

# Modifying Peng-Robinson Equation of State to Consider Influence of Confinement on Fluid Phase Behavior

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## Abstract

The behavior of confined fluids in shale reservoirs is significantly different from that of bulk fluids due to the confinement of nanopores. The unique physicochemical properties of confined fluids invalidate the current available equations of state (EOS) used in such reservoirs. In this study, first, the molar volume term of the Peng-Robinson equation of state (PR-EOS) is modified to describe the phase behavior of fluid under confinement. Second, a new dimensionless parameter  $\beta$  is proposed to describe fluid adsorption in nanopores and its empirical correlation is given. Finally, based on the modified PR-EOS, a generalized analytical formula is proposed to calculate critical temperature and pressure shifts by considering fluid adsorption in the nanopores. The modified PR-EOS, new adsorption correlation, and generalized formulations have been validated to be accurate by comparing with the experimental and molecular simulation results. The modified PR-EOS can provide a consistent fluid phase behavior description over the macro-to nano-scale pore sizes.

Keywords: modified PR-EOS, nanopores, confined fluids, critical shifts

## Introduction

As an unconventional resource, shale oil point to a promising future. Despite the great success of some development methods (horizontal drilling and multi-stage fracturing), many challenges remain, such as inaccurate estimates of reserves and production due to unknown fluid phase- and flow-behavior within tiny pores. The fully understand of fluid phase behavior is critical for efficient production of all reservoirs. In both conventional and unconventional reservoirs, inappropriate characterization and erroneous phase behavior models are the main reasons for the industry to face many production problems(Salahshoor et al., 2018).

The diameter of pore throat in conventional reservoirs is more than 2  $\mu\text{m}$ , however, the shale reservoir is dominated by nanopores, and the diameter of pore throat tends to be 1-100nm(Nelson, 2009). As the system scale is reduced to the nanometer scale, the molecular-molecular and molecular-wall interactions are enhanced, that is, the confinement effect is significant, which leads to fundamental

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changes in the thermodynamic characteristics and phase equilibrium of the fluid(Kamari et al., 2018; Zhang et al., 2016; Zuo et al., 2018). Specifically, the critical properties of confined fluids in nanopores are more complex than those of bulk fluids(Islam et al., 2015; Pitakbunkate, 2014; Pitakbunkate, 2016; Tan et al., 2019; Wu et al., 2016).

It has become a consensus that spatial confinement can cause critical property shifts of fluids in nanopores, however, the extent and trend of these shifts remains controversial(Jana et al., 2009; Morishige and Shikimi, 1998; Singh and Singh, 2011; Wu et al., 2016; Zarragoicoechea and Kuz, 2004). Zarragoicoechea and Kuz (2004) utilize generalized van der Waals theory to conclude that the shifts of critical temperature and pressure of confined fluids in nanopore have the same behavior, and obtained two correlations, which is commonly accepted and widely applied(Dong et al., 2016; Li and Sheng, 2017; Mohammad et al., 2018; Zarragoicoechea and Kuz, 2004; Zhang et al., 2019; Zhang et al., 2016). However, the two correlations cannot be considered universal because they assumed that the walls are inert, this means that no fluid-walls interactions are considered in their models. Recent studies have cast doubt on this(Islam et al., 2015; Singh et al., 2009; Tan et al., 2019; Wu et al., 2016). Tan et al. (2019) found, for example, that temperature decrease was 1 order of magnitude smaller than the pressure decrease using a differential scanning calorimeter(Tan et al., 2019). Experimental investigation is the earliest method to research fluid phase behavior in nanopores. However, due to the complexity of nanopores and the limitations of equipment, experimental study is very difficult and of high uncertainty. Therefore, it is of great significance to develop an effective and reliable method for modeling and predicting confined fluid phase behavior.

In this study, first, the traditional PR-EOS is modified to describe the phase behavior of fluid under confinement by the modification of molar volume term. Second, a new dimensionless parameter  $\beta$  is proposed to describe fluid adsorption in nanopores and its empirical correlation is given. Finally, based on the modified PR-EOS, a generalized analytical formula is proposed to calculate critical temperature and pressure shifts by considering fluid adsorption in the nanopores.

## Adsorption and effective molar volume

In the pore network, fluid molecules are usually absorbed on the pore wall and kept unmoved. In large pore sizes, compared with the bulk number of liquid molecules, the limited number of absorbed molecules can be neglected. In tight reservoirs, absorption will be significant and greatly reduce the number of molecules in the fluid that can be moved. This is more pronounced in nanopores, because the total number of molecules is limited, the absorption may limit a large proportion of fluid molecules as shown in Fig.1. The reduction number of movable fluid molecules will lead to the change of effective molar volume, which requires modification of the effective molar volume term in the traditional PR-EOS, so as to apply it to the fluid in confined nanopores.

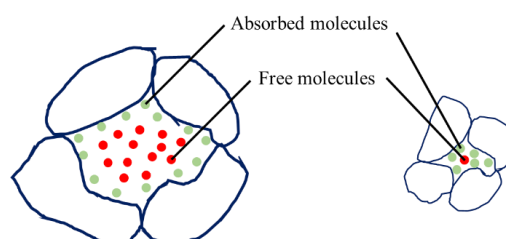


Fig. 1 Schematica of adsorption in pores. (left: large pore where adsorption is ignored, right: tiny pore where adsorption is significant)

Here, a cylindrical pore model is established to consider the effect of adsorption on effective molar volume, as shown in Fig.2. The pore model consists of two parts: Adsorption region and Free region.  $R_p$  is the pore radius,  $R_e$  is the effective radius,  $h$  is the thickness of adsorption region in radius direction,  $L$  is the length of the cylindrical pore. The effective molar volume should be the number of moles of the internal free fluid divided by the volume of the cylindrical pore.

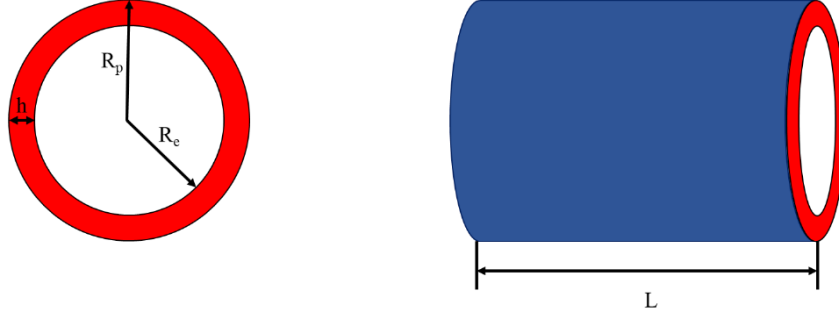


Fig. 2 Sketch map of pore model. (The adsorption region is shown in red, the center white area corresponds to free liquid.)

In this study, we assume that the fluid molecules are spherical. The adsorption region is defined as the section in which its local density deviates from the bulk, and density can be characterized by effective molecular volume coefficient  $\varepsilon$  which is defined by

$$\varepsilon = \frac{V_e}{V_{real}} \quad (1)$$

Where  $V_e$  is the effective volume of per fluid molecule,  $V_{real}$  is the real volume of per fluid molecule. The number of absorbed fluid molecule  $n_a$  can be describe as the ratio of adsorption volume ( $V_a$ ) and effective volume of per absorbed fluid molecule ( $V_e$ ).

$$n_a = \frac{V_a}{V_e} = \frac{\pi R_p^2 L - \pi R_e^2 L}{\varepsilon_a V_{real}} = \frac{\pi L (2R_p h - h^2)}{\varepsilon_a V_{real}} \quad (2)$$

Where  $\varepsilon_a$  is the effective molecular volume coefficient of adsorption region. The number of total fluid molecule  $n_t$  can be describe as the ratio of pore volume ( $V_p$ ) and effective volume of per free fluid molecule ( $V_e$ ).

$$n_t = \frac{V_p}{V_t} = \frac{\pi R_p^2 L}{\varepsilon_t V_{real}} \quad (3)$$

Where  $\varepsilon_t$  is the effective molecular volume coefficient without adsorption. The original molar volume  $V_m$  in PR-EOS is:

$$V_m = \frac{V_p}{n_t / N_A} \quad (4)$$

Where  $N_A$  is the Avogadro's number. The modified molar volume  $V'_m$  is:

$$V'_m = \frac{V_p}{(n_t - n_a)/N_A} \quad (5)$$

It can be rewritten as:

$$V'_m = \frac{n_t}{(n_t - n_a)} V_m = \frac{V_m}{1 - \frac{\varepsilon_t}{\varepsilon_a} \left( \frac{2h}{R_p} - \left( \frac{h}{R_p} \right)^2 \right)} \quad (6)$$

We define a parameter  $\beta$ , which is the ratio of  $\varepsilon_t$  to  $\varepsilon_a$  and is adjustable. Thus, the modified molar volume can be describe as:

$$V'_m = \frac{V_m}{1 - \beta \left( \frac{2h}{R_p} - \left( \frac{h}{R_p} \right)^2 \right)} \quad (7)$$

### Modifications of Peng-Robinson equation of state

The traditional Peng-Robinson equation of state (PR EOS) is as follows:

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m(V_m + b) + b(V_m - b)} \quad (8)$$

For fluids confined in a cylindrical nanopore, substitute the original molar volume by the modified one, then the modified PR-EOS can be listed as:

$$P = \frac{RT}{V'_m - b} - \frac{a}{V'_m (V'_m + b) + b(V'_m - b)} \quad (9)$$

Therefore,

$$P = \frac{RT}{\frac{V_m}{\left(1 - \beta \left( \frac{2h}{R_p} - \left( \frac{h}{R_p} \right)^2 \right)\right)} - b} - \frac{a}{\left[ \frac{V_m}{\left(1 - \beta \left( \frac{2h}{R_p} - \left( \frac{h}{R_p} \right)^2 \right)\right)} \right] \left[ \frac{V_m}{\left(1 - \beta \left( \frac{2h}{R_p} - \left( \frac{h}{R_p} \right)^2 \right)\right)} + b \right] + b \left[ \frac{V_m}{\left(1 - \beta \left( \frac{2h}{R_p} - \left( \frac{h}{R_p} \right)^2 \right)\right)} - b \right]} \quad (10)$$

Equation (10) is the modified PR-EOS for fluids confined in a cylindrical pore.

For any cubic equation of state, an inflection point exists at the critical point. Mathematically speaking, the first and second derivatives of pressure with respect to volume at a constant temperature are equal to zero at critical point:

$$\left( \frac{\partial P}{\partial v} \right)_{T=T_c} = \left( \frac{\partial^2 P}{\partial v^2} \right)_{T=T_c} = 0 \quad (11)$$

Imposing Equation (11) on Equation (10) and solving for parameters a and b yields.

$$a = 0.457235 \frac{R^2 T_c^2}{P_c} \quad (12)$$

$$b = \frac{0.0777969}{\left(1 - \beta \left(\frac{2h}{R_p} - \left(\frac{h}{R_p}\right)^2\right)\right)} \frac{RT_c}{P_c} \quad (13)$$

Then the expressions of critical pressure and critical temperature can be derived as follows:

$$P_{cm} = 0.01324 \frac{a}{b^2} \left(1 - \beta \left(\frac{2h}{R_p} - \left(\frac{h}{R_p}\right)^2\right)\right)^2 \quad (14)$$

$$T_{cm} = 0.17015 \frac{a}{bR} \left(1 - \beta \left(\frac{2h}{R_p} - \left(\frac{h}{R_p}\right)^2\right)\right) \quad (15)$$

Where  $P_{cm}$  and  $T_{cm}$  are the critical pressure and critical temperature calculated from the modified PR-EOS. With the critical pressure ( $P_c$ ) and critical temperature ( $T_c$ ) of the traditional PR EOS, the shift of critical properties are defined as follows:

$$\Delta P_c = \frac{P_c - P_{cm}}{P_c} = 1 - \left(1 - \beta \left(\frac{2h}{R_p} - \left(\frac{h}{R_p}\right)^2\right)\right)^2 \quad (16)$$

$$\Delta T_c = \frac{T_c - T_{cm}}{T_c} = \beta \left(\frac{2h}{R_p} - \left(\frac{h}{R_p}\right)^2\right) \quad (17)$$

### Correlation for critical property shift

Equation (14-17) indicate that the molecule-pore wall interaction leads to the shift of critical properties. Experimental and molecular dynamic simulation results have concluded that the critical properties decrease sharply with the decrease of poresize. Singh et al. studies the shift in the temperature as a function of the ratio of pore size to the molecule size.

In this studies, in order to eliminate the effect of molecular size, the ratio of effective molecule size ( $D_e$ ) to pore size ( $R_p$ ) is used in Fig.3. The effective molecular diameter is not the width or length of the molecule, but the diameter of the smallest cross section of the molecule.

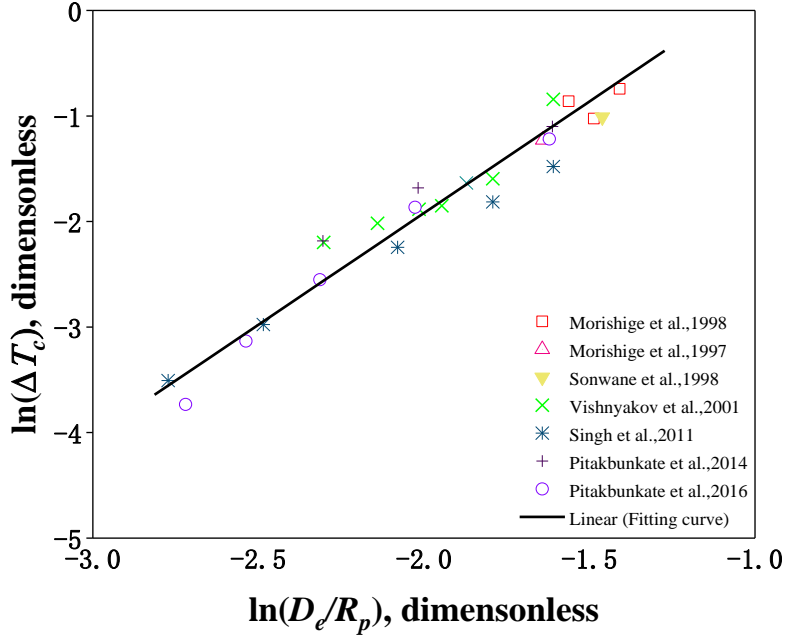


Fig. 3 Correlation of critical temperature shift versus dimensionless pore size.

There is a linear relationship between the natural logarithm of the critical temperature shift and the natural logarithm of the dimensionless pore size. The correlation of  $T_c$ -shift is quartic which is expressed as:

$$\ln(\Delta T_c) = 2.1161 \times \ln\left(\frac{D_e}{R_p}\right) + 2.3117 \quad (18)$$

The critical temperature shift can be then derived as:

$$\Delta T_c = 10.09156 \times \left(\frac{D_e}{R_p}\right)^{2.1161} \quad (19)$$

It can be seen from the above relationship and Fig. 3 that as the dimensionless pore size increases, the critical temperature change amplitude decreases, that is, as the pore size increases, the molecular wall interaction is significantly weakened.

If we substitute Equation (19) into the Equation (17), the parameter  $\beta$  for the modified PR-EOS can be calculated for any fluids as:

$$\beta = 10.09156 \frac{\left(\frac{D_e}{R_p}\right)^{2.1161}}{2\left(\frac{h}{R_p}\right) - \left(\frac{h}{R_p}\right)^2} \quad (20)$$

Where  $D_e$  set to  $h$  when single layer adsorption occurs. By determining the  $\beta$ -value of a particular pure component in a particular pore size, the modified PR-EOS can be solved to give the fluid properties of the component. For mixtures, similar approach can be used if reasonable mixing rules are given.

## Results and discussion

We have reproduced the critical property shifts for different components with our modified PR-EOS. The results have been further validated by the experiment and molecular simulation results, as shown in Fig.4 and Fig.5.

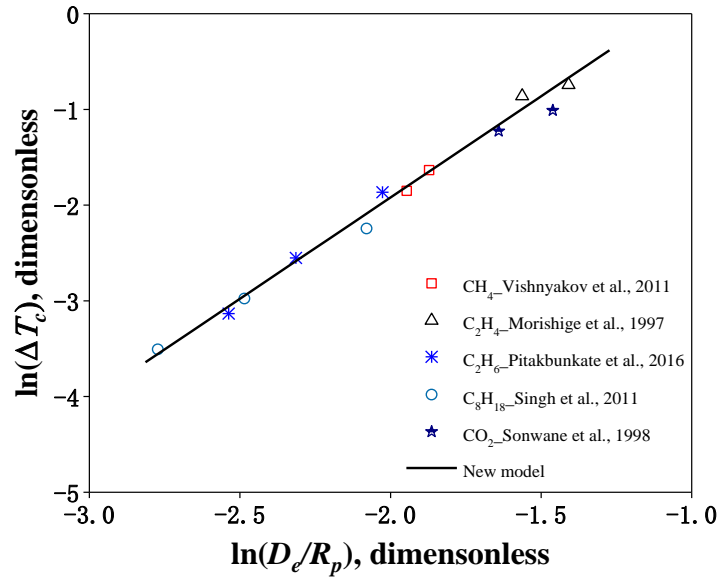


Fig. 4 Critical temperature shift from modified PR-EOS. (The symbols and lines represent, respectively, literature data and calculations.)

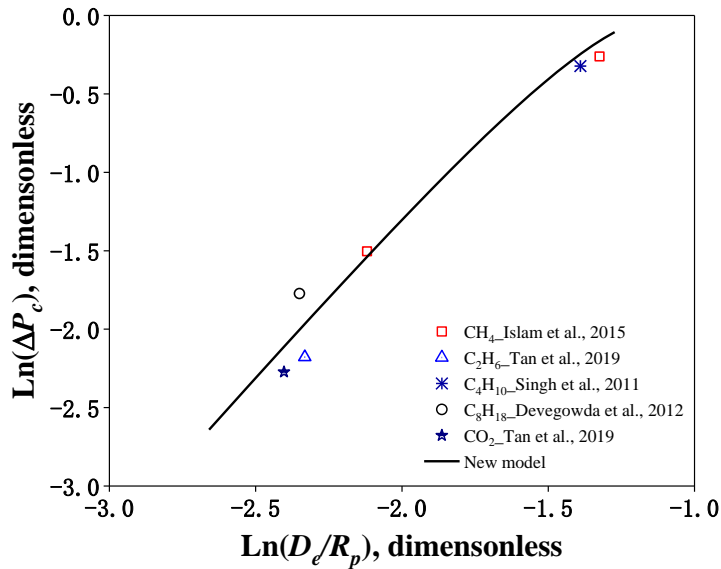


Fig. 5 Critical pressure shift from modified PR-EOS. (The symbols and lines represent, respectively, literature data and calculations.)

Fig.4 and Fig.5 shows that the relationship of critical temperature and pressure shifts and  $\frac{D_e}{R_p}$  is consistent with the results of many experiment and numerical simulation. It also shows that critical pressure is more sensitive to pore proximity than the critical temperature. Due to the molecular-molecular interaction and confinement effect, adsorption layer was formed on the inner surface of the nanopore, which changed the critical properties and affected the phase equilibrium. The critical property shifts starts at  $R_p < 100\text{nm}$  and increases significantly with the decrease of pore radius. In addition, the critical property shifts increases with pore radius reduction, and is more obvious at very small nanopores such as  $R_p = 1\text{ nm}$ .

## Conclusions

The change of fluid critical properties in nanopores has long been a consensus, but the current experimental methods cannot fully explore this phenomenon. In this work, the Peng-Robinson equation of state (PR-EOS) is modified by considering the effect of nanopore confinements on effective molar volume. Based on the modified PR-EOS and the proposed dimensionless adsorption parameters, a generalized equation is established to calculate the change of critical temperature and critical pressure with the adsorption amount of nanopores, which can accurately predict the relationship between the shifts of critical properties and dimensionless pore size. More experiments are needed to verify the performance of the modified PR-EOS on the critical pressure shifts.

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## Nomenclature

- $a$  = attraction parameter in PR-EOS,  $\text{kPa}\cdot\text{m}^3/\text{kmol}$
- $b$  = van der Waals volume,  $\text{m}^3/\text{kmol}$
- $P$  = pressure, MPa
- $T$  = temperature, K
- $T_r$  = reduced temperature
- $T_c$  = critical temperature of the original PR-EOS, K
- $P_c$  = critical pressure of the original PR-EOS, MPa
- $V_m$  = molar volume calculated by the original PR-EOS,  $\text{m}^3/\text{kmol}$
- $V'_m$  = molar volume calculated by the modified PR-EOS,  $\text{m}^3/\text{kmol}$



$R$  = gas constant,  $\text{dm}^3 \cdot \text{Pa} / (\text{mol} \cdot \text{K})$   
 $P_{cm}$  = critical pressure of the modified PR-EOS, MPa  
 $T_{cm}$  = critical temperature of the modified-PR EOS, K  
 $\Delta P_c$  = shift of critical pressure  
 $\Delta T_c$  = shift of critical temperature  
 $V_e$  = effective volume of per fluid molecule,  $\text{m}^3$   
 $V_{real}$  = the real volume of per fluid molecule,  $\text{m}^3$   
 $\varepsilon$  = effective molecular volume coefficient  
 $R_p$  = pore radius, m  
 $R_e$  = effective radius, m  
 $D_e$  = effective molecular diameter, m  
 $h$  = thickness of adsorption region, m  
 $L$  = length of the cylindrical pore, m  
 $n_a$  = number of absorbed fluid molecule  
 $n_t$  = number of total fluid molecule  
 $V_a$  = adsorption volume,  $\text{m}^3$   
 $\beta$  = adsorption parameters  
 $Z_V$  = compressibility factor of vapor phase  
 $Z_L$  = compressibility factor of liquid phase  
 $\delta_{ij}$  = binary interaction coefficient  
 $\varphi_V^i$  = fugacity coefficient of component  $i$  in the vapor phase  
 $\varphi_L^i$  = fugacity coefficient of component  $i$  in the liquid phase

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## Appendix

Rearranging modified PR-EOS into the compressibility factor form, gives

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

Where  $A = \frac{aP}{(RT)^2}$ ,  $B = \frac{bP}{RT} \left( 1 - \beta \left( \frac{2R_a}{R_t} - \left( \frac{R_a}{R_t} \right)^2 \right) \right)$ ,  $Z$  is the compressibility factor of liquid or vapor phase.

For a mixture, the van der Waals mixing rule is used for calculating constants  $a$  and  $b$ .

$$a = \sum_i \sum_j x_i x_j (a_i a_j)^{0.5} (1 - \delta_{ij}) \quad (2)$$

$$b = \sum_{i=1}^n x_i b_i \quad (3)$$

Where  $\delta_{ij}$  is the binary interaction coefficient of components  $i$  and  $j$ .  $\delta_{ij} = \delta_{ji}$ , and  $\delta_{ii} = \delta_{jj} = 0$ . From the EOS shown in Equation (3), the fugacity coefficient of a pure component is

$$\ln \varphi_{pure} = -\ln[Z - B] + (Z - 1) + \frac{A}{2\sqrt{2}B} \ln \left[ \frac{Z + B(1 + \sqrt{2})}{Z + B(1 - \sqrt{2})} \right] \quad (4)$$

For a mixture

$$\begin{aligned} \ln \varphi_V^i = & -\ln[Z_V - B_V] + \frac{b_i}{b} (Z_V - 1) \\ & + \frac{A_V}{2\sqrt{2}B_V} \left[ \frac{1}{a} \left( 2\sqrt{a_i} \sum_{j=1}^{nc} z_j \sqrt{a_i} (1 - \delta_{ij}) \right) - \frac{b_i}{b} \right] \ln \left[ \frac{Z_V + B_V(1 + \sqrt{2})}{Z_V + B_V(1 - \sqrt{2})} \right] \end{aligned} \quad (5)$$

$$\begin{aligned} \ln \varphi_L^i = & -\ln[Z_L - B_L] + \frac{b_i}{b} (Z_L - 1) \\ & + \frac{A_L}{2\sqrt{2}B_L} \left[ \frac{1}{a} \left( 2\sqrt{a_i} \sum_{j=1}^{nc} z_j \sqrt{a_i} (1 - \delta_{ij}) \right) - \frac{b_i}{b} \right] \ln \left[ \frac{Z_L + B_L(1 + \sqrt{2})}{Z_L + B_L(1 - \sqrt{2})} \right] \end{aligned} \quad (6)$$

where  $Z_V$  and  $Z_L$  are the compressibility factors of the vapor and liquid phases;  $A_i$  and  $B_i$  ( $i = V, L$ ) are the constants calculated from the vapor pressure or liquid pressure.

$$A_V = \frac{aP^V}{(RT)^2}, \quad B_V = \frac{bP^V}{RT} \left( 1 - \beta \left( \frac{2R_a}{R_t} - \left( \frac{R_a}{R_t} \right)^2 \right) \right) \quad (7)$$

$$A_L = \frac{aP^L}{(RT)^2}, \quad B_L = \frac{bP^L}{RT} \left( 1 - \beta \left( \frac{2R_a}{R_t} - \left( \frac{R_a}{R_t} \right)^2 \right) \right) \quad (8)$$