

Application of Peng-Robinson Equation of State for Calculating Solid-Vapor and Solid-Liquid Equilibrium of CH₄-CO₂ System

Gede Wibawa¹, Muhammad F. A. Nafi¹, Asti Permatasari¹ & Asalil Mustain²

¹ Department of Chemical Engineering, Faculty of Industrial Technology, Sepuluh Nopember Institute of Technology (ITS), Kampus ITS Sukolilo, Indonesia

² Department of Chemical Engineering, State Polytechnic of Malang, Indonesia

Correspondence: Gede Wibawa, Department of Chemical Engineering, Faculty of Industrial Technology, Sepuluh Nopember Institute of Technology (ITS), Kampus ITS Sukolilo, Surabaya 60111, Indonesia. E-mail: gwibawa@chem-eng.its.ac.id

Received: May 4, 2015

Accepted: June 5, 2015

Online Published: June 30, 2015

doi:10.5539/mas.v9n7p177

URL: <http://dx.doi.org/10.5539/mas.v9n7p177>

Abstract

In this study, the performances of Peng-Robinson Equation of State combined with the classical mixing rules were evaluated to calculate solid-vapor equilibrium (SVE) and solid-liquid equilibrium (SLE) of CH₄-CO₂ system. The evaluation was performed by comparing the calculated values with the literature data. In the calculation of SVE, the new binary interaction parameter values (k_{ij}) of CH₄-CO₂ mixtures were proposed in this work based on the experimental data. The proposed k_{ij} obtained in this work might increase the accuracy of Peng-Robinson Equation of State by reducing average absolute deviation in the temperatures between calculated values and literature data from (2.18% to 0.26%), (0.88% to 0.70%) and (0.61% to 0.44%) at CO₂ composition of 1%, 1.91% and 2.93%, respectively. Significant improvement was found at CO₂ composition of 1%. In the calculation of SLE, new parameters were not proposed since the calculation using the existing (literature) k_{ij} gives good results with an average absolute deviation of 0.5%.

Keywords: SVE, SLE, Peng-Robinson Equation of State, methane, carbon dioxide

1. Introduction

The increasing number of population and technology advancement encourages the world's rising energy consumption. One of the widely used energy is natural gas. The advantages of the using natural gas compared to other energy sources are energy generated from natural gas is more efficient, cleaner, and environmentally friendly. In addition, natural gas is also colorless, odorless, non-toxic, and non-corrosive (van Egteren, 1993). The composition of raw natural gas is depending on the reservoir source location. It is generally containing of 30% to 90% methane, with other light hydrocarbons (i.e., ethane, propane and other heavier hydrocarbons). On the other hand, some contaminants, such as water, carbon dioxide (CO₂), hydrogen sulfide, helium and nitrogen, are also contained in the natural gas (Scholes et al., 2012). CO₂ is one of greenhouse gas that causes global warming. CO₂ is also an acidic gas and reacts with water to form acidic compounds, namely strong carbonic acid (H₂CO₃) which can cause corrosion in piping systems.

Recently, there are so many methods to distribute natural gas. One of the promising methods used in the distribution of natural gas is liquefied natural gas (LNG). By using this method, the volume of natural gas can be reduced significantly after the liquefaction process that can make the natural gas transportation more efficient (Stringari et al., 2014). In the production of LNG, CO₂ must be removed from natural gas. One of CO₂ removal technology is controlled freeze out method. In this method, CO₂ is removed by utilizing behaviour of phase transitions among vapor, liquid and solid phases. To rational design and optimization condition of this type of separation method, solid-vapor equilibrium (SVE) and solid-liquid equilibrium (SLE) of CH₄-CO₂ system are necessary. In this work, The performance of Peng-Robinson Equation of State (Peng and Robinson, 1976) combined with the classical mixing rules in calculating phase equilibrium for SVE and SLE of CH₄-CO₂ system was evaluated.

2. Calculation Method

In this work, the standard form of Peng-Robinson Equation of State (PR-EoS) was used for the prediction of

solid-vapor and solid-liquid equilibrium for binary mixtures of CH₄-CO₂:

$$P = \frac{RT}{V - b_m} - \frac{a_m}{V(V + b_m) + b_m(V - b_m)} \quad (1)$$

Eq. (1) in cubic form can be written as the following form:

$$Z^3 - (1 - B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \quad (2)$$

where

$$A = \frac{a_m P}{R^2 T^2} \quad (3)$$

$$B = \frac{b_m P}{RT} \quad (4)$$

The values of a_m and b_m of the mixtures were calculated using the classical mixing rules to apply PR-EoS to the mixtures based on the following description:

$$a_m = \sum_{i=1}^N \sum_{j=1}^N z_i z_j (a_i a_j)^{0.5} (1 - k_{ij}) \quad (5)$$

$$b_m = \sum_{i=1}^N z_i b_i \quad (6)$$

$$a_i = 0.45274 \frac{R^2 T_{ci}^2}{P_{ci}} \left[1 + m_i \left(1 - \left(\frac{T}{T_{ci}} \right)^{0.5} \right) \right]^2 \quad (7)$$

$$b_i = 0.0778 \frac{RT_{ci}}{P_{ci}} \quad (8)$$

$$m_i = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2 \quad (9)$$

where z_i are the mole fraction of component i , ω_i are the acentric factor of component i and k_{ij} are the binary interaction parameter characterizing molecular interactions between molecules i and j .

2.1 Solid-Vapor Equilibrium

The fugacity coefficient of a component in the mixture can be calculated using PR-EoS by the following equation:

$$\varphi_i = \exp \left(\frac{b_i}{b_m} (Z - 1) - \ln(Z - B) - \frac{A}{2\sqrt{2}B} \left(\frac{2 \sum_j z_j (a_i a_j)^{0.5} (1 - k_{ij})}{a_m} - \frac{b_i}{b_m} \right) \ln \left(\frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B} \right) \right) \quad (10)$$

Due to the solid phase is almost containing of CO₂ only, the assumption of pure solid CO₂ formation was used. So, the equilibrium relationship between solid and vapor phase in the CO₂ freezing phenomena can be described below:

$$x_2 \varphi_2^v P = P_{2Solid}^{sat} \varphi_2^{sat} \exp \left(\frac{V_{2Solid} (P - P_{2Solid}^{sat})}{RT} \right) \quad (11)$$

The CO₂ vapor pressure was calculated using the exponential equation as described below:

$$P_{2Solid}^{sat} = 9.44 \cdot 10^8 \exp \left(-\frac{3108.2}{T} \right) \quad (12)$$

Although Eq. (11) derived from equating partial fugacity describes the necessary condition for solid CO₂ formation, but it is not sufficient to show the stability of the produced solids. So, the following condition should also be checked in this case:

$$T \leq T^{TP} \quad (13)$$

where T^{TP} is the triple point temperature (for CO_2 , $T^{TP} = 216.55$ K). There are several cases where solids formation is thermodynamically predicted, but the temperature is too high for a stable solid (ZareNezhad and Eggeman, 2006).

2.2 Solid-Liquid Equilibrium

The fugacity coefficient of a component in the mixture can be calculated using PR-EoS by the following equation:

$$\phi_i = \exp \left(\frac{b_i}{b_m} (Z-1) - \ln(Z-B) - \frac{A}{2\sqrt{2}B} \left(\frac{2\sum_j z_j (a_i a_j)^{0.5} (1-k_{ij})}{a_m} - \frac{b_i}{b_m} \right) \ln \left(\frac{Z + (1+\sqrt{2})B}{Z + (1-\sqrt{2})B} \right) \right) \quad (14)$$

Assuming solid phase is pure CO_2 , the solubility of solid CO_2 (2) in the CH_4 (1) can be described by the following equilibrium relationship:

$$x_2 \phi_2^l P = P_{2\text{Solid}}^{\text{sat}} \phi_2^{\text{sat}} \exp \left(\frac{V_{2\text{Solid}} (P - P_{2\text{Solid}}^{\text{sat}})}{RT} \right) \quad (15)$$

To find the solubility of CO_2 , Eq. (15) can be simplified into the following equation (Shen et al., 2012):

$$x_2 = \frac{P_{2\text{Solid}}^{\text{sat}} \phi_2^{\text{sat}} \exp \left(\frac{V_{2\text{Solid}} (P - P_{2\text{Solid}}^{\text{sat}})}{RT} \right)}{\phi_2^l P} \quad (16)$$

3. Results and Discussion

In this work, the calculation of frost points have been made using PR-EoS for the binary CH_4 - CO_2 system with the CO_2 compositions of 1%; 1.91%; and 2.93%. The results were compared with the experimental data determined by Le and Trebble (2007). The best fitted binary interaction parameters based on the classical mixing rule of PR-EoS obtained in this work for the calculation of SVE of CH_4 - CO_2 system are presented in Table 1 together with the literature k_{ij} data as comparison.

Table 1. The best fitted binary interaction parameters obtained in this work for SVE of CH_4 - CO_2 system

CO ₂ Composition	k_{ij}	
	ZareNezhad and Eggeman, 2006	This Work
1%	$-36.134/T^2 + 5.4835/T + 0.0998$	$-5 \cdot 10^{-7}/T^2 - 6 \cdot 10^{-9}/T + 0.6344$
1.91%	$-36.134/T^2 + 5.4835/T + 0.0998$	$-23220/T^2 + 270.84/T - 0.6691$
2.93%	$-36.134/T^2 + 5.4835/T + 0.0998$	$-45967/T^2 + 521.46/T - 1.3487$

The frost points calculated using the binary interaction parameters obtained in this work and using those obtained by ZareNezhad and Eggeman (2006) were compared with the experimental data (Le and Trebble, 2007) as shown in Table 2. As shown in this table, the significant improvement of accuracy was found for CO_2 concentration of 1% by reducing AAD from (2.18% to 0.26%). However for other CO_2 concentrations studied, the improvements were not significant because the calculation using existing k_{ij} also gave a little bit same magnitude of errors with the experimental data. In addition, the proposed present k_{ij} values in this work gave high accuracy for the correlation at lower CO_2 concentration. The illustrations of the improvements were presented in Figures 1 to 3.

Table 2. Average absolute deviation between calculated and experimental (Le and Trebble, 2007) frost point data using present and literature k_{ij} for SVE of CH₄-CO₂ system

CO ₂ Composition	AAD (%)	
	ZareNezhad and Enggeman, 2006	This Work
1%	2.18	0.26
1.91%	0.88	0.70
2.93%	0.61	0.44

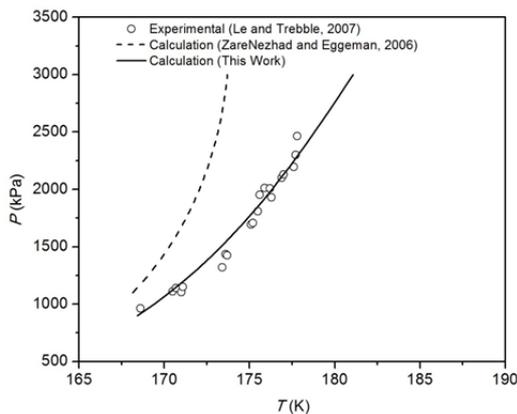


Figure 1. Comparison of calculated frost points using present and literature k_{ij} with experimental data (Le and Trebble, 2007) for SVE of CH₄ (1) + CO₂ (2) system for $x_2 = 1\%$

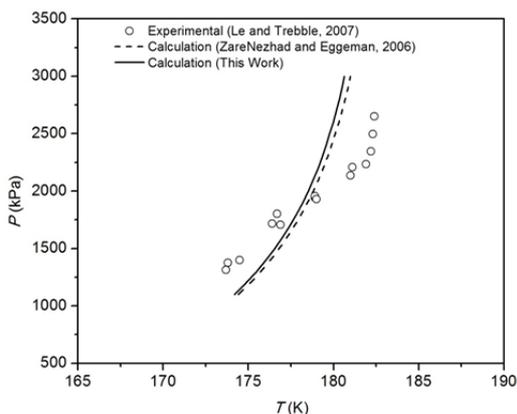


Figure 2. Comparison of calculated frost points using present and literature k_{ij} with experimental data (Le and Trebble, 2007) for SVE of CH₄ (1) + CO₂ (2) system for $x_2 = 1.91\%$

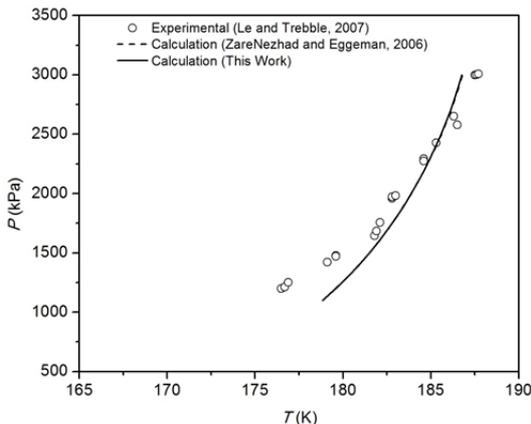


Figure 3. Comparison of calculated frost points using present and literature k_{ij} with experimental data (Le and Trebble, 2007) for SVE of CH₄ (1) + CO₂ (2) system for $x_2 = 2.93\%$

PR-EoS was also applied to calculate SLE in term of solubility of CO₂ (x₂) for CH₄ (1) + CO₂ (2) system with k_{ij} proposed by ZareNezhad and Eggeman (2006). The results were compared with the experimental data obtained by Shen et al. (2012) and giving a good accuracy with average absolute deviation of 0.5% between calculated and experimental solubility data. The comparison was presented in Figure 4.

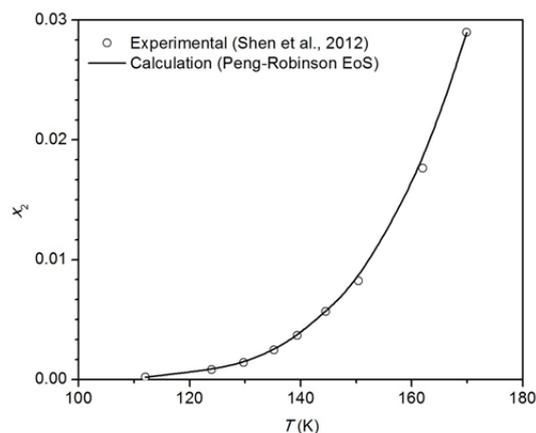


Figure 4. Comparison between calculated solubility of CO₂ (2) in CH₄ (1) using the Peng-Robinson Equation of State and experimental data obtained by Shen et al. (2012)

4. Conclusion

The proposed k_{ij} obtained in this work might improve the accuracy of Peng-Robinson Equation of State combined with classical mixing rules in calculation of SVE of CH₄ (1) + CO₂ (2) system by reducing average absolute deviation (AAD) from (2.18% to 0.26%) for the CO₂ composition of 1%, (0.88% to 0.70%) for the CO₂ composition of 1.91%, and (0.61% to 0.44%) for the CO₂ composition of 2.93%. The significant improvement was found for CO₂ concentration of 1%. The calculation of SLE based in the literature k_{ij} gave absolute average deviation of 0.5% between calculated and literature data for solubility of CO₂ in CH₄-CO₂ system.

Nomenclature

A	Peng-Robinson Equation of State parameter
a	Peng-Robinson Equation of State parameter
B	Peng-Robinson Equation of State parameter
b	Peng-Robinson Equation of State parameter
k	Binary interaction coefficient
m	Peng-Robinson Equation of State parameter
N	Number of component
P	System pressure (kPa)
P_2^{sat}	Saturated vapor pressure of solid CO ₂ at system temperature (kPa)
R	Universal gas constant (=8.314 J·mol ⁻¹ ·K ⁻¹)
T	System temperature (K)
V	Molar volume (m ³ ·mol ⁻¹)
z	Mole fraction of component
Z	Compressibility factor

Greek letters

φ	Fugacity coefficient
ω	Acentric factor

Subscripts

c	Critical condition
-----	--------------------

<i>i</i>	Component <i>i</i>
<i>j</i>	Component <i>j</i>
<i>m</i>	Mixtures
1	Methane
2	Carbon dioxide

Superscripts

<i>v</i>	Vapor phase
<i>l</i>	Liquid phase
<i>sat</i>	Saturated condition
<i>TP</i>	Triple point

References

- Le, T. T., & Trebble, M. A. (2007). Measurement of carbon dioxide freezing in mixtures of methane, ethane, and nitrogen in the solid–vapor equilibrium region. *Journal of Chemical & Engineering Data*, *52*, 683-686. <http://dx.doi.org/10.1021/je060194j>
- Peng, D. Y., & Robinson, D. B. (1976). A new two-constant equation of state. *Industrial & Engineering Chemistry Fundamentals*, *15*, 59-64. <http://dx.doi.org/10.1021/i160057a011>
- Scholes, C. A., Stevens, G. W., & Kentish, S. E. (2012). Membrane gas separation applications in natural gas processing. *Fuel*, *96*, 15-28. <http://dx.doi.org/10.1016/j.fuel.2011.12.074>
- Shen, T., Gao, T., Lin, W., & Gu, A. (2012). Determination of CO₂ solubility in saturated liquid CH₄+ N₂ and CH₄ + C₂H₆ mixtures above atmospheric pressure. *Journal of Chemical & Engineering Data*, *57*, 2296-2303. <http://dx.doi.org/10.1021/je3002859>
- Stringari, P., Campestrini, M., Coquelet, C., & Arpentinier, P. (2014). An equation of state for solid–liquid–vapor equilibrium applied to gas processing and natural gas liquefaction. *Fluid Phase Equilibria*, *362*, 258-267. <http://dx.doi.org/10.1016/j.fluid.2013.10.020>
- van Egteren, M. (1993). Natural gas for electric power generation: Advantages, availability and reliability. *Utilities Policy*, *3*, 145-153. [http://dx.doi.org/10.1016/0957-1787\(93\)90006-I](http://dx.doi.org/10.1016/0957-1787(93)90006-I)
- ZareNezhad, B., & Eggeman, T. (2006). Application of Peng–Robinson Equation of State for CO₂ freezing prediction of hydrocarbon mixtures at cryogenic conditions of gas plants. *Cryogenics*, *46*, 840-845. <http://dx.doi.org/10.1016/j.cryogenics.2006.07.010>

Copyrights

Copyright for this article is retained by the author(s), with first publication rights granted to the journal.

This is an open-access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/3.0/>).