Evaluation of Updated Volume-translation Peng-Robinson Model for Estimating Volumetric Properties of Hydrocarbon Mixtures at High Pressure High Temperature

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Abstract-
A volume-translation function by the authors with arguments of reduced pressure and temperature was assessed for binary and multicomponent mixtures. The correlation is not a generalised function and reduced-pressure as an argument. Thereby, ensuring high performance at high pressure and temperature (HPHT) in the class of other volume-translation function for cubic equations of state. The function was compared to non-cubic equations of states (nCEoS) of PC-SAFT, GERG-2004, GERG-2008 and AGA8-DC92 for the prediction of molar-volume at HPHT with reasonable results.

Keywords: Peng-Robinson; molar-volume; equations of state; volume translation; PC-SAFT; GERG-2008

1. Introduction
The simple nature of the mathematical expression of the cubic equation of state (CEoS) has endeared its use in the petroleum engineering industry despite the shortcomings [1, 2]. Notable amongst the inaccuracies of CEoS is predicting density. This has been resolved by the volume-translation (VT) concept of Peneloux et al. [3]. Application of VT though commonly applied for the sub-critical region has gained application in the supercritical region with established works by Baled et al. [1] and Ungerer and Batut [4] for hydrocarbons and CO2 by Hekayati et al. [5]. VT for the supercritical region of the authors was applied by Bamgbade et al. [6], Bugress et al. [7], Bugress et al. [8] and de Sant’ Anab et al. [9]. Peng-Robinson (PR) and Soave-Redlick-Kwong (SRK) CEoS are the common two parameter models applied for VT. Kunz and Wagner [2] had stated that VT-CEoS is limited to application for only the liquid phase. However, the successful prediction of density at the supercritical region by Baled et al. [1] within 7-276 MPa and 278-533 K respectively has further opened the doors for other researchers to follow. PR and SRK are widely applied and still relevant in the oil and gas industry, while numerous modifications of the PR-CEoS model exist in literature with a publication celebrating the 40 years of the model [10]. Non CEoS (nCEoS) models abound for accurate estimation of thermodynamic properties. These models are PC-SAFT [11], GERG-2004 [12], GERG-2008 [2] and AGA8-DC92 [13]. Baled et al. had ruled on the favourable performance of their model over that of PC-SAFT, but PC-SAFT is more promising based on the concept and its formulation for further modification. Except for PC-SAFT, the other nCEoS have not been compared to the VT model of CEoS at the supercritical region to the best of the knowledge of the authors. Also, these models are specifically designed for natural gas and are industry standards.
This study seeks to evaluate the performance of the model by Orodu et al. [14] for the first time on binary and multicomponent mixtures in predicting molar-volume. The model was confined during formulation to high pressure high temperature (HPHT). HPHT by the definition of De
Brujin et al. [15] covers the range of 300 °F (422 K) - 400 °F (477.6 K) and 10,000 psi (68.9 MPa) – 20,000 psi (137.9 MPa) [16]. Hence, HPHT is a subset of the supercritical region. However, the focus for this study is pressure and temperature of 50 ≤ P ≤ 150 MPa, and 300 ≤ T ≤ 500 K. HPHT is the current frontier for natural gas exploration and production to meet the global energy mix consisting of renewables and natural gas for power generation.

2. **High Pressure High Temperature (HPHT) Volume Translation EoS Models**

The widely applied equations of state (EoS) for natural gas and hydrocarbons can be grouped into cubic EoS (CEoS) and non-cubic EoS (nCEoS). And as previously alluded, nCEoS is gaining grounds in application due to their accuracy in predicting volumetric properties. However, nCEoS models have high computational requirement/cost compared to CEoS models. Common volume-translation forms, concerning the arguments of the function, are presented in Table 1 for HPHT application and other temperature and pressure region. HPHT volume-translation gleaned from literature for CEoS and in particular for Peng Robinson CEoS are thus presented.

2.1 **VT-CEoS Models for Peng-Robinson (PR)**

**Ungerer and Batut [4];**

The authors modelled volume-translation term (molar volume deviation, ‘c’) as a function of molecular weight and temperature to develop a generalised equation for hydrocarbon components. Formulation by regression analysis was calibrated with ‘c’ at HPHT (223.15 to 527.15 K and 20 to 160 MPa). The equations are:

For C₆ – C₁₃:

\[ C(T) = (0.023 - 0.00056M_w)T + (-34.5 + 0.4666M_w) \]  \hspace{1cm} (1)

For C₁₃>:

\[ C(T) = M_w - M_{ref} = (0.023 - 0.02056M_w)(T - T_{ref}) \]  \hspace{1cm} (2)

where c(T) is temperature dependent volume-translation (cm³/mol); T and Tref , the temperature for computation and reference point respectively (K); Mw, molecular weight (g/mol); and vm, molar volume at the reference point.

**Pedersen et al. [17];**

Pedersen et al. [17] developed a set of equations to account for the volume-translated term of C₇+ components subdivided into pseudo-components. These equations are:

\[ c_{oi} = \frac{M_{wi}}{\rho_i} - v_i^{\text{EoS}} \]  \hspace{1cm} (3)

where \( \rho_i \) is density at 15 °C and atmospheric pressure (Kg/m³); \( v_i^{\text{EoS}} \), is molar volume predicted at same conditions for both PR-EoS and Soave-Redlick-Kwong (SRK) EoS; \( M_w \) is molecular weight (Kg/ Kg mole); and c in m³/ Kg mole. ASTM 1250–80 correlation is used for the conversion to appropriate thermodynamic conditions. This is;
\[ \rho_{T_1} = \rho_{T_0} e^{\left[-A(T_1 - T_0)\right] \left[1 + 0.8A(T_1 - T_0)\right]} \]  \hspace{1cm} (4)

where: \(T_0\) and \(T_1\) are reference temperature and temperature for the required computation and associated density (K) respectively.

\[ A = 613.9723 \frac{1}{\rho_{T_0}^2} \]

The temperature dependent ‘c’ is;

\[ c_i = c_{0i} + c_{1i}(T - 288.15) \]  \hspace{1cm} (5)

where \(T\) is temperature (K); \(c_{0i}\) is from Eq. (3); \(c_{1i}\) from Eq.(5) for \(\rho T1\) and its conversion to ‘c’ in molar volume is by \(c = Mw_i / \rho_i\). Favourable results were obtained. Previous equation did not account for volume translation in this manner for \(C_{7+}\) pseudo-components.

Baled et al. [1];

Baled et al. [1] developed a new volume translation ‘c’ based on a correlation formulated with data at HPHT,

\[ c = \Delta v = v_{EoS} - v_{exp} = A + B \cdot T_r \]  \hspace{1cm} (6)

where \(A\) and \(B\) are constants obtained by regressing 17 pure components from \(C_1\) to \(C_{40}\); \(T_r\), reduced temperature; \(v_{EoS}\) and \(v_{exp}\) is molar volume from CEoS and experiment respectively.

\[ A, B = f(M_w, \omega) = k_0 + k_1 \exp \left(\frac{-1}{k_2 M_w \omega}\right) + k_3 \exp \left(\frac{-1}{k_4 M_w \omega}\right) + k_5 \exp \left(\frac{-1}{k_6 M_w \omega}\right) \]  \hspace{1cm} (7)

Hekayati et al. [5];

An important development noteworthy of investigating is the temperature and pressure dependent volume-translation by Hekayati et al. [5]. The authors’ volume-translation for PR-EoS was specifically adopted for supercritical CO\(_2\). Error analysis based on deviation from experimental values showed less departure from zero at high and extremely high temperature, though slightly higher deviation for high pressure as compared to temperature. The inclusion of molecular weight cannot be overlooked for the application of this approach as seen in Eq. 8 for multicomponent gases. By so doing, the equation becomes generalised and not component specific to CO\(_2\).

\[ c \left(\frac{cm^3}{mol}\right) = A_1 + A_2 \ln \rho \left(A_3 - \ln \rho r + A_4 \frac{\ln T_r}{\ln \rho r}\right) - A_5 \ln T_r \]  \hspace{1cm} (8)

where \(P_r\) and \(T_r\) are both reduced pressure and reduced temperature respectively; \(A_1, A_2, A_3, A_4\) and \(A_5\) are constants of the equation.
Orodu et al. [14]; The existing volume-translation models of CEoS for HPHT are scarce as earlier highlighted and are not comparable with the nCEoS models. However, the Baled et al. [1] is recognised and globally applied. Orodu et al. [14] model has not been tested on binary and multicomponent mixtures. The model is as given in Eq. 9.

\[ c = A_1 + A_2 T_r + A_3 P_r + A_4 T_r^2 + A_5 P_r^2 + A_6 T_r P_r \]  

(9)

where \( T_r \) and \( P_r \) are reduced temperature and reduced pressure respectively; \( A_1, A_2, A_3, A_4, A_5 \) and \( A_6 \) are constants specific to Eq. 9 for hydrocarbon components including CO2 and N2. The constants of Eq. 9 are as presented in Table 2, and the volume-translation term applies to the Peng-Robinson EoS, that is Eq. 10. Eq. 12 is the equation for computing the corrected molar volume (\( \nu_{\text{true}} \)) based on that computed by Peng-Robinson CEoS and volume-translation ‘c’.

\[ P = \frac{RT}{V-b} - \frac{aT_r \alpha(T_r)}{(v+eb)(v+\sigma b)} \]  

(10)

where \( a \) is the attraction; \( b \), repulsion parameter; \( P \), pressure; \( T \), temperature; \( V \), volume; \( e \) and \( \sigma \), are for any CEoS. For Peng-Robinson (PR) of 1976, \( e = 1+\sqrt{2} \), \( \sigma = 1-\sqrt{2} \), \( a = 0.42747 \frac{R^2T_c^2}{P_c} \), and \( b = 0.08664 \frac{RT_c}{R} \). \( \alpha(T_r) \) is an alpha-function based on reduced-temperature \( (T_r) \) and acentric factor \( (\omega) \). The acentric factor used is that made popular by Soave-Redlick-Kwong.

For PR,

\[ \alpha(T_r) = [1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1 - \sqrt{T_r})]^2 \]  

(11)

\[ \nu_{\text{true}} = \nu_{\text{PR-CEoS}} - c \]  

(12)

The application of Eq. 9 - 10 for binary and multicomponent mixtures require the introduction of the following equations.

\[ a\alpha(T_r) = \sum_{i=1}^{n} \sum_{j=1}^{n} (x_i x_j a_i a_j \alpha_i \alpha_j)^{1/2} (1 - K_{ij}) \]  

(13)

\[ b = \sum_{i=1}^{n} x_i b_i \]
(14)

\[ c = \sum_{i=1}^{n} x_i c_i \]

(15)

where \( x \) is mole fraction of components; \( c \), volume translation; \( \alpha \), alpha term; \( K_{ij} \), binary interaction parameter (BIP) between component \( i \) and component \( j \) of the mixture; and \( n \), number of components of the mixture.
Table 1: Variants of volume-translation with focus on HPHT (modified after; Orodu et al. [14])

| Volume-translation function | Reference | Application |
|-----------------------------|-----------|-------------|
| \( c = f(T_r, p_r) \)       | Hekayati et al. [5] | HPHT applicable; only CO2 |
| \( c = v_{\text{sat,EoS}}(T_r = 0.8) = \frac{RT_c}{P_c} z_{RA}^{(1+0.5z^2)} \) | Guennec et al. [18] | Low Pressure, Low to High Temperature |
| \( c = f(T_c, p_c, \omega) \) | Forero and Velasquez [19] | Low Pressure; Low Temperature |
| \( c = f(p, x) \)          | Singh et al. [20] | Low Pressure, Low Temperature |
| \( c = f(Z_{RA}, T_c, P_c) \) | Nazarzadeh and Moshfeghian [21] | Low Pressure |
| \( c = f(T_r, Z_{RA}, P_c, T_c, \omega) \) | Nazarzadeh and Moshfeghian [21] | Low Pressure |
| \( \nu = v_{\text{EoS}} - c - \delta_c \left( \frac{\eta}{\eta + \delta} \right) \) | Chou and Prasnitz [22], Abudour et al. [23, 24] | Low to Moderate Pressure, Low to Moderate Temperature; near critical point region |
| \( c = f(Z_{RA}, T_c, P_c); c = f(\omega); \) | Loria et al. [25] | Low Pressure, Low Temperature; adapted for bitumen |
| \( c = f(T_r, Z_{RA}, P_c, M_w) \) | Pedersen et al. [17] | HPHT, adapted for C7+ |
| \( c = f(T, M_w) \)        | Ungerer and Batut [4] | HPHT |
| \( c = f(T_r, \omega) \)   | Soreide [27] | Low Pressure, Low Temperature |
| \( c = f(M_w) \)           | Jhaveri and Youngren [28] | Low-Pressure, Low-Temperature; adapted for heavy hydrocarbons |

where: \( v_{\text{EoS}} = \) molar volume computed from CEoS; \( v_{\text{exp}} = \) molar volume from experiment; \( \omega = \) acentric factor; \( c = \) molar volume deviation; \( T_r \) and \( p_r \), reduced temperature and pressure; \( T_c, P_c, \) and \( Z_c \), critical temperature, pressure, and gas compressibility factor; \( Z_{RA} = \) Rackett value; \( \rho = \) density; \( M_w = \) molecular weight; \( v_l = \) molar liquid volume; \( d = \) distance function; \( R = \) universal gas constant
Table 2: Constants of Eq. 9 (Orodu et al., [14])

| Comp. | A₁ | A₂ | A₃ | A₄ | A₅ | A₆ | Applicable Pressure Range |
|-------|----|----|----|----|----|----|---------------------------|
| C₁    | -3.210 | 0.488 | -0.15391 | 0.000 | 0.00411 | -0.02611 | 50 ≤ P ≤ 150 MPa |
| C₂    | -1.254 | -6.499 | 0.04968 | 1.712 | 0.00119 | -0.06189 | 50 ≤ P ≤ 900 MPa |
| C₃    | -1.003 | -8.660 | 0.04660 | 2.409 | -0.00003 | -0.00492 | 50 ≤ P ≤ 200 MPa |
| nC₄   | 4.246 | -20.480 | 0.08632 | 8.100 | 0.00165 | -0.13336 | 50 ≤ P ≤ 200 MPa |
| iC₄   | 2.802 | -17.690 | 0.05117 | 4.174 | 0.00054 | -0.01550 | 50 ≤ P ≤ 200 MPa |
| nC₅   | 8.532 | -24.989 | 0.02141 | 7.989 | 0.00196 | -0.06735 | 50 ≤ P ≤ 100 MPa |
| C₁₀   | 41.610 | -66.652 | 0.03767 | 17.917 | 0.00026 | 0.07012 | 50 ≤ P ≤ 150 MPa |
| CO₂   | -4.272 | 3.976 | -0.10600 | 1.262 | 0.00132 | -0.01876 | 50 ≤ P ≤ 150 MPa |
| N₂    | -3.367 | -0.079 | -0.08831 | 0.000 | 0.00163 | 0.00418 | 50 ≤ P ≤ 150 MPa |

2.2 nC EOS Models

The nC EOS used for comparison of the model developed in Orodu et al. [14] are EOS based on molecular theory (GERG–2004, GERG–2008, and PC–SAFT). Gross and Sadowski [11] developed PC – SAFT; GERG – 2008 by Kunz and Wagner [2]; GERG – 2004 by Kunz et al. (2007). GERG–2008 being the later version of GERG–2004 and all the models are valid for the supercritical region of which HPHT is a subset. Furthermore, the range of validity for GER-2008 and GERG-2004 is (a normal range of 90–450 K and P≤35 MPa and an extended range of 60–700 K and P≤70 MPa) and (normal range of 90–450 K and P≤35 MPa) respectively. It should be noted that these EOS by GERG are explicit in Helmholtz free energy. The other nC EOS is AGA8-DC92 [29], an extended viral type of EOS. AGA8 is applicable for only the gas phase of hydrocarbons (natural gas). The typical range of application is within the temperature of 143 – 673 K and pressure up to 280 MPa.

3. Results and Discussion

3.1 Multicomponent Synthetic Natural Gas – Atilhan et al. [30, 31]

The developed VT PR-EOS model in this work is tested on a synthetic lean natural gas of Atilhan et al. [30, 31]. The composition of the gas is given in Table 3 for Mixture-1 and Mixture-3. Binary Interaction Parameter (BIP) used is as computed by Brusilovsky [32]. The BIP was specifically obtained for high-pressure PR-EOS.

Results of relative molar volume deviation are presented in Figures 1a to 1f. Figures 1a, 1c and 1e for Mixture-1, and Figures 1b, 1d and 1f for Mixture-2. The comparison is made with computed values by the authors for GERG-2004 and AGA-8. Performance of VT PR-EOS is quite impressive and exceptional at temperatures of 250 and 350 K and clearly within the league of the other two models.
Table 3: Composition of Synthetic Lean Natural Gas – Sample 1 to 4 (Atilhan et al., [30, 31])

| Component | Mixture 1   | Mixture 3   |
|-----------|-------------|-------------|
| C1        | CH$_3$      | 0.89982     | 0.89975     |
| C2        | C$_2$H$_6$  | 0.03009     | 0.02855     |
| C3        | C$_3$H$_8$  | 0.01506     | 0.01427     |
| iC$_4$    | 2-CH$_3$C$_3$H$_7$ | 0.00752 | 0.00709     |
| nC$_4$    | C$_4$H$_{10}$ | 0.00753     | 0.00722     |
| nC$_5$    | 2-CH$_3$C$_4$H$_{10}$ | 0.00300 | 0.0045      |
| C$_5$     | C$_5$H$_{12}$ | 0.00300     | 0.0045      |
| N$_2$     | N$_2$       | 0.01697     | 0.01713     |
| CO$_2$    | CO$_2$      | 0.01701     | 0.01699     |
| M/g·mol$^{-1}$ |            | 18.536      | 18.631      |

3.2 Binary Mixtures of CH$_4$ + N$_2$ – Gomez – Osorio et al. [33]

The molar volume of binary mixtures of varying compositions of CH$_4$ and N$_2$ at approximately 25% CH$_4$, 50% CH$_4$, and 75% CH$_4$ are computed. Computation is at temperatures of 350, 400 and 450 K, and pressure up to 150 MPa in testing the VT PR-EoS model. The GERG-2008 model relative deviation % outperformed the VT PR-EoS. Meanwhile Orodu et al. [14] model performed within the capacity of AGA-08 and GERG–2008. Surprisingly, at below 50 MPa, the VT PR-EoS of this study had better fit in most of the compositions as observed in Figures 2a to 2f. It should be noted that based on Table 2, the volume-translation model was for between pressures of 50 MPa and 150 MPa.
Figure 1: Experimental molar volume deviation at temperatures 250 – 450 K, Mixture – 1 and Mixture 3 of Atilhan et al. [30, 31] based on Volume translated PR-EoS
Figure 2: Experimental molar volume deviation at temperatures 304, 350, 400 and 450 K for different binary mixtures of CH₄ and N₂ of Gomez-Osorio et al. [33] based on Volume translated PR-EoS
3.3 Binary Mixture of CH₄ + N₂ – Seitz et al. [34]

The first reported data for CH₄ + N₂ binary mixture is that of the work by Seitz et al. [34] for pressure above 40 MPa, that is, HPHT range in some instances (39.93 ≤ P ≤ 99.93 MPa and 323.15 ≤ T ≤ 573.15 K). Prior studies by Gomez – Osorio et al. (2016) and Kunz and Wagner (2012) reported relative density deviation of 0.2 to 1.15 % and -0.5 to 1 % respectively of computed density by the GERG-2008 model from the experimental data by Seitz et al. The relative density deviation from this work applied to the dataset is as presented in Seitz et al. [34] is -1.5 to 1%. A graphical presentation is as seen in Figure 3.

Figure 3. Relative density deviation computed from this study for a binary mixture of CH₄+N₂ (39.93 ≤ P ≤ 99.93 MPa and 323.15 ≤ T ≤ 573.15 K).
The result from this study is thus at par with that of GERG – 2008 as against the earlier results in sub-section 3.2 (Figures 2a – 2j). However, Kunz and Wagner [2] stated that the large deviation is because of the uncertainty of the experimental apparatus used by Seitz et al. The dataset range covers the compositions 90% CH₄ + 10% N₂, 80% CH₄ + 20% N₂, 70% CH₄ + 30% N₂, 60% CH₄ + 40% N₂, 50% CH₄ + 50% N₂, 40% CH₄ + 60% N₂, 30% CH₄ + 70% N₂, 20% CH₄ + 80% N₂, and 10% CH₄ + 90% N₂. This covers a broader range to that of Gomez – Osorio et al. [33]. Though the molar volume deviation covers the pressure region of 50 to 150 MPa for nitrogen and methane, the relative density deviation in Figure 3 shows better prediction at 39.94 MPa than 60 and 100 MPa that is within the range of data used in developing the model.

This stated case goes a long way in necessitating the provision and stating the uncertainty of equipment used in experimental setups alongside the results of models used in fitting the data and likewise predicting it. The importance of this specific binary mixture is due to the presence of these components in no small measure in natural gas.

3.4 Binary Mixture of C₃H₈ + C₁₀H₂₂ – Bamgbade et al. [6]

Also, binary mixtures of C₃H₈ and C₁₀H₂₂ at approximately 16% C₃H₈, 42% C₃H₈, 60% C₃H₈ and 82% C₃H₈ are used to test the developed VT PR-EoS model further. Relative molar volume deviations are all approximately within ±1.0 % (Figures 4a to 4d) except at temperatures above 500 K in which the model upper boundary for applicability is 500 K. All results were computed at K_ij ≠ 0 (BIP). Other computations made was with K_ij = 0 for the sole purpose of comparison with existing values in Bamgbade et al. [6] for PC – SAFT and Bamgbade et al. application of the VT PR-EoS of Baled et al. [1].

Results obtained and as presented in Table 4 and viewed at first glance with in-depth understanding from Figures 5a to 5d shows a favourable comparison with PC – SAFT and Baled et al. [1] models. An exception of the commendable result is at the composition of 60 % - C₃H₈ and 40 % - C₁₀H₂₂. PC – SAFT model produced higher relative molar deviation at the extremes of 16% - 84% (C₃H₈ - C₁₀H₂₂) and 82% - 18% (C₃H₈ - C₁₀H₂₂) where either of the components in the binary mixture dominates. Thereby indicating but not confirmed of the preferable range of applicability of PC – SAFT or optimisation study to re-evaluate the binary interaction parameter. However, BIP was not used for the computation.
Fig. 4a: Experimental molar volume deviation, 16% C₃H₈ and 84% C₁₀H₂₂ based on Volume translated PR-EoS

Fig. 4b: Experimental molar volume deviation, 42% C₃H₈ and 58% C₁₀H₂₂ based on Volume translated PR-EoS

Fig. 4c: Experimental molar volume deviation, 60% C₃H₈ and 40% C₁₀H₂₂ based on Volume translated PR-EoS

Fig. 4d: Experimental molar volume deviation, 82% C₃H₈ and 18% C₁₀H₂₂ based on Volume translated PR-EoS

Figure 4: Experimental molar volume deviation of binary mixtures of C₃H₈ and C₁₀H₂₂ based on Volume translated PR-EoS and data from Bamgbade et al. [6] with kij ≠ 0
Table 4: Average Absolute Deviation (AAD) % of PR-EoS volume translation models from ThisWork and Bamgbade et al. [6], and PC-SAFT of Gross and Sadowski [11] for binary mixtures of Propane (C3) and Decane (C10), \( k_{ij} = 0 \)

| Binary Comp. | T/K | Data Points | ThisWork | Bamgbade et al. (2015) – Baled Model | PC-SAFT | ThisWork (P>=50MPa); Data Points = 15 |
|--------------|-----|-------------|----------|--------------------------------------|--------|---------------------------------------|
| C3-C10       |     |             |          |                                      |        |                                       |
| 16-84%       | 444.3 | 21         | 0.54     | 0.20                                 | 2.47   | 0.45                                  |
|              | 510.5 | 20         | 1.55     | 1.66                                 | 1.36   | 1.28                                  |
| 42-58%       | 344.2 | 24         | 0.54     | 0.62                                 | 1.17   | 0.55                                  |
|              | 444.4 | 18         | 1.50     | 1.11                                 | 0.97   | 2.08                                  |
|              | 511.0 | 23         | 1.73     | 1.48                                 | 1.22   | 2.09                                  |
| 60-40%       | 344.3 | 22         | 2.53     | 1.90                                 | 0.54   | 3.28                                  |
|              | 513.2 | 21         | 3.07     | 2.48                                 | 0.64   | 2.84                                  |
| 82-18%       | 344.2 | 20         | 1.25     | 1.31                                 | 3.04   | 1.30                                  |
|              | 444.3 | 25         | 1.96     | 0.84                                 | 1.69   | 0.36                                  |
Figure 5a: Comparison of predictive capability at 16% $\text{C}_3\text{H}_8$ and 84% $\text{C}_{10}\text{H}_{22}$ for This Work, Bamgbade et al. [6], PC-SAFT and This Work for Pressure greater than and equal to 50MPa.

Figure 5b: Comparison of predictive capability at 42% $\text{C}_3\text{H}_8$ and 58% $\text{C}_{10}\text{H}_{22}$ for This Work, Bamgbade et al. [6], PC-SAFT and This Work for Pressure greater than and equal to 50MPa.

Figure 5c: Comparison of predictive capability at 60% $\text{C}_3\text{H}_8$ and 40% $\text{C}_{10}\text{H}_{22}$ for This Work, Bamgbade et al. [6], PC-SAFT and This Work for Pressure greater than and equal to 50MPa.

Figure 5d: Comparison of predictive capability at 82% $\text{C}_3\text{H}_8$ and 18% $\text{C}_{10}\text{H}_{22}$ for This Work, Bamgbade et al. [6], PC-SAFT and This Work for Pressure greater than and equal to 50MPa.
3.5 **Binary Mixture of CH$_4$ + C$_{10}$H$_{22}$ – Regueira et al. [35]**

Binary mixtures with the composition in Figures 6a to 6f are tested with results of relative molar volume given in the same figures. Further comparison necessitated the plot of Figures 7a and 7b. The composition at 0 % CH$_4$ has relative volume deviation (RVD) range of -0.1 to 0.3 with the cluster of data points around 0.1 to 0.2. RVD for 60.17 % CH$_4$ has RVD from -2.0 to -0.5, the cluster (main distribution) of RVD is around -1.0 %. These distributions of RVD for the two scenarios indicated in Figures 7a and Figure 7b is a clear reflection of the prediction of both molar volume and fluid density by the VT PR-EoS model in this study. Hence molar volume prediction for binary mixture consisting of 70.85 % CH$_4$ is similar to 60.17 % CH$_4$ and 84.96 % CH$_4$ lower than 60.17 % CH$_4$.

VT PR-EoS of this study is compared with the performance of PC-SAFT as computed by Regueira et al. [35]. Comparison is based on the entire data set that contains data points of pressure below 50 MPa, knowing that the developed model in this study was calibrated with P ≥ 50 Mpa.
The other is with the removal of data points with pressure less than 50 MPa. Hence the basis for averaging AAD% is slightly affected. Notwithstanding, presented in Table 5 is the AAD% used as the basis for the comparison in the above paragraph.

Table 5: Comparison of Average Absolute Deviation % for prediction of molar volume for PC-SAFT according to Regueira et al. [35], and This Work for Volume Translation PR-EoS.

| Binary Comp. | AAD%    |                  |                  |
|--------------|---------|------------------|------------------|
| CH4 – C10H22 | PC-SAFT | PR-EOS ThisWork  | PR-EoS ThisWork  |
|              | kij=0.0172 | kij=0.045        | kij=0.045        |
| 0% - 100 %   | 1.085   | 9.526            | 0.184            |
| 22.72 % - 77.28 % | 1.036 | 0.466            | 0.179            |
| 45.20 % - 54.80 % | 0.842 | 0.653            | 0.428            |
| 60.17 % - 39.83 % | 0.623 | 1.084            | 0.958            |
| 70.85 % - 29.15 % | 0.648 | 0.828            | 0.765            |
| 84.96 % - 15.04 % | 0.648 | 2.03             | 1.824            |
4. Conclusion

A volume-translation expression with arguments of reduced-pressure and reduced-temperature, developed by the authors in an earlier article was evaluated for the first time for binary and multicomponent mixtures. Its use involves the estimation of molar-volume at high pressure and temperature (HPHT) and comparison with cubic and non-cubic equations of state (EoS). The following major conclusions are drawn from the study:

i. The accuracy of the experimental data of molar-volume affects the assessment of EoS models. This has partially affected the evaluation and comparison of GERG-2008 and volume-translation model under study.

ii. The adaptation of a consistent alpha-function at high-temperature may improve the accuracy of the volume-translation model of two parameter cubic equations of state.

iii. Performance of the volume-translation model is at par with AGA8-DC92 and GERG-2004, and comparable to that of PC-SAFT.

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