# A Molecular-Based Equation of State for Vapour-liquid Equilibrium of Pure Substances

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Based on an analysis of the virial coefficients of some hard-sphere fluids models, a molecular equation of state was developed for modelling the vapour-liquid data of pure substances. The superiority of the equation of state employed here is its mathematical simplicity. The molecular parameters were obtained to real fluids by correlating the density dependence of the attraction term to vapour-liquid data of a reference fluid. The resulting attraction term is mathematically rather simple which fulfils the structural requirements given by the physical background. Through this model, vapour-liquid equilibrium data of pure substances were correlated. The systems under study were n-alkanes, 1-alkanols, acetone and carbon dioxide. The results were compared with those obtained by PR (Peng-Robinson), SRK (Soave-Redlich-Kwon) and RM (Riazi-Mansoori) equations of state. On the basis of the results, the saturated liquid density for n-alkanes, and 1-alkanols can be predicted within about 1.2%, and 4%, respectively.

**Keywords:** Equation of state, Statistical mechanics, Polar fluids, the Reduced dipole moment, Molecular thermodynamics

## INTRODUCTION

The development of equations of state (EoS) for the description of thermodynamic properties of fluids and fluid mixtures has a long history. Two approaches are most widely used in chemical engineering applications. One approach is the empirical further development of the cubic equations of state such as the Redlich-Kwong-Soave [1] or Peng-Robinson [2] equation. Most cubic equations of state are based on the van der Waals equation of state. In particular, the repulsion term of the van der Waals equation usually remains unchanged while most modifications affect the attraction term. The resulting equations fulfill the requirements of both simplicity and accuracy since they require little input information, but they are empirical correlations and an insight in molecular properties of the system is limited. On the other hand, in recent decades, a large number of molecular based equations of state have

been developed based on the framework of statistical mechanics [3-13]. Due to the mathematical techniques required for the derivation of such equations, the resulting terms are usually mathematically complicated. Consequently, the Peng-Robinson and Soave-Redlich-Kwong equations are widely used in industry, and often yield a more accurate representation than other alternatives.

Furthermore, problems can appear even though the equations are molecular based. The resulting equations can lead to unphysical behavior due to their mathematical complexity. This may occur if a model is used out its range of validity of the underlying theory. In general, the probability of such unreliable behavior decreases with decreasing mathematical complexity. This is an important argument motivating the development of simplified equation of state models.

The aim of this paper is to develop a molecular based equation of state with a mathematically simple form. The origin of this work is finding that simple molecular model equations are able to play an expanding role in the accurate calculation of fluid-phase equilibria [14].

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This equation is able to describe the spherical and non-spherical molecular fluids, chain molecules, as well as dipolar model fluids. With the van der Waals attraction term, these equations yield a biquadratic equation of state for the molar volume or density. The van der Waals attraction term is a truncated virial series and approximates only the second virial coefficients of the attraction. Here, we complete successfully the attraction term with respect to the description of real fluid data. In addition, several physical requirements have been taken into account to present an effective attraction term.

The development of an equation of state describing VLE data has several challenges, such as description of the saturated liquid density. Cubic equations of state are often not accurate enough for the saturated liquid densities, so, they are improved by empirical methods. For example, the volume translation technique [15] adds a constant to the molar volume shifting the saturated liquid branch closer to the experimental data. Detailed investigations have shown that a temperature dependent volume translation leads to unphysical behavior [16]. For a volume translation with a temperature independent parameter, however, virial coefficient mostly shifts towards the theoretical values [17]. Such approach is a possibility of changing the repulsion term towards the hard-sphere fluid. However, for an accurate description of the hard sphere fluid the Carnahan-Starling equation of state [18] or similar approaches [19] should be used. The advantage of the constant volume translation is that the mathematical structure of the cubic equations of state is maintained. The disadvantage of such volume translation is that it affects all virial coefficients simultaneously. As a result, it is not possible to reproduce the theoretical values for all virial coefficients, one can rather shift the values of the higher virial coefficients towards the correct order of magnitude. In this work we prefer to use a hard-sphere equation rather the volume translated cubic equation. The reason for this choice is the necessity of a mathematically higher order equation for accounting the specific molecular interactions such as dipole-dipole interactions. Since the cubic structure cannot be maintained for such interactions, a volume-translated van der Waals repulsion does not have any advantages over the use of a hard-sphere term.

## EQUATION OF STATE

The equation of state presented here is based on a simplified molecular model published by Yelash and Kraska [20]. This equation has been derived by a mapping of the properties of molecular equation of state models onto a mathematically simplified parametric equation $P_{map}$ (Eq. (1)). In combination with the van der Waals attraction term, this equation can be rearranged into a fourth order polynomial in the density or the molar volume. The general form of the equation of state is given in Eqs. (1) and (2).

$$P_{map} = \frac{RT}{V_m}\left(1 + c\ m\ \frac{D_1 y + D_2 y^2 + D_3 y^3}{(1-y)(3-4y)(1+c_1 y)}\right) \tag{1}$$

$$D_1 = A - 3c_1 + 7 \qquad D_2 = B + 7c_1 - 4 \qquad D_3 = C - 4c_1 \tag{2}$$

where $T$ is the temperature, $P$ the pressure, $V_m$ the molar volume, and $y = mb/4V_m$ the packing fraction with the chain length parameter $m$ and the covolume parameter $b$, and $c$ obtained for the best-fit values. The coefficients $A$, $B$, $C$ and $C_1$ depend on the molecular parameters which are here the chain length parameter $m$ and the reduced dipole moment $\mu^*$ according to Eqs. (3) to (10):

$$A = \frac{1}{4}(2 + 18m) - 1.9(\mu^*)^4 - 0.07(\mu^*)^6 - 0.04(\mu^*)^8 \tag{3}$$

$$B = \frac{1}{4}(45m - 21) + 9.5(\mu^*)^4 - (\mu^*)^6 + 0.07(\mu^*)^8 \tag{4}$$

$$C = 1.7(\mu^*)^4 + 2(\mu^*)^6 - 0.08(\mu^*)^8 \tag{5}$$

$$c_1 = 0.7(\mu^*)^4 \tag{6}$$

$$\mu^* = \frac{\mu}{\sqrt{mk_B T\sigma^3}} \equiv \frac{\hat{\mu}}{\sqrt{T}} \tag{7}$$

$$T^* = T\frac{bR}{4a} \tag{8}$$
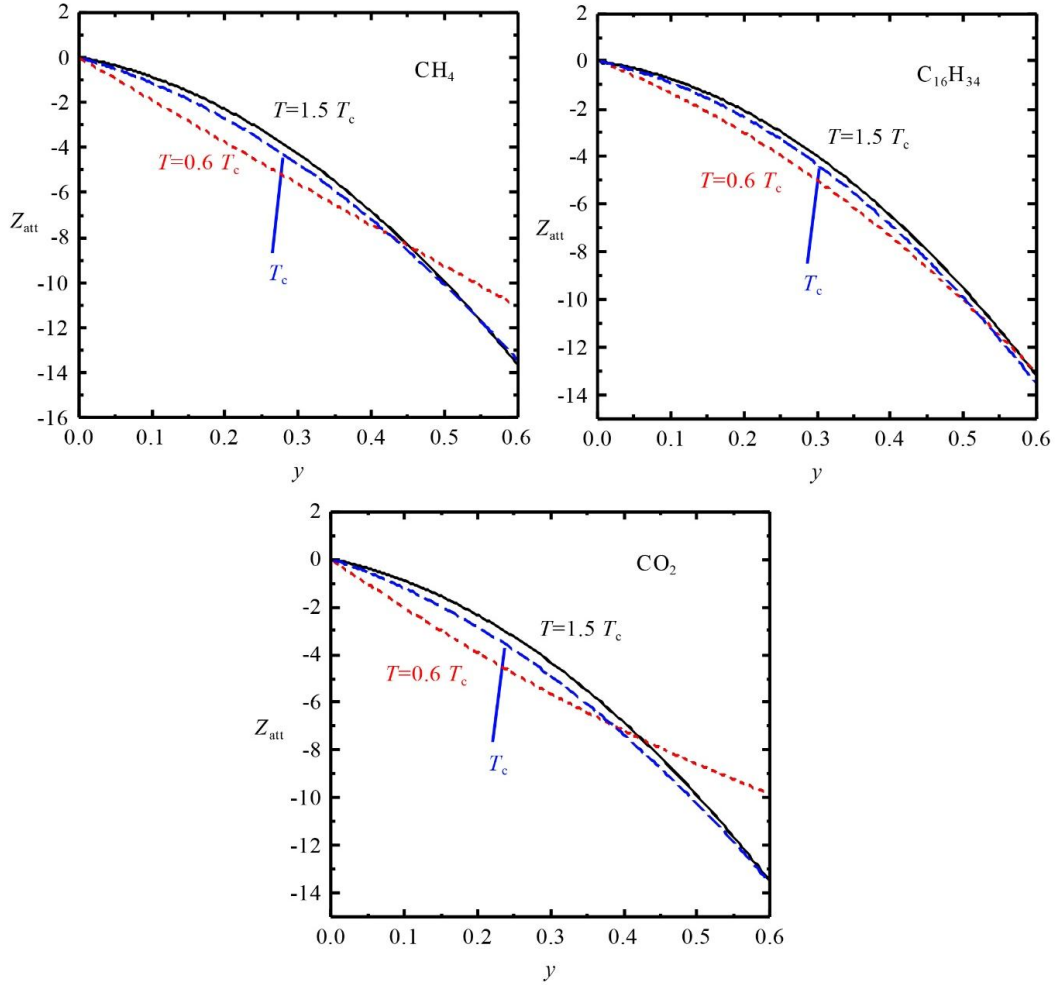
$$p^* = p\frac{b^2}{16a} \tag{9}$$

**Fig. 1.** Density dependence of the attraction term given by Eq. (11) at three temperatures.

$$\mu = 0.3308 \hat{\mu} \sqrt{m \cdot b} \cdot \qquad (10)$$

The units of the variables in Eq. (10) are $[\hat{\mu}] = K^{1/2}$, $[b] = dm^3 mol^{-1}$ and $[\mu] = D$. The resulting repulsion term is given by the combination of Eqs. (1) to (10) with the van der Waals attraction term. Experimental data [21,22] of the coexistence region of methane are used as the reference data for adjusting the attraction term. The resulting expression is given as:

$$P_{att} = -\frac{16a}{b^2} y^2 \left(a_1(T^*) + a_2(T^*)y^2\right) \qquad (11)$$

$$a_1(T^*) = 330.14416 + \frac{213465.26}{T^*} + 2.6581428 \, T^* \qquad (12)$$

$$a_2(T^*) = 3729.9723 - \frac{891532.07}{T^*} + 25.507962 \, T^* \qquad (13)$$

The resulting attraction term is an adjusting term, however, as shown in Fig. 1 the density dependences behave topologically correct (continuous change in shapes of the figures), *e.g.* show monotonous behaviour.

## RESULTS

The parameters of the equation of state proposed here have been adjusted to vapour pressure data and saturated liquid density data for n-alkanes, 1-alkanols, carbon dioxide, acetone and stearic acid. Since the equation of state

**Table 1.** Adjusted Equation of State Parameters

| Substance | $A$ ( bar dm$^6$ mol$^{-2}$) | $B$ (dm$^3$ mol$^{-1}$) | $m$ | $c$ | $\mu$ (D) |
|---|---|---|---|---|---|
| CH$_4$ | 0.0012786 | 0.067184 | 1.0000 | 0.9000 | |
| C$_2$H$_6$ | 0.0019055 | 0.067887 | 1.3333 | 0.7607 | |
| C$_3$H$_8$ | 0.0021763 | 0.072459 | 1.6666 | 0.6054 | |
| n-C$_4$H$_{10}$ | 0.0024561 | 0.074474 | 1.9639 | 0.5406 | |
| n-C$_5$H$_{12}$ | 0.0025959 | 0.075967 | 2.2719 | 0.4762 | |
| n-C$_6$H$_{14}$ | 0.0027072 | 0.077061 | 2.5486 | 0.4360 | |
| n-C$_7$H$_{16}$ | 0.0029000 | 0.080000 | 2.7625 | 0.4094 | |
| n-C$_8$H$_{18}$ | 0.0031001 | 0.082000 | 2.9369 | 0.3921 | |
| n-C$_9$H$_{20}$ | 0.0033519 | 0.084206 | 3.1179 | 0.3824 | |
| n-C$_{10}$H$_{22}$ | 0.0036534 | 0.086074 | 3.2258 | 0.3887 | |
| n-C$_{11}$H$_{24}$ | 0.0038698 | 0.087430 | 3.4401 | 0.3807 | |
| n-C$_{12}$H$_{26}$ | 0.0040931 | 0.087517 | 3.6053 | 0.3837 | |
| n-C$_{13}$H$_{28}$ | 0.0041550 | 0.088950 | 3.7966 | 0.3632 | |
| n-C$_{14}$H$_{30}$ | 0.0043384 | 0.091219 | 3.8898 | 0.3560 | |
| n-C$_{15}$H$_{32}$ | 0.0045660 | 0.092179 | 4.0103 | 0.3577 | |
| n-C$_{16}$H$_{34}$ | 0.0048391 | 0.093527 | 4.2077 | 0.3568 | |
| n-C$_{17}$H$_{36}$ | 0.0049984 | 0.093032 | 4.3782 | 0.3568 | |
| n-C$_{18}$H$_{38}$ | 0.0049984 | 0.093052 | 4.4978 | 0.3479 | |
| n-C$_{19}$H$_{40}$ | 0.0050000 | 0.093100 | 4.7170 | 0.3326 | |
| n-C$_{20}$H$_{42}$ | 0.0050000 | 0.093200 | 4.9645 | 0.3166 | |
| CH$_3$OH | 0.0028760 | 0.053791 | 1.3038 | 0.9994 | 1.76 |
| C$_2$H$_5$OH | 0.0031147 | 0.060418 | 1.5454 | 0.8776 | 1.86 |
| n-C$_3$H$_7$OH | 0.0034436 | 0.066187 | 1.7495 | 0.7837 | 1.81 |
| n-C4H$_9$OH | 0.0036240 | 0.069634 | 1.9840 | 0.7082 | 1.89 |
| n-C$_5$H$_{11}$OH | 0.0038507 | 0.075585 | 2.1790 | 0.6372 | 2.27 |
| n-C$_6$H$_{13}$OH | 0.0040255 | 0.080584 | 2.3907 | 0.5590 | 2.35 |
| n-C$_7$H$_{15}$OH | 0.0041875 | 0.081220 | 2.5868 | 0.5371 | 2.35 |
| n-C$_8$H$_{17}$OH | 0.0042093 | 0.087687 | 2.8471 | 0.4696 | 3.15 |
| n-C$_9$H$_{19}$OH | 0.0044217 | 0.090888 | 3.0567 | 0.4257 | 3.51 |
| n-C$_{10}$H$_{21}$OH | 0.0042941 | 0.087217 | 3.2709 | 0.4220 | 3.28 |
| Stearic acid | 0.0069781 | 0.120510 | 4.3408 | 0.3571 | 4.57 |
| Acetone | 0.0040367 | 0.086129 | 1.4882 | 0.7493 | 1.77 |
| CO$_2$ | 0.0013420 | 0.041275 | 1.2701 | 0.9575 | |
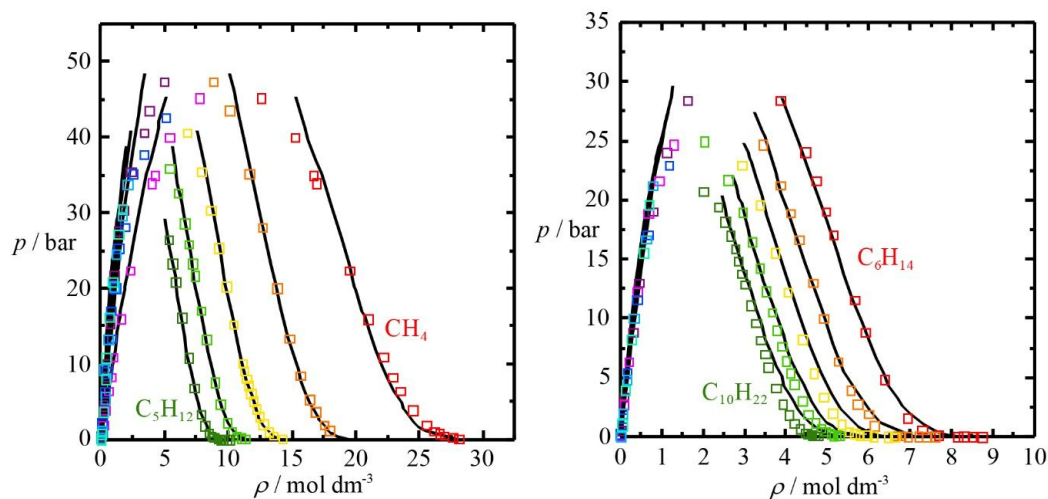
**Fig. 2.** Correlated vapour-liquid coexistence curves of the n-alkanes from methane to n-decane. The comparison is shown in the temperature-density as well as in the pressure-density projection. The data were taken from reference [21]. The solid lines show our calculated values and the symbols stand for the experimental ones.

does not include the effect of association, this effect is covered effectively by dipolar interactions. The adjusted parameters are listed in Table 1. In Fig. 2, correlations for the n-alkanes from methane to n-decane are shown in the temperature-density and pressure-density diagrams.

As seen, the data are well represented in both projections by the equation of state. As usual for classical equations of state the deviations between the model and the experimental data increases towards the critical point. Figure 3 shows the comparison for the saturated liquid densities of the alkanes from n-dodecane to n-eicosane in both projections $P$-$\rho$ and $T$-$\rho$. The agreement between the experimental and calculated data is also shown in Fig. 3 for the n-alkanes from methane to n-eicosane in the $P$-$T$-projection. The results show that the model is able to well-describe the vapour-liquid coexistence data in all projections.

Figures 4 and 5 show the correlations for the 1-alkanols from methanol to 1-dodecanol in the $P$-$\rho$, $T$-$\rho$ and $P$-$T$ projections. For the correlation of 1-alkanols the dipole moment has been included as an adjustable parameter. The resulting values are listed in Table 1 and reasonably agree with the experimentally obtained dipole moments for the

gas phase.

The differences can be related to induction effects as discussed later. The agreement between the calculations on the experimental data is similar as for the n-alkanes, whereas the agreement for the n-alkanes is a little bit better. Figure 6 shows the correlation for stearic acid. The pressure and temperature range of experimental data are limited, however, since stearic acid is important as a model solute for the investigation of the processes in supercritical fluids, it has been included in our work. The comparison shows a good agreement for the available data in all three projections. Further substances of interest are carbon dioxide and acetone which are similarly represented by the model.

Figure 7 shows the dependence of the equation of state parameters within the homologous series of the n-alkanes and 1-alkanols. As seen, there is a systematic dependence of the parameters on the number of carbon atoms. The $m$-parameter exhibits a nearly linear dependence on the number of carbon atoms which is almost identical for the n-alkanes and the 1-alkanoles. The $a$ and $b$ parameters exhibit different dependences on the number of carbon atoms for the n-alkanes and 1-alkanoles which can be explained by the
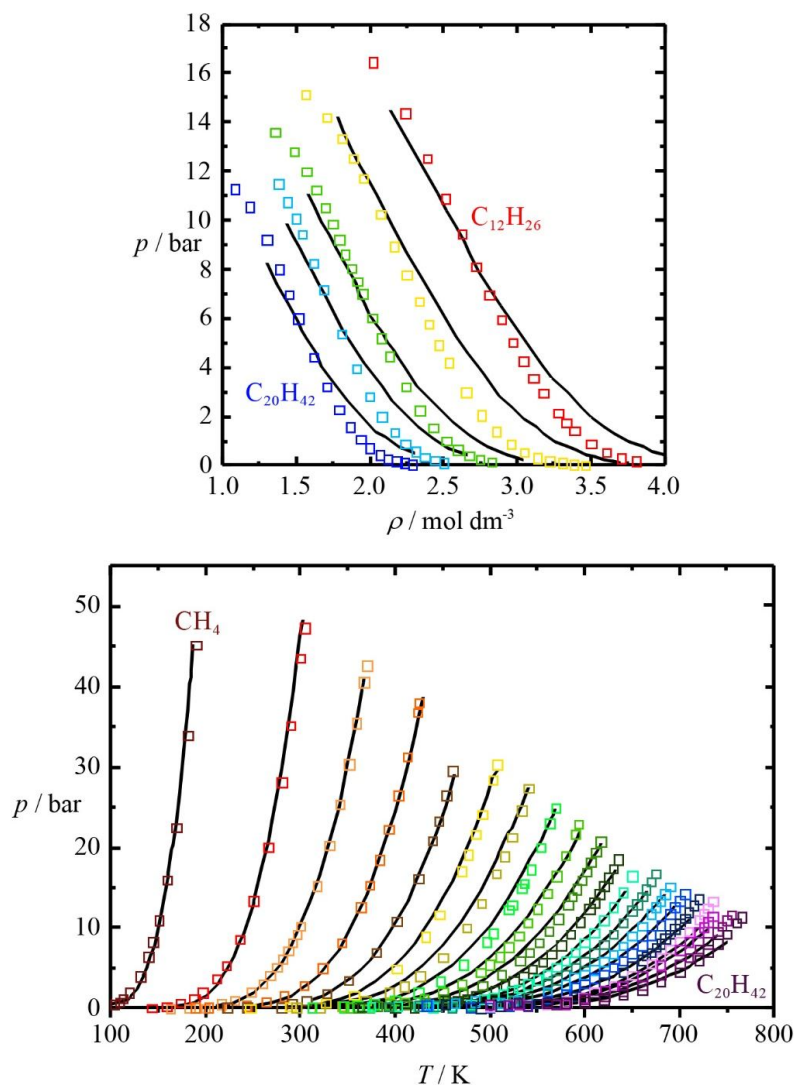
**Fig. 3.** Correlated saturated liquid density of some higher n-alkanes. The comparison is also shown for the correlated vapour pressure curves with the experimental data for the n-alkanes with 12, 14, 16, 18 and 20 carbon atoms. The data were taken from reference [22]. The solid lines show our calculated values and the symbols stand for the experimental ones.

interactions of the *OH* group. One can also see that the correlated dipole moments of the 1-alkanols agree well with the experimental values for the gas phase dipole moment. The correlated values are about 10% to 30% above the gas phase values which is related to the induction effects at liquid densities [24,25]. For the higher 1-alkanols the resulting dipole moment are higher.

To verify the accuracy of the new equation of state, we report calculation for the phase behaviour of eicosane in Fig. 8.

The molar volumes of saturated liquids calculated using various equations of state are compared to those using
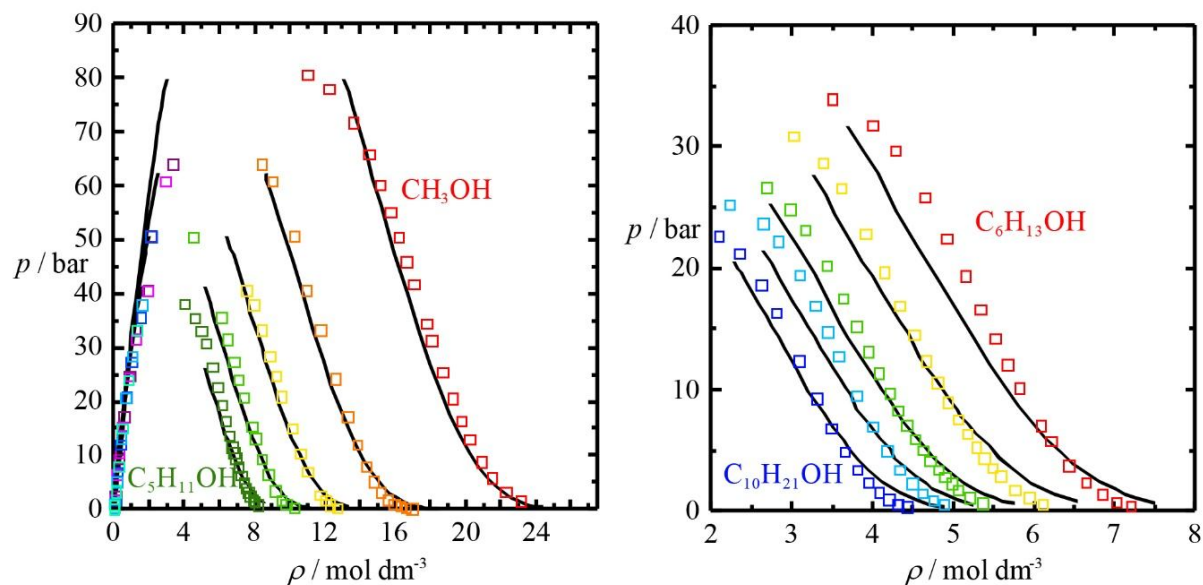
**Fig. 4.** Correlated vapor-liquid coexistence curves of the 1-alkanoles from methanol to 1-decanol. The comparison is shown in the temperature-density as well as in the pressure density projection. The data were taken from references [21,22]. The solid lines show our calculated values and the symbols stand for the experimental ones.
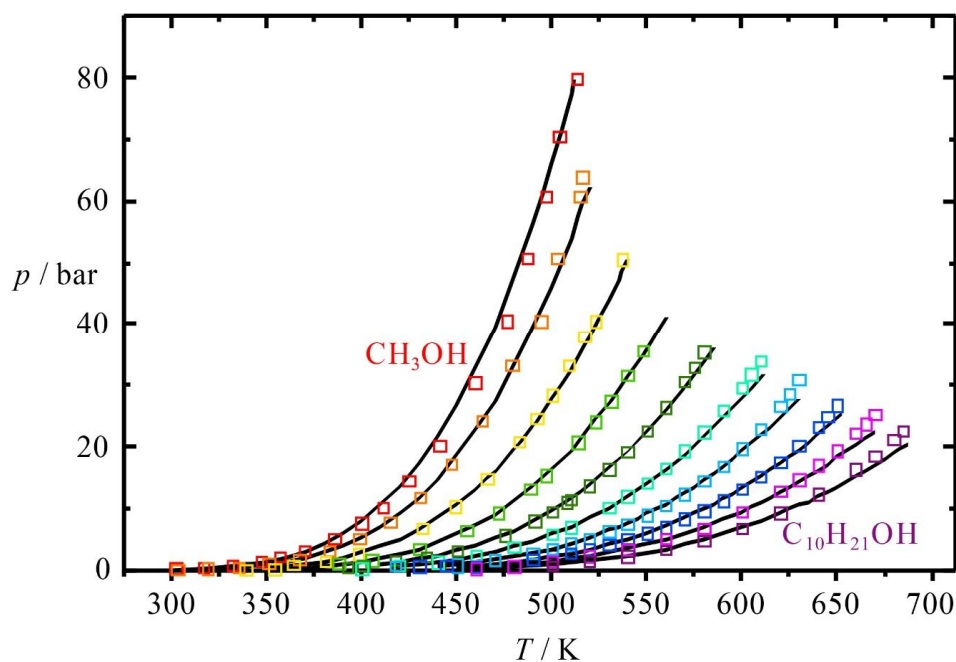


**Fig. 5.** Comparison of the correlated vapour pressure curves with the experimental data for n-alkanols. The data were taken from reference [25,26]. The solid lines show our calculated values and the symbols stand for experimental ones.
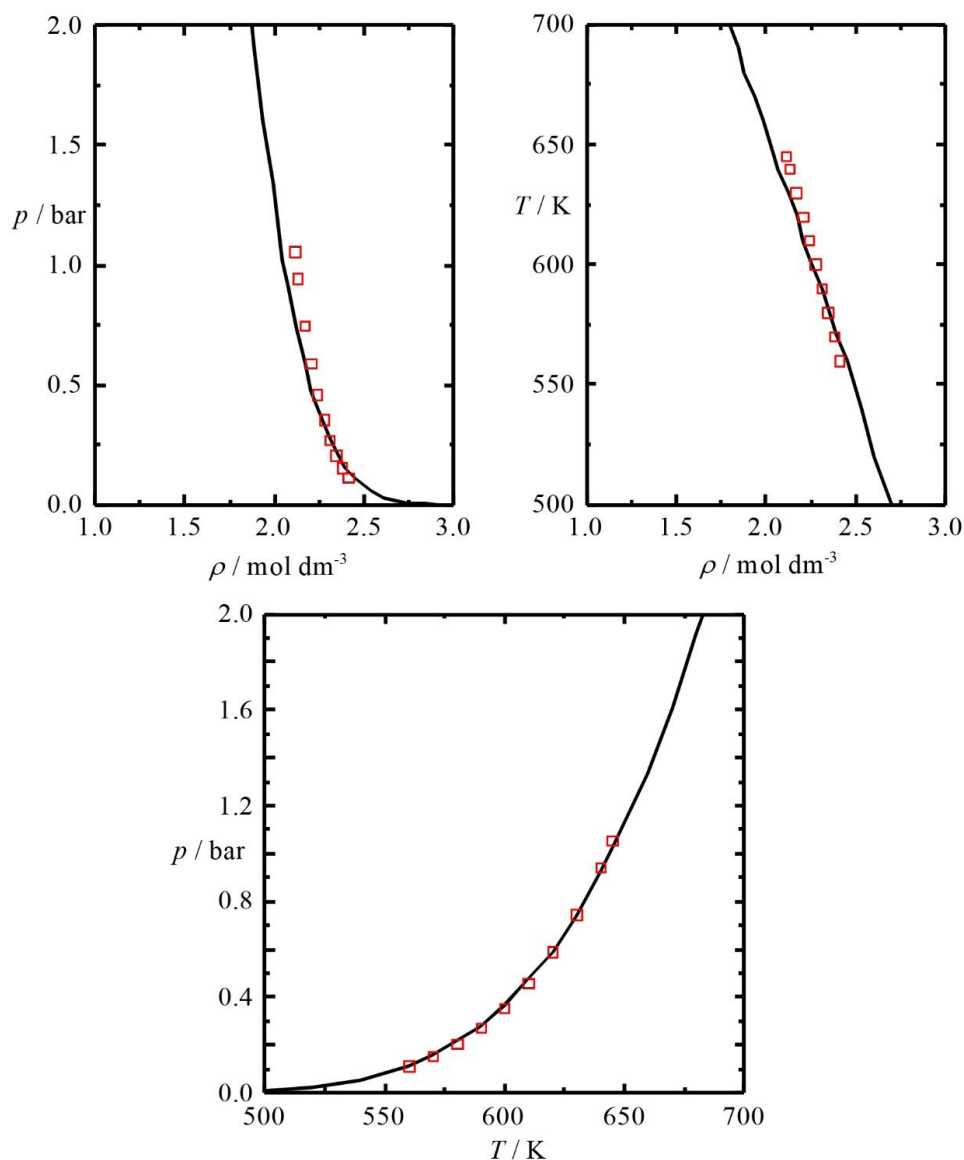
**Fig. 6.** Correlated vapor-liquid coexistence curves of stearic acid. The data were taken from reference [23]. The solid lines show our calculated values and the symbols stand for experimental ones.

an accurate correlation proposed by Thomson [23]. The percentage of average absolute deviations (*AAD*%) of the equations are presented in Table 2. According to this table, the performance of RM [26] equation of state is better than that for the other equations. The RM and this equation are actually one order of magnitude more accurate than the other equations. It must be also pointed out that this

equation is more accurate than the PR equation and SRK equation.

The average absolute deviations (*AAD*) of various equations of state in predicting vapor pressures of carbon dioxide and *n*-alkanes are presented in Table 3. According to this table, prediction by the SRK equation is one order of magnitude superior to the other equations. However, it must
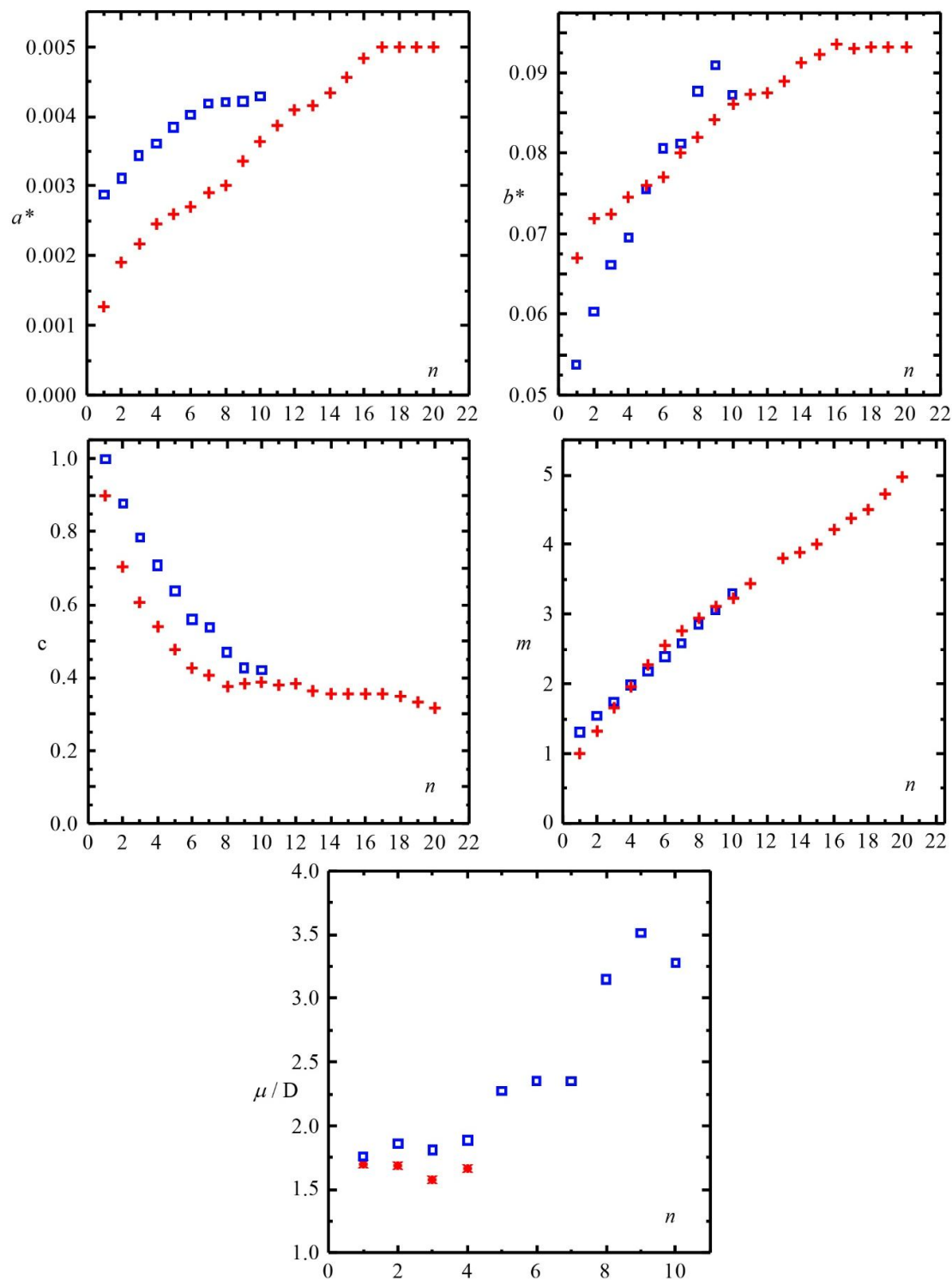
**Fig. 7.** Dependence of the equation of state parameters on the carbon number with $b^* = b$ (dm$^3$ mol$^{-1}$) and $a^* = a$ (bar dm$^6$ mol$^{-2}$. (+: n-alkanes, □: 1-alkanols).
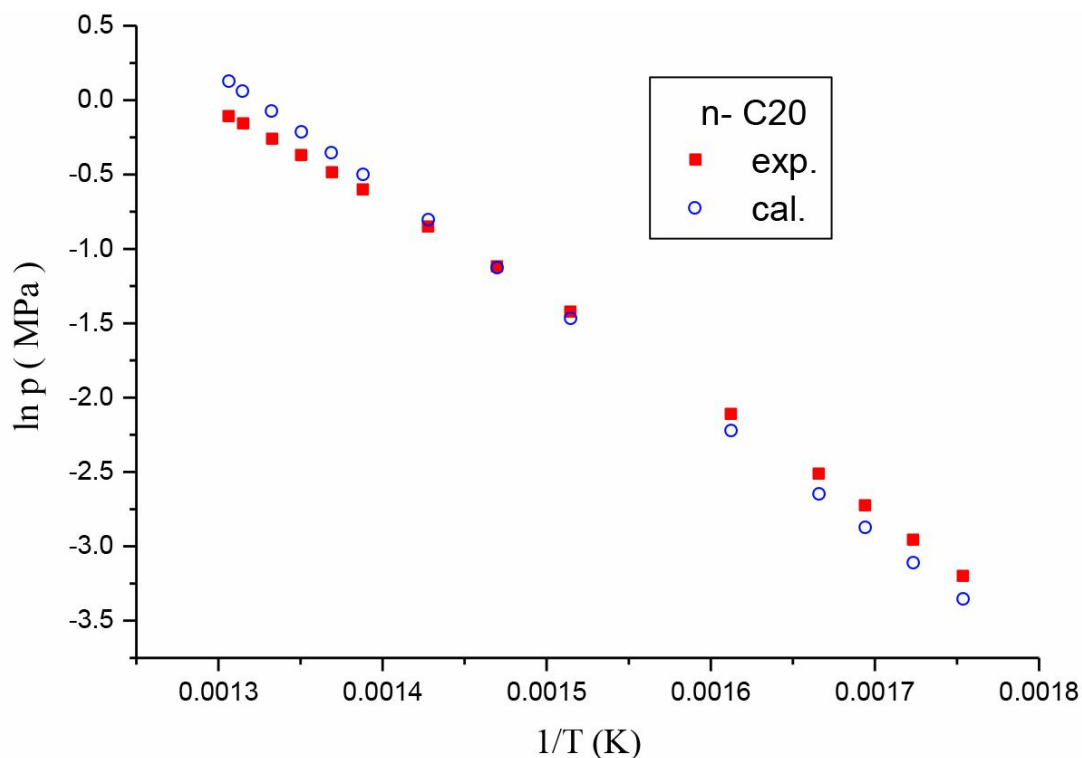
**Fig. 8.** Comparison of the experimental phase behaviour of eicosane (n-$C_{20}$) with the equation of state predictions from the boiling point ($b_p$) to the critical point (cp). The data were taken from reference [21,22]. The solid lines show our calculated values and the symbols stand for the experimental ones.

be pointed out that the PR and SRK equations are developed by fitting to the vapor pressure data. In Tables 4 and 5, the vapor pressure and saturated liquid molar volumes for 1-alkanols are compared with experimental data. The deviation between calculated and experimental data is within 4%.

## CONCLUSIONS

In this work, we explored the possibility of developing a simple equation of state to model the coexistence curves of several different substances. Considering the dependency of density to the attraction term, we developed a semi-empirical attraction term in order to develop a recently presented simplified molecular-based equation of state for fluids. Through this equation of state, a good correlation

was obtained for all three projections ($P$-$\rho$, $T$-$\rho$, $P$-$T$) of the coexistence curves. The extension of the equation of state proposed here to the mixtures is in progress and will be the subject of the following paper.

The liquid molar volumes and vapor pressures of carbon dioxide and $n$-alkanes were also calculated using various equations of state. The RM and equations of state proposed here showed higher accuracy for predicting the molar volume, and the SRK equation of state showed higher accuracy for predicting the vapor pressure.

## ACKNOWLEDGEMENTS

**Table 2.** The Average Absolute Deviations of Various Equations of State in Predicting Saturated Liquid Molar Volumes of Pure Compounds Compared with Experimental Data [25,26] and those Calculated Using the Hankinson and Thomson (1982) Correlation [23]

| Substance | $T_r$ rang | RM | This work | PR | SRK |
|---|---|---|---|---|---|
| $CH_4$ | 0.48-0.99 | 4.5 | 11.4 | 8.6 | 4.5 |
| $C_2H_6$ | 0.33-0.99 | 6.4 | 1.7 | 6.0 | 9.2 |
| $C_3H_8$ | 0.35-0.98 | 3.9 | 1.2 | 5.3 | 9.2 |
| $n-C_4H_{10}$ | 0.36-0.96 | 3.0 | 2.1 | 3.6 | 10.3 |
| $n-C_5H_{12}$ | 0.47-0.99 | 2.4 | 2.0 | 3.4 | 12.5 |
| $n-C_6H_{14}$ | 0.39-0.99 | 2.2 | 2.4 | 2.2 | 14.8 |
| $n-C_7H_{16}$ | 0.41-0.99 | 1.4 | 2.8 | 2.7 | 16.0 |
| $n-C_8H_{18}$ | 0.41-0.99 | 1.2 | 4.4 | 4.2 | 17.7 |
| $n-C_9H_{20}$ | 0.42-0.98 | 0.8 | 8.8 | 5.1 | 18.7 |
| $n-C_{10}H_{22}$ | 0.43-0.98 | 0.7 | 11.9 | 7.0 | 20.8 |
| $n-C_{11}H_{24}$ | 0.55-0.78 | 0.3 | 3.40 | 7.4 | 21.3 |
| $n-C_{12}H_{26}$ | 0.54-0.89 | 0.4 | 3.00 | 10.1 | 24.3 |
| $n-C_{13}H_{28}$ | 0.56-0.80 | 0.2 | 5.16 | 11.4 | 25.8 |
| $n-C_{14}H_{30}$ | 0.54-0.85 | 1.2 | 5.33 | 15.0 | 29.9 |
| $n-C_{15}H_{32}$ | 0.58-0.82 | 1.2 | 5.26 | 16.7 | 31.8 |
| $n-C_{16}H_{34}$ | 0.56-0.81 | 1.8 | 5.26 | 19.7 | 35.1 |
| $n-C_{17}H_{36}$ | 0.59-0.83 | 3.9 | 5.71 | 24.3 | 40.3 |
| $n-C_{18}H_{38}$ | 0.55-0.84 | 4.0 | 5.45 | 26.9 | 43.1 |
| $n-C_{19}H_{40}$ | 0.56-0.85 | 4.4 | 17.87 | 29.6 | 46.1 |
| $n-C_{20}H_{42}$ | 0.57-0.85 | 4.8 | 3.0 | 32.2 | 49.0 |
| $CO_2$ | 0.71-1.00 | 19.5 | 2.1 | 4.7 | 0.8 |
| | | | | | |
| Overall | | 3.2 | 5.2 | 11.7 | 22.9 |

**Table 3.** The Average Absolute Deviations of Various Equations of State in Predicting Vapor Pressures of Pure Compounds Compared with Experimental Data [21,22]

| Substance | $T_r$ rang (No. of data) | RM | This work | SRK | PR |
|---|---|---|---|---|---|
| $CH_4$ | 0.48-0.99 (84) | 17.2 | 13.4 | 2.9 | 0.7 |
| $C_2H_6$ | 0.33-0.99 (114) | 11.9 | 26.1 | 2.6 | 3.0 |
| $C_3H_8$ | 0.35-0.98 (101) | 8.3 | 9.6 | 1.9 | 3.0 |
| n-$C_4H_{10}$ | 0.36-0.96 (130) | 7.0 | 14.2 | 1.9 | 5.6 |
| n-$C_5H_{12}$ | 0.47-0.99 (91) | 9.9 | 8.7 | 1.5 | 0.8 |
| n-$C_6H_{14}$ | 0.39-0.99 (88) | 16.5 | 13.9 | 1.9 | 3.1 |
| n-$C_7H_{16}$ | 0.41-0.99 (80) | 20.7 | 17.5 | 1.2 | 2.4 |
| n-$C_8H_{18}$ | 0.41-0.99 (87) | 28.9 | 18.9 | 1.2 | 2.7 |
| n-$C_9H_{20}$ | 0.42-0.98 (82) | 33.3 | 19.6 | 1.5 | 2.1 |
| n-$C_{10}H_{22}$ | 0.43-0.98 (86) | 37.4 | 25.0 | 1.2 | 3.1 |
| n-$C_{11}H_{24}$ | 0.55-0.78 (27) | 37.7 | 10.9 | 4.4 | 6.6 |
| n-$C_{12}H_{26}$ | 0.54-0.89 (40) | 31.7 | 8.1 | 0.4 | 2.9 |
| n-$C_{13}H_{28}$ | 0.56-0.80 (27) | 28.8 | 10.6 | 0.5 | 3.3 |
| n-$C_{14}H_{30}$ | 0.54-0.85 (42) | 30.3 | 16.8 | 2.5 | 5.8 |
| n-$C_{15}H_{32}$ | 0.58-0.82 (27) | 23.4 | 13.7 | 0.6 | 4.0 |
| n-$C_{16}H_{34}$ | 0.56-0.81 (45) | 29.3 | 13.7 | 0.9 | 5.6 |
| n-$C_{17}H_{36}$ | 0.59-0.83 (43) | 23.9 | 6.5 | 1.6 | 6.2 |
| n-$C_{18}H_{38}$ | 0.55-0.84 (44) | 30.2 | 7.8 | 3.0 | 9.2 |
| n-$C_{19}H_{40}$ | 0.56-0.85 (42) | 30.4 | 8.7 | 3.6 | 10.4 |
| n-$C_{20}H_{42}$ | 0.57-0.85 (42) | 33.0 | 12.6 | 2.4 | 8.8 |
| $CO_2$ | 0.71-1.00 (47) | 19.1 | 6.0 | 0.5 | 0.8 |
| Overall | | 24.2 | 13.4 | 1.82 | 4.29 |

**Table 4.** The Average Absolute Deviations of Vapor Pressures Compared with Experimental Data [21,22]

| Substance | No. of data | $T_r$ rang | AAD |
|-----------|-------------|------------|-----|
| $CH_3OH$ | 15 | 0.65-1.00 | 7.1 |
| $C_2H_5OH$ | 13 | 0.68-1.00 | 3.4 |
| n-$C_3H_7OH$ | 14 | 0.68-1.00 | 1.8 |
| n-$C_4H_9OH$ | 12 | 0.69-0.98 | 1.2 |
| n-$C_5H_{11}OH$ | 16 | 0.71-0.99 | 2.0 |
| n-$C_6H_{13}OH$ | 14 | 0.71-0.99 | 2.5 |
| n-$C_7H_{15}OH$ | 18 | 0.66-0.99 | 2.9 |
| n-$C_8H_{17}OH$ | 20 | 0.69-0.99 | 3.3 |
| n-$C_9H_{19}OH$ | 15 | 0.69-1.00 | 4.7 |
| n-$C_{10}H_{21}OH$ | 14 | 0.67-1.0 | 4.8 |
| | | | |
| Overall | | | 3.4 |

**Table 5.** The Average Absolute Deviations of Saturated Liquid Molar Volumes with Experimental Data [21,22] and those Calculated Using the Hankinson and Thomson (1982) Correlation [23]

| Substance | No. of data | $T_r$ rang | AAD |
|-----------|-------------|------------|-----|
| $CH_3OH$ | 13 | 0.69-0.99 | 3.6 |
| $C_2H_5OH$ | 16 | 0.58-1.00 | 3.8 |
| n-$C_3H_7OH$ | 13 | 0.68-0.97 | 5.9 |
| n-$C4H_9OH$ | 13 | 0.63-0.98 | 4.1 |
| n-$C_5H_{11}OH$ | 20 | 0.71-0.99 | 3.9 |
| n-$C_6H_{13}OH$ | 16 | 0.69-1.00 | 4.2 |
| n-$C_7H_{15}OH$ | 18 | 0.70-1.00 | 3.2 |
| n-$C_8H_{17}OH$ | 20 | 0.69-0.99 | 3.5 |
| n-$C_9H_{19}OH$ | 15 | 0.69-1.00 | 4.6 |
| n-$C_{10}H_{21}OH$ | 14 | 0.67-1.00 | 4.5 |
| | | | |
| Overall | | | 4.1 |

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