Modeling the Viscosity for \((nC_5+nC_8), (nC_5+nC_{10}), (nC_8+nC_{10})\) and \((nC_5+nC_8+nC_{10})\) Systems with Peng-Robinson Viscosity Equation of State

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Abstract
The aim of this modeling study is to improve the performance of the Peng-Robinson viscosity equation of state. To achieve this aim, the couple of Peng-Robinson viscosity equation of state and the proposed mixing rules has been applied for modeling the viscosities of the binary and ternary systems containing \((nC_5+nC_8), (nC_5+nC_{10}), (nC_8+nC_{10})\) and \((nC_5+nC_8+nC_{10})\) for temperatures and pressures ranged \((297.75-373.35)\) K and \((49.95-246.26)\) bar, respectively. First, the pressure temperature-dependent and constant expressions for the binary interaction coefficients of binary systems have been determined. Subsequently, these empirical correlations of binary interaction coefficients have been applied to predict the viscosities for ternary mixture of \((nC_5+nC_8+nC_{10})\). For this ternary mixture, the results of model show acceptable accuracy (overall AAD~7.77 % and 8.02 for mixing rule 1 and 2, respectively).

Keywords
Viscosity, Equation of state, mixture, mixing rule, viscosity model, Peng Robinson

1 Introduction
Viscosity is a transport property which can be related to the strength of the forces acting between the molecules. Viscosity modelling is of high importance in many engineering purposes such as designing petrochemical equipments, the underground movement of the oil, heat and mass transfer rate and the numerical modeling of fluid flow. Since viscosity is a significant parameter in diffusion analysis and the hydrodynamic processes modeling require the accurate dynamic viscosities, the precise values of viscosity over wide ranges of pressure and temperature are of fundamental importance. Although the reliable viscosities can be determined with the experimental methods, it is not possible for researchers to determine the viscosity values for all mixtures by using experimental measurements (especially at high pressures); therefore, according to this limitation, the viscosity must be described by applying numerical simulation methods [1,2].

Several methods exist for modeling the viscosities of the mixtures such as the empirical correlations [3] and thermodynamical methods [4,5,6]. The empirical correlation of Lohrenz et al. [3] and the corresponding states model of [7] are conventional approaches to describe the viscosity of hydrocarbon mixtures. The narrow ranges of the thermodynamic conditions in their application and the requirement of fluid densities to calculate viscosities are two main limitations of these methods hindering their usage. On the other hand, the statistical physics approaches are very complicated and they are insufficiently developed to describe the viscosity of mixtures. According to the similarities between the \(PvT\) and \(T_{\mu}P\) relationships and diagrams, several researchers have developed the viscosity equations of state. The viscosity equations of state can be applied for pure components and their mixtures at high and low pressures. The main advantage of using viscosity equations of state is that no fluid density is needed for modeling the viscosity [4]. In recent years, several researches have been conducted on modeling the viscosity of hydrocarbons and their mixtures. Khosharay [6] proposed a mixing rule for the viscosity based Peng-Robinson equation of state to compute the viscosity of light liquid hydrocarbon mixtures. The results of this model
proved that it worked well for binary, ternary, quaternary and five-component hydrocarbon mixtures (AAD=4.83 %). Fan and Wang [4] suggested the Peng-Robinson model to describe the viscosity for pure light hydrocarbons and their mixtures. The proposed model was successfully applied for computing viscosities of light hydrocarbons and their mixtures (AAD=9.47 %). Wang et al. [8] utilized the PR viscosity EOS for hydrocarbons containing heptane, octane, nonane, hexyl benzene and their ternary mixtures. The results of the proposed model showed the good performance of model for specified systems (AAD=0.13 %). Guo et al. [9] suggested two viscosity EOSs containing Petal–Teja and PR EOSs. Guo et al. [10] used Peng-Robinson viscosity EOS for pure hydrocarbons and their mixtures. This model could be applied for both high and low pressures. Derevich [5] applied a thermodynamic model for describing the viscosities of pure hydrocarbons and their mixtures. This model successfully reproduced the experimental viscosities not only pure components in vapor and liquid phases but also solutions in the wide ranges of thermodynamic conditions with AAD of 6 %. Tan et al. [11] applied Friction theory in combination with statistical associating fluid theory (SAFT1 and PC-SAFT) to model the viscosities of \( n \)-Alkane mixtures. Based on the results of the model, the accuracy was adequate for engineering applications. Lawal [12] proposed a four-parameter viscosity EOS based on Lawal–Lake–Silberberg model for pure hydrocarbons and their mixtures.

Since the applied model in the work of Khosharay [6] can be applied for limited light liquid hydrocarbon mixtures, in this modeling investigation, two suggested mixing rules have been coupled with the PR\( \mu \) model. In these two mixing rules, the binary interaction parameters have been considered, taking advantage of the well described viscosity. These binary interaction parameters have been determined based on the experimental viscosities for binary mixtures of \((nC_7+nC_8)\), \((nC_8+nC_{10})\), \((nC_9+nC_{10})\) binary systems. These binary interaction parameters have been utilized for modeling the viscosities of \((nC_5+nC_9+nC_{10})\) ternary liquid hydrocarbon system. The performance of this model has been compared with the previous model [6].

\[ T' = \frac{R'P}{\mu - b} + \frac{a}{\mu^2 + 2b \mu - b} \] (1)

In Eq. (1), a presumptive temperature, \( T' \), is computed by using following equations:

\[ T' = T - T_d \] (2)

\[ T_d = 0.45T_c \] (3)

where \( P \) shows the pressure, \( T \) is the temperature of system, \( \mu \) represents the viscosity and subscript \( c \) is the critical state. According to the minimum deviation of the modeled viscosities from the experimental viscosities, the coefficient of 0.45 has been chosen for \( T_d \) [4].

The coefficients of \( a, b \) and \( r_c \) are computed as follows:

\[ a = 0.45724 \frac{(r_c P_c)^2}{T_c} \] (4)

\[ b = 0.0778 \frac{r_c P_c}{T_c} \] (5)

\[ r_c = \frac{p_c T_c}{0.3074P_c} \] (6)

Based on the [13], the critical viscosity, \( \mu_c \), is calculated in terms of critical temperature \( (T_c) \), critical pressure \( (P_c) \) and molecular weight \( (M_w) \):

\[ \mu_c = 7.7T_c^{-1/6}M_w^{1/2}P_c^{2/3} \] (7)

In Eq. (7), \( \mu_c \) has been expressed in terms of micropoise.

In Eq. (1), \( R' \) is computed as follows:

\[ R' = \beta (P) r_c \] (8)

In Eq. (8), \( \beta (P) \) is a function of pressure. The value of this parameter is 1 at critical pressure and it is determined as follows:

\[ \beta (P) = \frac{\rho (1 - P_c^{-1})}{0.02715P_c^{-1}((P_c + 0.25)^{-1} - 0.8) + P_c^{-1}} \] (9)

In Eq. (9),

\[ \rho = 0.03192 - 3.3125 \times 10^{-4} M_w \omega \] (10)

The above viscosity model developed from PR EOS is named PR\( \mu \) model.

2.2 PR\( \mu \) model

The PR\( \mu \) model poorly represented liquid viscosity so that the correction of viscosity must be applied. This correction is written as follows:

\[ \mu = \mu^{PR} + \varphi_0 + \varphi \] (11)
In Eq. (11), \( \mu^{PR} \) shows the viscosity that is calculated by using Eq. (1) and \( c_0 \) shows the parameter which is a function of reduced pressure.

\[
c_0 = 6.714(P_r - 1) - 127.8\left((P_r + 1)^{-0.5}\right)
\]

In Eq. (11), the parameter of \( c \) is a function \( \mu^{PR} \) and it can be expressed by Eq. (21).

\[
\mu = \frac{\mu^{PR}}{\mu_c}
\]

\[
c = c_1 \ln \mu + c_2 \left( (\mu + 1.25)^{-1} - 0.4444 \right)
\]

The parameters of \( e_1, e_4 \) and \( e_7 \) are functions of molecular weight and acentric factor and they are computed as follows:

\[
e_3 = 3337.201 - 717.955M_w \omega
\]

\[
e_4 = 17000 \quad \omega \geq 0.3
\]

\[
e_6 = 216.643 + 0.231e_3 \quad \omega < 0.3
\]

\[
e_7 = 4130.636
\]

\[
e_1 = \left( \frac{e_5}{(e_1 + 1.25)^{-1}} - e_5 \right)
\]

In Eq. (19), \( e_1 \) is a function of acentric factor and can be calculated as follows:

\[
e_1 = 1.767 + 18.384\omega - 32.728\omega^2 + 80.299\omega^3
\]

This model of viscosity correction is PR\( \mu \) viscosity model.

### 2.3 Mixing Rules

According to the modeling investigation of Fan and Wang [4], the viscosity equation of state can be applied for the mixtures by this mixing rule:

\[
z_m = \sum_i z_i x_i \quad z = a, b, c, r, T_d \text{ and } \beta
\]


\[
z_m = \sum_i \sum_j z_i^o x_j \quad z = a, b, c, r, T_d \text{ and } \beta
\]

\[
c_m = \sum_i c_i x_i
\]

In Eq. (22)

\[
z_{ij} = \sqrt{z_i z_j}
\]

In this study, two mixing rules have been applied for viscosity equation of state. The first mixing rule (mixing rule 1) is expressed as follows:

\[
z_m = \sum_i \sum_j z_i^o x_j x_i \quad z = a, b, r_e
\]

Also, this expression has been used to calculate \( z_m \):

\[
z_{ij} = \sqrt{z_i z_j}
\]

Since the viscosity depends on the strength of the forces acting between the molecules, in this work, the binary interaction parameters is considered as an applicable factor for improving the performance of the present model. To achieve this aim, the binary interaction parameters of the model are used as follows:

\[
T_{dm} = \sum_i \sum_j x_i x_j \sqrt{T_d T_{d_j} \left(1 - k_{ij}\right)}
\]

\[
\beta_m = \sum_i \sum_j x_i x_j \sqrt{\beta_i \beta_j \left(1 - l_{ij}\right)}
\]

In Eqs. (28) and (29), \( k_{ij} \) and \( l_{ij} \) are the binary interaction parameters. These parameters are determined according to the minimization of the average absolute deviation (AAD) of viscosity data for binary systems.

The second mixing rule (mixing rule 2) is suggested as follows:

\[
z_m = \sum_i \sum_j z_i^o x_j x_i \quad z = a, b, c, r_e
\]

\[
z_{ij} = \frac{\left(\left(z_i^o\right)^{1/2} + \left(z_j^o\right)^{1/2}\right)^3}{8}
\]

\[
T_{dm} = \sum_i \sum_j x_i x_j \frac{\left(T_d^{1/2} + T_{d_j}^{1/2}\right)^3}{8} \left(1 - k_{ij}\right)
\]

\[
\beta_m = \sum_i \sum_j x_i x_j \frac{\left(\beta_i^{1/2} + \beta_j^{1/2}\right)^3}{8} \left(1 - l_{ij}\right)
\]

Also, \( k_{ij} \) is considered as a constant parameter and \( l_{ij} \) have been considered as a pressure dependant parameter.

\[
l_{ij} = a_0 + a_1 P + a_2 P^2
\]
3 Results and discussions

3.1 Binary mixtures

In this section, three binary mixtures have been considered. First of all, the binary mixture of (nC$_5$+nC$_8$) has been considered. The acentric factor and critical properties are taken from [14]. The experimental viscosities of this binary mixture are given from the experimental investigation of Barrufet et al. [15]. The experimental viscosities used for modeling purpose are in the temperatures range (297.95-373.35) K and pressures range (1.01-246.26) bar. The composition of this mixture is in the range of (10.48-89.46) mole% of nC$_5$. A part of experimental viscosities and modeling results (by using mixing rule 1) are reported in Fig. 1. The AAD of the viscosities are calculated based on the following equation:

$$ \text{AAD} = \frac{1}{N_p} \sum_{i=1}^{N_p} \left( \frac{\mu_i^{\text{exp}} - \mu_i^{\text{calc}}}{\mu_i^{\text{exp}}} \right) \times 100 \quad (35) $$

The overall absolute deviations of the applied model for (nC$_5$+nC$_8$) mixture are 2.61 % and 2.90 % for mixing rule 1 and mixing rule 2, respectively. The binary interaction parameters of the model are presented in Table 1. To our knowledge, the AAD of this system was 9.8 % by using PRVIS model [16] in previous work. The results prove that the application of binary interaction parameter is necessary for PR viscosity equation of state.

The second binary mixture considered in this study is (nC$_5$+nC$_{10}$) mixture. The experimental viscosity data have been given from the experimental study of Estrada-Baltazar et al. [17]. The modeling study has been conducted for viscosity data in the temperatures range of (297.95-373.35) K and pressure range of (1.01-246.26) bar. The composition of this binary system changes from 10.31 to 90.08 mole% of nC$_5$. As it is shown in Table 1, the average absolute deviations of the present model for (nC$_5$+nC$_{10}$) mixture are 3.01 % and 3.42 % by using mixing rule 1 and mixing rule 2, respectively. Also, Fig. 2 compares the experimental and modeled viscosities for (nC$_5$+nC$_{10}$) mixture by using mixing rule 1.

The third binary system studied in this work contains (nC$_8$+nC$_{10}$). The experimental viscosity data for this binary mixture are from Estrada-Baltazar et al. [18]. The present model is used in order to reproduce viscosities in the temperatures ranged (297.95-373.35) K and pressures ranged (1.01-246.26) bar. The composition of this binary system is in the range of (13.84-88.58) mole% of nC$_8$. Similar to two previous binary mixtures, the adjustable parameters ($l_{ij}$ and $k_{ij}$) are determined for this binary system and they have been shown in Table 1. The experimental data and modeling results (by using mixing rule 1) are compared in Fig. 3. The average absolute deviations

<table>
<thead>
<tr>
<th>Mixture</th>
<th>$k_{ij}$</th>
<th>$l_{ij}$</th>
<th>$r$</th>
<th>$r^2$</th>
<th>AAD</th>
<th>$k_{ij}$</th>
<th>$l_{ij}$</th>
<th>$r$</th>
<th>$r^2$</th>
<th>AAD</th>
</tr>
</thead>
<tbody>
<tr>
<td>nC$_5$+nC$_8$</td>
<td>-0.07145</td>
<td>-12.51</td>
<td>0.003125</td>
<td>-0.2821</td>
<td>2.61 %</td>
<td>-0.0494</td>
<td>-15.58</td>
<td>0.00393</td>
<td>-0.3390</td>
<td>2.90 %</td>
</tr>
<tr>
<td>nC$<em>5$+nC$</em>{10}$</td>
<td>-0.1779</td>
<td>-9.761</td>
<td>0.001458</td>
<td>-0.03259</td>
<td>3.01 %</td>
<td>-0.0721</td>
<td>-6.884</td>
<td>0.00073</td>
<td>-0.3657</td>
<td>3.42 %</td>
</tr>
<tr>
<td>nC$<em>8$+nC$</em>{10}$</td>
<td>-0.07811</td>
<td>-11.31</td>
<td>0.001130</td>
<td>-0.00148</td>
<td>2.90 %</td>
<td>-0.0643</td>
<td>-10.25</td>
<td>0.00078</td>
<td>-0.0460</td>
<td>3.00 %</td>
</tr>
</tbody>
</table>

Fig. 1 Viscosity versus pressure for the binary mixture of (0.8946 nC$_5$+0.1054 nC$_8$)

Fig. 2 Viscosity versus pressure for the binary mixture of (0.1031 nC$_5$+0.8969 nC$_{10}$)
of the viscosity equation of state for \( (nC_5+nC_8) \), \( (nC_5+nC_{10}) \), \( (nC_8+nC_{10}) \) and \( (nC_5+nC_{12}) \) mixtures are 2.90 % and 3.00 % in combination with the mixing rule 1 and mixing rule 2, respectively.

In order to demonstrate the central hypothesis of this proposed mixing rule, the binary interaction coefficients of the present model are set to zero \((k_{ij} = 0\) and \(l_{ij} = 0\)). The results reported in Table 2 indicate that the present model is not reliable for \( (nC_5+nC_8) \), \( (nC_5+nC_{10}) \) and \( (nC_8+nC_{10}) \) binary systems without binary interaction coefficients. Also, the AAD of PRVIS model [16] was 5.69 % and 12.7 % for second and third binary systems, respectively.

### Table 2

Comparison of the applied mixing rules with and without binary interaction coefficients (AAD)

<table>
<thead>
<tr>
<th>Mixture</th>
<th>( N_p )</th>
<th>( k_{ij} ) &amp; ( l_{ij} = 0 )</th>
<th>( k_{ij} ) &amp; ( l_{ij} \neq 0 )</th>
<th>( k_{ij} ) &amp; ( l_{ij} = 0 )</th>
<th>( k_{ij} ) &amp; ( l_{ij} \neq 0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( nC_5+nC_8 )</td>
<td>295</td>
<td>8.25 %</td>
<td>2.61 %</td>
<td>8.54 %</td>
<td>2.90 %</td>
</tr>
<tr>
<td>( nC_5+nC_{10} )</td>
<td>312</td>
<td>14.74 %</td>
<td>14.74 %</td>
<td>15.35 %</td>
<td>3.42 %</td>
</tr>
<tr>
<td>( nC_8+nC_{10} )</td>
<td>324</td>
<td>10.36 %</td>
<td>10.36 %</td>
<td>10.37 %</td>
<td>3.00 %</td>
</tr>
</tbody>
</table>

### 3.2 The \( (nC_5+nC_8+nC_{10}) \) Ternary System

In the previous part of this study, the results obtained for the \( (nC_5+nC_8) \), \( (nC_5+nC_{10}) \) and \( (nC_8+nC_{10}) \) binary systems prove that the viscosity equation of state in combination with the proposed mixing rules works well for these binary systems. Hence, the present model can be applicable for \( (nC_5+nC_8+nC_{10}) \) ternary mixture. The experimental viscosities of this ternary system are given from the experimental investigation of Iglesias-Silva et al. [19] who have measured the liquid viscosity for \( (nC_5+nC_8+nC_{10}) \) ternary mixture in the temperatures ranged \((297.95-373.35) \) K and pressures ranged \((1.01-246.26) \) bar for 530 points. The compositions of this mixture are represented in Table 3.

In this section, the adjustable parameters of the model \((l_{ij} \) and \( k_{ij} \)) obtained in previous section have been applied in order to predict the viscosities of \( (nC_5+nC_8+nC_{10}) \) ternary mixture. The pressure and temperature range of experimental data are given in Table 3. Also, a part of experimental viscosities and modeling results (by using mixing rule 1) are reported in Fig. 4. The average absolute deviations of these systems are 7.77 % and 8.02 % for the mixing rule 1 and mixing rule 2, respectively; therefore, the present model performed well for these two ternary mixtures. The AAD of PRVIS model [16] was 7.41 % for this system. The AAD of previous model is 10.1 % for this system.

### Table 3

Components of \((nC_5(1)+nC_8(2)+nC_{10}(3))\) ternary mixture

<table>
<thead>
<tr>
<th>( x_1 )</th>
<th>( x_2 )</th>
<th>T range (K)</th>
<th>P range (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6014</td>
<td>0.2505</td>
<td>297.79-373.35</td>
<td>1.01-246.26</td>
</tr>
<tr>
<td>0.1489</td>
<td>0.7033</td>
<td>297.79-373.35</td>
<td>1.01-246.26</td>
</tr>
<tr>
<td>0.3008</td>
<td>0.5425</td>
<td>297.79-373.35</td>
<td>1.01-246.26</td>
</tr>
<tr>
<td>0.4487</td>
<td>0.3989</td>
<td>297.79-373.35</td>
<td>1.01-246.26</td>
</tr>
<tr>
<td>0.7507</td>
<td>0.1001</td>
<td>297.79-373.35</td>
<td>1.01-246.26</td>
</tr>
<tr>
<td>0.1499</td>
<td>0.5407</td>
<td>297.79-373.35</td>
<td>1.01-246.26</td>
</tr>
<tr>
<td>0.3008</td>
<td>0.4001</td>
<td>297.79-373.35</td>
<td>1.01-246.26</td>
</tr>
<tr>
<td>0.4483</td>
<td>0.2488</td>
<td>297.79-373.35</td>
<td>1.01-246.26</td>
</tr>
<tr>
<td>0.5994</td>
<td>0.0998</td>
<td>297.79-373.35</td>
<td>1.01-246.26</td>
</tr>
<tr>
<td>0.1498</td>
<td>0.4013</td>
<td>297.79-373.35</td>
<td>1.01-246.26</td>
</tr>
<tr>
<td>0.3002</td>
<td>0.2494</td>
<td>297.79-373.35</td>
<td>1.01-246.26</td>
</tr>
<tr>
<td>0.4485</td>
<td>0.0999</td>
<td>297.79-373.35</td>
<td>1.01-246.26</td>
</tr>
<tr>
<td>0.1502</td>
<td>0.2500</td>
<td>297.79-373.35</td>
<td>1.01-246.26</td>
</tr>
<tr>
<td>0.5007</td>
<td>0.0996</td>
<td>297.79-373.35</td>
<td>1.01-246.26</td>
</tr>
<tr>
<td>0.1501</td>
<td>0.0994</td>
<td>297.79-373.35</td>
<td>1.01-246.26</td>
</tr>
</tbody>
</table>

Fig. 4 Viscosity versus pressure for the ternary mixture of \((0.6014 nC_5+0.2505 nC_8+0.1481 nC_{10})\)
4 Conclusions

The coupling of the Peng-Robinson viscosity equation of state and two proposed mixing rules have been applied for describing the viscosities of (nC₈⁺+nC₁₀), (nC₈⁺+nC₁₀), (nC₆⁺+nC₁₀), and (nC₆⁺+nC₁₀) mixtures. Also, the pressure dependent and constant expressions for the binary interaction coefficients of binary systems containing (nC₈⁺+nC₆⁺), (nC₈⁺+nC₆⁺), (nC₆⁺+nC₁₀), and (nC₆⁺+nC₁₀) are determined, taking the advantage of well described viscosity for these binary systems. The obtained binary interaction coefficients are applied for describing the viscosity of (nC₈⁺+nC₁₀) mixture. The results of the model prove that the present model successfully describes the viscosities of these mixtures.

Nomenclature

- \( \alpha \): energy parameter for PR equation of state (K.s²·Pa⁻¹)
- \( b \): volumetric parameter for PR equation of state (Pa.s)
- \( c, c' \): parameters of viscosity
- \( e \): constant parameters of the model
- \( M_w \): molecular mass (gr/mol)
- \( N_p \): number of experimental data
- \( P \): pressure (bar)
- \( r_c \): parameter of the PRµ model (K.s)
- \( R \): universal gas constant (Jmol/K)
- \( R' \): parameter of the PRµ model (Jmol/K)
- \( T \): Temperature (K)
- \( T_d \): a specific temperature for calculated viscosities (K)
- \( T' \): a presumptive temperature (K)
- \( v \): molar volume (mol/m³)
- \( x \): liquid mole fraction
- \( PR \): Peng Robinson
- \( EOS \): Equation Of State
- \( SAFT \): Statistical Associating Fluid Theory
- \( PC-SAFT \): perturbed-chain statistical associating fluid theory

Greek letters

- \( \beta(P) \): pressure dependent function in PRµ model
- \( \mu \): dynamic viscosity (nPa s)
- \( \omega \): acentric factor

Subscripts

- \( c \): critical property
- \( m \): mixture property
- \( r \): reduced property

References

