other components, such as hydrocarbons, gases or H2O. The H2O-CO2 mixture does not only appear during the CO2 transport process via pipelines but also in the aqueous reservoirs. Obviously, the phase behavior of n-alkanes draws great attention from scientists or engineers in the oil industry [3]. It can affect the pumping of oil significantly since the precipitation of waxes in pipelines causes serious operation issues [4]. In practice, even pure n-alkanes phase behavior can be very complicated.

The equation of state (EOS) approach has been used successfully as a characterization model for phase behavior like saturation pressure. Among all kinds of EOS, Peng-Robinson EOS (PR-EOS) is the most popular and widely used in different mixtures. Duarte et al. [5] have reported the performance of a modified PR-EOS prediction for asymmetric alkane + alkane binary systems. Their study covered methane-alkane mixture from C1 to C36. The results showed the prediction value fit well with the measured data. The progress made in statistical mechanics has promoted the development of molecular-based type EOSes [6, 7]. Among them, PC-SAFT EOS has been successfully applied to predict the thermodynamic properties both for pure-fluids and mixtures [8]. Leekumjorn and Krejbjer...
[9] employed PC-SAFT EOS to model the phase behavior of reservoir fluids. The compressibility factor prediction of Soave-Redlich-Kwong (SRK) EOS for the oil mixture used in their study are overestimated at a low pressure range of 100–200 bar but underestimated at a high-pressure range of 400–500 bar. While the prediction of PC-SAFT fit the experimental data well without obvious deviation through all pressure ranges.

However, all research data has not examined the performance of PC-SAFT EOS on CH$_4$-CO$_2$-H$_2$O system at a temperature between 600K to 800 K and pressure between 1000 bar to 2400 bar and as for CH$_4$-C$_6$H$_{14}$ mixture at 300–430 K and 60–180 bar. The CO$_2$-DMC mixing system is used to test the performance of PC-SAFT on the relatively rare chemical component mixture. In this paper, the phase behavior of all the three above-mentioned types of mixtures and other two usual mixtures used in chemical industry is further studied. The saturation pressure prediction accuracy of PC-SAFT EOS under high temperature and elevated pressure condition are evaluated and compared with both experimental data and PR-EOS prediction used in the original works.

2. Thermodynamic Models

2.1 Peng-Robinson EOS (PR-EOS)

Peng and Robinson developed PR-EOS in 1976 [10]:

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

where \( P, T, v \) and \( R \) stand for pressure, temperature, the molar volume and the universal gas constant, respectively. \( a \) and \( b \) stand for EOS parameters. The following PR-EOS parameters are defined for a pure component:

\[
a_i = 0.45724 \frac{R^2 T_i^2}{P_c} \left[1 + c_i (1 - T_i^{0.5})\right]^2
\]

\[
b_i = 0.07780 \frac{R T_i}{P_c}
\]

where

\[
c_i = 0.37464 + 1.54226 \omega_i - 0.26992 \omega_i^2
\]

and \( T_r \) is the reduced temperature, \( T_c \) is the critical temperature, \( P_c \) is the critical pressure, and \( \omega \) is the acentric factor.

In this work, the mixture PR-EOS parameters are determined by the following mixing rules:

\[
a = \sum_i \sum_j x_i x_j a_{ij}
\]

\[
b = \sum_i x_i b_i
\]

where

\[
a_{ij} = (1 - k_{ij}) (a_i a_j)^{0.5}
\]

and \( k_{ij} \) is the binary interaction parameter between components \( i \) and \( j \).

2.2 PC-SAFT EOS

In the PC-SAFT EOS, the chains consist of spherical segments represent the molecules [8]. The square-well potential model is used to describe the pair potential between the segments. Non-associating molecules are characterized by three pure component parameters \( \sigma, \epsilon, m \), which are the segment diameter independent of temperature, the potential depth and the number of segments per chain,
respectively.

The residual Helmholtz energy is expressed by the sum of hard-chain reference contribution and dispersion contribution in PC-SAFT EOS.

\[ \tilde{a}_{\text{res}} = \tilde{a}_{\text{hc}} + \tilde{a}_{\text{disp}} \]  
(8)

\[ \tilde{a}_{\text{hc}} = \bar{m} \tilde{a}_{\text{hs}} - \sum_{i} \chi_{i} (m_{i} - 1) \ln g_{i}^{\text{hs}} (\sigma_{i}) \]  
(9)

\[ \tilde{a}_{\text{disp}} = -2 \pi \rho I_{1} (\eta, \bar{m}) m_{i}^{2} \varepsilon \sigma_{i}^{3} - \pi \rho \bar{m} C_{1} I_{2} (\eta, \bar{m}) m_{i}^{2} \varepsilon^{2} \sigma_{i}^{3} \]  
(10)

In this paper, only the key equations in PC-SAFT EOS are presented. The full detailed equation expressions can be found in Gross and Sadowski’s original work [8].

2.3 Thermodynamic Condition

The equality of the fugacity of each component in different phases is the thermodynamic requirement for vapor liquid-equilibria (VLE), which can be expressed as:

\[ f_{i}^{V} = f_{i}^{L} \]  
(11)

where \( f_{i}^{V} \) and \( f_{i}^{L} \) are the fugacity of component \( i \) in the vapor and liquid phase, respectively.

2.4 Absolute Average Relative Deviation

The absolute average relative deviation (AARD) between the predicted value and the measured value is used to evaluate the performance of PC-SAFT prediction.

\[ \text{AARD} = \frac{1}{n} \sum_{i=1}^{n} \frac{|X_{i}^{\text{calcd}} - X_{i}^{\text{exp}}|}{X_{i}^{\text{exp}}} \]  
(12)

where \( n \), \( X_{i}^{\text{calcd}} \) and \( X_{i}^{\text{exp}} \) stand for the total number of data points, the calculated saturation pressure, and the measured saturation pressure, respectively.

2.5 Bubble Point Pressure Calculation

The data used in this study are cited from previous literature (Table 1). The procedures of utilizing PC-SAFT EOS to calculate the predicted bubble point pressure are presented in Figure 1.
**Figure 1.** Flowchart for calculation of bubble point pressure by using PC-SAFT EOS

**Table 1.** Saturation pressure data

| Mixture          | composition            | Feed number | Temperature, K | Pressure, bar | reference       |
|------------------|------------------------|-------------|----------------|---------------|----------------|
| CH₄-C₆H₁₄        | 30%-70% CH₄-C₆H₁₄     | 1           | 311.27         | 63.97         | Nojabaei et al., 2013 |
|                  |                        |             | 367.41         | 75.31         |                 |
|                  |                        |             | 422.05         | 78.39         |                 |
| CH₄-C₆H₁₄        | 50%-50% CH₄-C₆H₁₄     | 2           | 311.76         | 115.68        |                 |
|                  |                        |             | 367.16         | 130.76        |                 |
|                  |                        |             | 395.21         | 129.31        |                 |
| CH₄-C₆H₁₄        | 70%-30% CH₄-C₆H₁₄     | 3           | 311.15         | 174.51        |                 |
|                  |                        |             | 338.11         | 181.67        |                 |
|                  |                        |             | 336.52         | 178.73        |                 |
| CO₂-H₂O          | 20%-80% CO₂-H₂O       | 4           | 621.07         | 881.06        | Duan et al., 1992 |
|                  |                        |             | 705.72         | 1332.52       |                 |
|                  |                        |             | 782.07         | 1747.57       |                 |
|                  |                        |             | 845.14         | 2111.65       |                 |
| Mixture       | composition            | Feed number | Temperature, K | Pressure, bar | reference          |
|--------------|------------------------|-------------|----------------|--------------|--------------------|
| CH\textsubscript{4}-CO\textsubscript{2}-H\textsubscript{2}O | 4%-16%-80% CH\textsubscript{4}-CO\textsubscript{2}-H\textsubscript{2}O | 5           | 619.41         | 1055.83      |                    |
|              |                        |             | 699.91         | 1514.56      |                    |
|              |                        |             | 775.43         | 1973.30      |                    |
|              |                        |             | 833.52         | 2388.35      |                    |
| CO\textsubscript{2}-DMC                    | 91.4%-8.6% CO\textsubscript{2}-DMC | 6           | 307.13         | 66.72         |                    |
|              |                        |             | 316.82         | 80.85         |                    |
|              |                        |             | 326.87         | 94.41         |                    |
|              |                        |             | 337.28         | 105.22        |                    |
| CO\textsubscript{2}-DMC                    | 88.2%-11.8% CO\textsubscript{2}-DMC | 7           | 307.13         | 57.73         | Hou et al., 2010   |
|              |                        |             | 316.82         | 70.01         |                    |
|              |                        |             | 326.87         | 84.63         |                    |
|              |                        |             | 337.28         | 97.58         |                    |
|              |                        |             | 833.52         | 2388.35       |                    |
| CO\textsubscript{2}-DMC                    | 85.2%-14.8% CO\textsubscript{2}-DMC | 8           | 307.13         | 55.66         |                    |
|              |                        |             | 316.82         | 67.53         |                    |
|              |                        |             | 326.87         | 81.61         |                    |
|              |                        |             | 337.28         | 94.52         |                    |
| C\textsubscript{3}H\textsubscript{8}-CH\textsubscript{2}CF\textsubscript{3} | 88.28%-11.72% C\textsubscript{3}H\textsubscript{8}-CH\textsubscript{2}CF\textsubscript{3} | 9           | 263.15         | 5.03           |                    |
|              |                        |             | 283.15         | 8.69          |                    |
|              |                        |             | 298.15         | 12.66         |                    |
|              |                        |             | 313.15         | 17.64         |                    |
|              |                        |             | 333.15         | 26.61         |                    |
| C\textsubscript{3}H\textsubscript{8}-CH\textsubscript{2}CF\textsubscript{3} | 73.2%-26.8% C\textsubscript{3}H\textsubscript{8}-CH\textsubscript{2}CF\textsubscript{3} | 10          | 263.15         | 5.84           | Takagi et al., 2003|
|              |                        |             | 283.15         | 10.17         |                    |
|              |                        |             | 298.15         | 14.79         |                    |
|              |                        |             | 313.15         | 20.57         |                    |
|              |                        |             | 333.15         | 38.66         |                    |
| Methanol-MTP | 47.53%-52.47% C\textsubscript{3}H\textsubscript{8}-CH\textsubscript{2}CF\textsubscript{3} | 11          | 263.15         | 6.27           |                    |
|              |                        |             | 283.15         | 11.14         |                    |
|              |                        |             | 298.15         | 16.28         |                    |
|              |                        |             | 313.15         | 23.34         |                    |
|              |                        |             | 333.15         | 37.10         |                    |
| Methanol-MTP | 17.28%-82.72% C\textsubscript{3}H\textsubscript{8}-CH\textsubscript{2}CF\textsubscript{3} | 12          | 263.15         | 5.97           |                    |
|              |                        |             | 283.15         | 10.75         |                    |
|              |                        |             | 298.15         | 15.92         |                    |
|              |                        |             | 313.15         | 22.53         |                    |
|              |                        |             | 333.15         | 34.39         |                    |
| Methanol-MTP | 16.48%-83.52% Methanol-MTP | 13          | 392.62         | 4.52           |                    |
|              |                        |             | 402.84         | 5.81          |                    |
|              |                        |             | 423.86         | 9.26          |                    |
|              |                        |             | 444.59         | 14.02         |                    |
| Methanol-MTP | 29.27%-70.73% Methanol-MTP | 14          | 387.37         | 4.57           | Shariati et al., 2016|
|              |                        |             | 402.70         | 6.75          |                    |
|              |                        |             | 423.86         | 10.77         |                    |
|              |                        |             | 444.74         | 16.35         |                    |
| Methanol-MTP | 85.71%-14.29% Methanol-MTP | 15          | 381.53         | 4.74           |                    |
|              |                        |             | 402.70         | 8.37          |                    |
|              |                        |             | 423.43         | 13.95         |                    |
|              |                        |             | 444.30         | 22.26         |                    |

### Table 1. Saturation pressure data (Cont.)

#### 3. Results and Discussion

##### 3.1 Methane and Hexane System

For methane (C\textsubscript{1}) and hexane (C\textsubscript{6}) system, the data provided by Nojabaei [12] is studied. There are three
different composition \( \text{C}_1\text{-C}_6 \) systems which conclude 30%, 50% and 70% \( \text{C}_1 \), respectively. In the original work, Nojabaei [12] provided the phase envelop for \( \text{C}_1/\text{C}_6 \) mixtures with and without the capillary pressure (\( P_c \)) effect. The phase envelop is shrunk when there is \( P_c \) effect.

In the present research, only the phase behavior of \( \text{C}_1/\text{C}_6 \) mixtures without \( P_c \) effect is studied. Figure 2 shows the saturation pressure profiles at bubble points of 30%-70% \( \text{C}_1/\text{C}_6 \), and 50%-50% \( \text{C}_1/\text{C}_6 \) and 70%-30% \( \text{C}_1/\text{C}_6 \) mixtures, respectively. The saturation pressure increases significantly with \( \text{C}_1 \) composition increase at a similar temperature. It’s also interesting that the prediction accuracy is better without the binary interaction parameter (BIP) tuning. The BIP is cited from Gross and Sadowski [8]. It could be caused by the experimental method effect since the original work by Nojabaei [12] mainly focuses on the \( P_c \) effect. The BIP proposed by Gross and Sadowski [8] didn’t take the \( P_c \) effect into account. And the bubble pressure lines of \( \text{C}_1/\text{C}_6 \) mixture trend to be horizontal with the increase of \( \text{C}_1 \) composition. It tells that the mixture is more stabilized with more \( \text{C}_1 \) in the \( \text{C}_1/\text{C}_6 \) mixture and takes more pressurization work to compress \( \text{C}_1/\text{C}_6 \) into liquid. It’s reasonable since the \( \text{C}_1 \) is lighter than \( \text{C}_6 \) so the mixture contains more \( \text{C}_1 \) are more favor in the vapor phase.

![Figure 2. Comparison of the measured and predicted saturation pressures for \( \text{CH}_4/\text{C}_6\text{H}_{14} \) mixture](image)

### 3.2 Methane-carbon Dioxide-water System

For methane-carbon dioxide-water system, the data provided by Duan [13] is studied. There are one binary mixture of 20%-80% \( \text{CO}_2/\text{H}_2\text{O} \) and one ternary mixture of 4%-16%-80% \( \text{CH}_4/\text{CO}_2/\text{H}_2\text{O} \). In the original work, Duan [13] didn’t provide the exact value of experimental data and EOS prediction. The qtiplot data reading software is used in the present study to process the data in Duan’s work. And the AARD of Duan’s prediction value between experimental data is 4%.

Figure 3 shows the saturation pressure profiles for \( \text{CO}_2/\text{H}_2\text{O} \) and \( \text{CH}_4/\text{CO}_2/\text{H}_2\text{O} \) mixtures, respectively. The BIP used for the \( \text{CO}_2/\text{H}_2\text{O} \) pair is found in Diamantinis and Economou’s work [2]. The saturation pressure is higher when the mixture contains \( \text{CH}_4 \) while the major composition of water remains the same. And the prediction value shows more deviation when the temperature is approaching to the mixture critical region.
3.3 Carbon Dioxide + Dimethyl Carbonate System
For carbon dioxide (CO2)-dimethyl carbonate (DMC) system, the data provided by Chen [14] is studied. There are three different mixing compositions which are 91.4%-8.6% CO2-DMC, 88.2%-11.8% CO2-DMC and 85.2%-14.8% CO2-DMC, respectively. The PC-SAFT parameter for DMC is cited from Im’s paper [15]. Figure 4 shows the saturation pressure profile predicted by PC-SAFT EOS for CO2-DMC binary mixture. The saturation pressure drops significantly with a small increment in DMC composition and with more DMC composition in the mixture.

3.4 Propane + Pentfluoroethane and Methanol + Methyl Propionate Systems
Due to the lack of previous research, the PC-SAFT parameters for pentafluoroethane and methyl propionate are determined by the method introduced by Pouya Hosseinifar [16]. The specific calculation could be found in the original paper. The calculated pentafluoroethane and methyl propionate PC-SAFT parameters are listed in Table 2.
Table 2. PC-SAFT parameters for pentafluoroethane and methyl propionate

|          | Pentafluoroethane | Methyl propionate |
|----------|-------------------|-------------------|
| m        | 3.82              | 3.03              |
| σ        | 3.71              | 3.78              |
| ε/k      | 222.45            | 245.16            |

The data provided by Takagi [17] and Shariati [18] are used to study the predict accuracy of PC-SAFT EOS for C₃H₈-PFE and methanol + MTP mixtures, respectively. PC-SAFT parameters for pentafluoroethane and methyl propionate could found in Gross’ paper [8] and Gross’ paper [19], respectively. The comparison of experimental data between PC-SAFT EOS prediction for C₃H₈-PFE and methanol + MTP mixtures are given in Figures 5 and 6. The overall AARDs of C₃H₈-PFE and methanol + MTP mixtures are 6.76% and 5.5%, respectively. The results show the PC-SAFT EOS successfully predict the bubble point pressure for common substances used in chemical industry.

![Figure 5. Comparison of the measured and predicted saturation pressures for C₃H₈-CHF₂CF₃ mixture](image1)

![Figure 6. Comparison of the measured and predicted saturation pressures for Methanol-MTP mixture](image2)

4. Conclusion
In this study, the performance of PC-SAFT on predicting the saturation pressure of n-alkane-n-alkane
binary mixture, CH$_4$-CO$_2$-H$_2$O, CO$_2$-DMC, C$_3$H$_8$-PFE and methanol + MTP mixtures are successful. The AARDs for Feed #1~3 are 1.51%, 2.68% and 4.87%, respectively. The prediction accuracy is better when the mixture contains less CH$_4$. The AARD for an aqueous mixture of CO$_2$-H$_2$O and CH$_4$-CO$_2$-H$_2$O are 1.27% and 4.14%, respectively. As for CO$_2$-DMC mixtures, the AARDs for Feed 6~8 are 0.78%, 0.72% and 0.91%, respectively. PC-SAFT has been successfully applied to predict the n-alkane mixture and alkane containing water mixture. Since the CO$_2$-H$_2$O system is one of the most important geological fluids on earth [20]. The phase behavior of the mixture contains CO$_2$ and H$_2$O is crucial in many industrial fields and need to be studied more through in the future. The overall AARDs of C$_3$H$_8$-pentafluoroethane and methanol-methyl propionate show that the prediction accuracy of PC-SAFT EOS on relatively rare chemical mixture is still high. Still the prediction of PC-SAFT on other relatively rare chemical components mixture is still needed in the future research.

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