Critical properties of binary mixtures of hydrocarbons for linear hard sphere models of molecules based on ISPT, Nezbeda and Boublík equations of state, and the chain equation of state of R J Sadus

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Abstract The predicted results of virial coefficients from different equations of state of hard body fluids such as linearly tangent hard spheres, hard ellipsoidals or hard spherocylinders have been used to calculate the values of nonsphericity factor and the van der Waals parameters. The parameters of these equations of state testify the predicted critical properties satisfactorily. The improved accuracy of the predicted results has been observed by incorporating the chain concept with the shape of the molecules of binary mixtures of hydrocarbons.

1. Introduction
Critical properties of fluids or fluid mixtures [1-5] are essential for describing the phase behavior of fluids. The experimental determination of critical properties or critical state of the composition of a system, in which two phases become indistinguishable, is not easy and therefore reliable thermodynamic property calculations need the development of an adequate equation of state (EoS) for reference purpose. The knowledge of critical properties of fluids or fluid mixtures is essential for the development of equations of state (EoSs), for design of supercritical extraction process and also for prediction of the physical properties. Critical properties, especially the critical temperature and pressure are important input parameters for EoS and generalized correlations in order to estimate physical and thermodynamic properties of fluids. The precise knowledge of this is important for the calculation of the amount of fluid in a place and their recovery by “gas cycling technique” or by “hydrocarbon solvent injection technique” [1-3, 6]. The critical behavior of mixtures helps to determine the operating ranges successfully in the process equipment. The oil and natural gas industry try to obtain reliable high accuracy phase equilibrium and procuring the pressure-density-temperature data at different steps between exploration and its use. Two-component (or binary) systems are the basis for the understanding of multi-component systems. In contrast to single component, binary systems present an additional variable as composition of the mixture. The composition of the binary mixture is a major factor in the determination of the thermodynamic and physical properties of the mixture, and it is commonly expressed in mole or weight fraction. A small error in prediction of these properties greatly affects the calculated physical properties. For binary mixture, it is possible to observe coexistence of the two phases at pressures higher than the critical pressures of the individual components. The area in which two phases coexist is limited by the bubble point and dew point curves. The point at which these two curves are connected is by definition the critical point, a junction between bubble and dew-point curves. The maximum pressure and temperature on the envelope of a binary mixture are called cricondenbar and cricondentherm, respectively.
Although experimental critical properties are available for commonly used pure substances and mixtures, but the experimental investigation of critical properties of every possible fluid mixture is impractical because of the limitations in terms of time and cost [5, 6]. Besides the direct measurements, the critical properties of mixtures are often estimated using various correlation methods. The basis of the existing correlation methods [4] can be divided into a) excess property (a result of empirical methods) b) graphical techniques (Gibbs energy-mole fraction diagram) c) group contribution (structure of the molecule is a function of some property of the substance) d) conformal solution (the components of the mixture conform to certain simple postulates of statistical mechanics) and e) equation of state (a P,V,T relation describing phase behavior and critical properties of a single-component and multi-component mixtures).

In chemical industry the importance of thermo physical data cannot be denied and availability of these data for all mixtures is not possible because of a dearth of carrying out experiments for all ranges of temperature, pressure and composition. To avoid the non-availability of experimental data, thermodynamic models are relied upon to predict results. Different models of cubic EoS typically provide fast and reliable predictions. Cubic equations of state methods have been applied to estimate the critical properties of single components and mixtures. This method was first used by Joffe and Zundkevitch [7] in 1967 and Spear et al [8] in 1969. They used the Redlich-Kwong equation of state to predict the critical properties and found qualitative results for the critical properties of binary mixtures. Later on in 1976, Huron [9] and in 1978 Huron et al [10] used the Soave-Redlich-Kwong equation of state together with the adjustable parameters and predicted the critical points and vapour liquid equilibria correctly. In 1977, Peng and Robinson [11] predicted the critical properties of a total of 32 multicomponent mixtures using Gibbs free energy criterion. In 1980, Heidemann and Khalil [12] used the Soave-Redlich-Kwong equation of state with Helmholtz free energy concept and presented their calculations for prediction of critical properties of binary mixtures. In 1981 a modification in the Heidemann and Khalil [12] approach to reduce the computational time in the calculation was presented by Michelson and Heidemann [13]. In 1983, Teja et al [14] used the Teja-Patel and the Peng-Robinson equations of state to predict the critical properties of mixtures using the Heidemann and Khalil procedure. It is well understood that the Heidemann-Khalil method is superior as compared to the Peng-Robinson method and easily computational as it uses the Helmholtz free energy concept instead of Gibbs energy concept. In 1987, Sadus, Young and Svejda [15] calculated the critical properties of binary mixtures from an equation of state for hard convex bodies and Guggenheim’s equation of state for hard spheres. The results of both equations were found to agree well with experimental data [15]. In 1988, Mainwaring et al. [17] used the Deister equation of state to calculate the critical properties of over 50 binary mixtures and used the Guggenheim equation of state [16] for comparison purposes. They found that Deiters equation of state [18-20] gives good results for mixtures of moderately different size molecules, whereas Guggenheim’s equation is superior for dissimilar size molecules. In 1992, Gracia-Sánchez et al. [21] used the simplified perturbed hard chain theory equation of state to analyze its ability for the prediction of the critical points of reservoir fluids using the procedure of Heidemann and Khalil. The performance of this equation was demonstrated for four oil reservoir fluid systems containing up to 48 components. In 1997, Eishah et al. [1] using the PRSV-2 equation of state and adopting the procedure of Heidemann and Khalil [12] predicted the critical properties of binary mixtures for 20 polar and non-polar molecules. In 2018, Akhouri and Kaur [22] predicted the critical properties of binary mixtures of n-alkanes using the hard convex chain equation of state of RJSadus and they found an improvement in the predictions even incorporating the shape factor in chain concept.

Many refinements to the perfect gas EoS have been proposed because of the physical factors, which must be responsible for deviations from the perfect gas equation, are the finite size of the molecules, and the mutual attraction (or repulsion) between them. The two constants a and b introduced in the van der Waals EoS (1873) represent attractive and repulsive intermolecular forces, respectively. In the van der Waals EoS, the values of a and b parameters are determined using the experimentally determined critical constants of the fluid. The two constants of the equation of state, the parameters a and b, can be expressed uniquely in terms of the critical constants of a pure fluid. The values of the
critical constants specified for that fluid are reproduced exactly through the conditions at the critical point. For mixtures, the determination of the value $a$ and $b$ is more complicated because critical property data for mixtures is rarely available and critical point criterion are more complex. Many attempts have been made to produce a more satisfactory equation of state than the equation of van der Waals. Some attempts have been made to improve the accuracy of equation of state by considering the molecular shape of fluids.

The aim of this work is to evaluate the HCB equations of state proposed by ISPT [23], Boublík [25-27] and Nezbeda[28] and HCB chain equation of state [29]for the prediction of the gas- liquid critical properties for binary mixtures for hard sphere models of molecules (hard linearly tangent spheres, HLNTs, hard ellipsoids, HEs and hard spherocylinders, HSPs). The gas-liquid critical properties of several hydrocarbon mixtures[30-34] have been calculated from the proposed HCB and HCB chain equations of state. The hydrocarbons form the largest group of organic compounds. At standard conditions (20°C and 1 atm), the first four alkane series i.e. methane, ethane, propane, and butane are in gaseous form while pentane to hexadecane are in liquid form. Alkanes are open, straight-chain saturated hydrocarbons and napthenes or cycloalkanes are ring or cyclic saturated hydrocarbons. The straight line between the ends of carbon atoms are called core. The core values of molecules and molecular parameters are summarized in Table A1. Experimental values of critical properties have been reported for a large number of pure substances. However, for hydrocarbon compounds, because of thermal cracking that occur at higher temperatures, critical properties have been measured up to $C_{18}$. For heavier hydrocarbons (>C_{18}), with very high critical temperatures but correspondingly low critical pressures, direct measurements are not possible due to thermal cracking of the hydrocarbons above about 500°C or even as low as 350°C for more reactive hydrocarbons. Critical properties can also be obtained indirectly from other measurements, e.g. by regression of vapour pressure data. Ambrose and Young [35] method for the experimental determination of critical properties is only reliable if the pure component is thermally stable around the critical condition. Ribeiro et al [36] gave a method of indirect measurements of critical properties used particularly for mixtures. A number of correlations have been developed for prediction of critical temperature and pressure[37-39]. Hard body models of molecules can be used as reference systems in perturbation treatments of molecules with repulsive and attractive interactions [40-41]. Hard linear molecules such as hard ellipsoids or sphero-cylinders have been regularly studied and their virial coefficients [42-43] and EoS are well known. Wertheim theory of associated fluid [44-46] may be used to predict the chains of tangent hard spheres and it has successfully predicted the virial coefficients and EoS. The three models, hard linear tangent spheres (Figure 1), hard ellipsoidal (Figure 2), and hard spherocylinder(Figure 2), reduces to hard sphere model when $\alpha = 1$. As a result, the values of virial coefficients for $\alpha$ close to one are very similar to these three geometries. This idea is justified for small $\alpha$ (i.e., $\alpha < 1$) but not for large $\alpha$, as for large $\alpha$ virial coefficients are sensitive to the details of the shape.

![Figure 1](image1.png)

(a) Hard linearly tangent spheres  
(b) Hard spherical molecules
The scheme of the work is as follows. In section 2, the theoretical predictions are given which presents the calculations of the virial coefficients by using the three forms of EoSs and the virial coefficients values are then used to calculate the nonsphericity parameters $\alpha$ and the van der Waals constants of hard body models of the molecules i.e. HLTSs, HEs, and HSPs. This section also includes the calculation of the nonsphericity parameters $\alpha$ and the van der Waals constants of chain models of the molecule in the three geometries by using the known values of virial coefficients. Section 3 has the tables of calculated critical properties of binary mixtures for both hard convex body models and hard convex body chain models in HLTS, HEs, and HSPs configurations. The results and discussions are given in section 4 and the conclusions are in section 5.

2. Theoretical Predictions

Perturbation theories and empirical equations of state usually divide the total pressure into two parts, one is a contribution arising from the repulsive forces, and the other arising from the attractive ones. Therefore, it is quite important to have good equations of state for the repulsive parts. The following equations of state [equations (1)-(5)] have different repulsive parts in order to search a good equation for critical properties predictions of binary mixtures. The critical properties of various binary mixtures have been successfully calculated by using the Guggenheim two parameter equation of state[16,17], which has the form

$$P = \frac{RT}{v} \left( 1 - \frac{b}{4v} \right) - \frac{a}{v^2}$$

(1)

Several EoS have been proposed for HLTS. These equations of state are the result of Boublik modifications. Boublik [23] modified the scaled particle theory of hard convex bodies of Gibbons [24] and proposed an improved version of EoS, called, ISPT. Later Boublik [25] modified the EoS of Nezbeda [28], by analyzing the virial coefficients of HSP models. These EoSs are written in the form

ISPT EoS

$$P = \frac{RT}{v} \left[ 1 + \left( 3\alpha - 2 \right) y + \left( 3\alpha^2 - 3\alpha + 1 \right) y^2 - \alpha^2 y^3 \right] \frac{a}{v^2}$$

(2)

Nezbeda EoS

$$P = \frac{RT}{v} \left[ 1 + \left( 3\alpha - 2 \right) y + \left( \alpha^2 + \alpha - 1 \right) y^2 - \alpha(5\alpha - 4) y^3 \right] \frac{a}{v^2}$$

(3)
BoublkEoS

\[
P = \left( \frac{RT}{v} \right) \left[ 1 + \left( 3\alpha - 2 \right) y + \left( 3\alpha^2 - 3\alpha + 1 \right) y^2 - \alpha(6\alpha - 5)y^3 \right] \frac{a}{v^2}
\]  

(4)

R J SadusEoS is expressed as

\[
P = \left( \frac{RT}{v} \right) \left[ m \left( 1 + \left( 3\alpha - 2 \right) y + \left( 3\alpha^2 - 3\alpha + 1 \right) y^2 - \alpha^2 y^3 \right) \right] \frac{a}{v^2}
\]

\[
\left( m-1 \right) \left[ 1 + \frac{2.5S_H}{V} - \frac{S_H}{V} y^2 \right] \left( 1-y \right) \left( 1-(3-2.5S_H)y + (3-3S_H)y^2 -(1-S_H)y^3 \right) \]  

(5)

The above expressions of equation of state has a quantity \( a \) which estimates the attractive forces between the molecules, and the other quantity \( b/4 \) and \( V^* \) estimates the molar volume of hard sphere and the hard convex body molecules, respectively. The packing fraction \( y \) is defined as, \( y = \frac{V^*}{V} \), where \( V^* \) is the molar volume of the hard convex bodies and \( V \) the molar volume of the fluid. Also, \( V^* \) is given by the product of Avogadro number \( N \) and the volume, \( V^* \) i.e. \( V^* = NV^* \). The deviation from non-spherical geometry is defined by the \( \alpha \) parameter,

\[
\alpha = \frac{R^*S^*}{3V^*}
\]  

(6)

In equation (6), the mean curvature \( R^* \), the surface area \( S^* \) and the volume \( V^* \) are the three characteristic geometrical quantities of one hard convex body. The parameter, \( \alpha = 1 \), for a sphere and \( \alpha > 1 \), for a hard convex body. The diameter of HCB is supposed to be equal to the diameter of HS. In equation (5), the quantity \( S_R \) is defined as, \( S_R = \frac{S_{HCB}}{S_{eq}} \), where \( S_{HCB} \) is the actual surface area of HCB and \( S_{eq} \) is the surface area of hard spheres, and the diameter of the HCB is supposed to be equal to the diameter of the HS. The constraint on \( S_R \) can be written as, \( S_R > \frac{3\alpha + 1}{2.5(1-1/m)} \) Since \( \alpha > 1 \) and \( m > 1 \), and therefore, \( S_R > 1 \). The repulsive parts of each of the equations (2-4) has the form as the ISPT EoS or NezbedaEoS or BoublkEoS, respectively and the attractive parts have the similar van der Waals form as \( a/v^2 \). In equation (5), the repulsive part containing \( m, V^* \) and \( S_R \) helps to investigate the property of hard convex body chain equation of state and the attractive part is the familiar van der Waals term as \( a/v^2 \). The parametric values \( a, v^*, S_R \) and \( m \) of the equations of state have been calculated and are given in Table B1 and Table B2. The above mentioned equations of state were derived assuming that we deal with a pure fluid. However, in technical practice, we often encounter mixtures of fluids, which need to be described as well. In order to use the existing equations of state for mixtures, their \( a \) and \( b \) parameters need to be calculated. The \( a \) and \( b \) parameters serve to effectively characterize the forces between the molecules in a fluid as being either repulsive or attractive. The parameter \( a \) is actually a measure of the intermolecular attractive forces, which are dominant over relatively large separations of the molecular centers i.e. long range interactions. The \( b \) parameter, also known as the effective molecular volume or co-volume term, serves to take into account the finite volumes possessed by molecules that give rise to repulsive interactions when the
molecules are in contact i.e. short-range interactions. It is a rough measure of the size of the hard sphere fluid molecules. Consequently, the fluid pressure can be viewed as being due to a combination of two types of contributions, as quantified by an attractive and a repulsive term. These and \( b \) parameters can be found by fitting the equation of state parameters to experimental pure component properties and then by using thermodynamic constraints imposed by critical point conditions. Three conditions hold at the critical point of a substance: the equation of state \( f(P,V,T) = 0 \), the condition of a horizontal tangent to the critical isotherm \( \frac{\partial P}{\partial V} = 0 \), and the condition of a point of inflection \( \frac{\partial^2 P}{\partial V^2} = 0 \). These are sufficient to permit evaluation of the three critical constants in terms of \( a \), \( b \), and \( c \) or conversely to express \( a \), \( b \), and \( c \) in terms of \( P_c \), \( n_c \) and \( T_c \). It can be done in various ways, depending on an equation and desired accuracy. In order to extend a pure fluid equation of state to fluid mixtures, the following combining rules are used:

\[
\lambda_{ij} = \frac{1}{2} \left( \frac{\lambda_i^{1/3} + \lambda_j^{1/3}}{\lambda_{ij}^{1/3}} \right)^3 \quad (7)
\]

\[
a_{ij} = \xi \lambda_{ij} \left( \frac{a_i a_{ij}}{\lambda_i \lambda_{ij}} \right)^{1/2} \quad (8)
\]

where \( \lambda \) stands either for \( b \) or \( v^* \) and \( \xi \) is an adjustable parameter or adjustable binary interaction parameter. In equations (7-8), the unlike parameters (\( \lambda_{ij} \) or \( a_{ij} \)) has been estimated by combining the pure component parameters (\( \lambda_i \) or \( a_{ij} \)). Here, the introduction of adjustable parameter is necessary to compensate the inadequacy of combining rule. The parameters \( \alpha \) and \( \alpha^2 \) in equations (2-5) are given by

\[
\alpha = \sum_i x_i \alpha_i \quad (9)
\]

\[
\alpha^2 = \sum_i x_i (\alpha_i)^2 \quad (10)
\]

where \( \alpha_i \) is the nonsphericity parameter of component \( i \), \( x \) is some measure of composition (usually mole fractions) and summations are performed over all the components in the mixture. Equation (10) is not exactly consistent with the theoretical prescription and it is found that the calculated properties either do not differ or differ negligibly. Actually the use of equation (10) expedites the calculation of critical properties of binary mixtures.

### 2.1 Determination of values of third virial coefficients \( B_3 \)

The virial coefficients have been calculated by using the equations (2-4). The equations have the \( y \)-coefficients in the form given in Table A2.

The equations of state can be represented as

\[
Z = \frac{1 + \kappa_1 y + \kappa_2 y^2 + \kappa_3 y^3}{(1 - y)^3} \quad (11)
\]

where \( y \) is the packing fraction defined as \( y = \rho V_m \), and \( \rho \) is the number density. Here, the coefficients \( \kappa_1 \), \( \kappa_2 \), and \( \kappa_3 \) are taken from the ISPT-EoS, Nezbeda-EoS and Boublik-EoS, respectively. The ISPT, Nezbedaand Boublik-EoSs predict a linear variation in \( \alpha \) for \( \kappa_1 \) and quadratic dependence of \( \kappa_2 \) and \( \kappa_3 \). All these three EoSs provide a fair prediction of \( B_3 \), \( B_3 \) is well represented by a linear
function of $\alpha$ and are given by,

$$B_3 = (\kappa_2 + 3\kappa_3) + 1.5(1-\kappa_1 - \kappa_2 - \kappa_3) + 4.5(1 - \kappa_1 - \kappa_2 - \kappa_3) \quad (12)$$

It can be shown that for hard convex body, the nonspHERicity parameter in terms of the second virial coefficient has the form

$$\alpha = \frac{B_2 - 1}{3} \quad (13)$$

For hard convex bodies equation (6) or equation (13) can be considered as the definition of $\alpha$ regardless of the shape of the molecule, and both yield identical results.

2.2 Determination of nonsphericity parameter $\alpha$ for three models of the molecules:

The third virial coefficients $B_3$ for any of the EoSs (equations (2)-(4)) is calculated from equation (12) using the known value of $\alpha$ from equation (6) or equation (13). The value of the virial coefficients [see Table A3] is then substituted in any of the equations (14-16) to obtain the nonsphericity $\alpha$ for a particular model. Thus each EoS will result three values of $\alpha$ corresponding to the three molecular models. The calculated $\alpha$ values for the three molecular models are given in Tables A4, Table A5, and Table A6.

The relation of third virial coefficient $B_3$ with the nonsphericity parameter $\alpha$ for the three molecular models, respectively are: For HLTS model of molecules,

$$B_3 = -3.17144 + 12.08706\alpha + 1.08437\alpha^2 \quad (14)$$

For HE model of molecules,

$$B_3 = -0.92666 + 10.02080\alpha + 0.90584\alpha^2 \quad (15)$$

For HSP model of molecules,

$$B_3 = -1.22719 + 10.37590\alpha + 0.85129\alpha^2 \quad (16)$$

For non convex bodies, for instance the HLTS model $R^*$ is not well defined. Boublik and Nezbeda[28] proposed for HLTS to take the mean radius of curvature of a convex body of similar shape to that of the original nonconvex molecules.

2.3 Determination of the van der Waals parameter $'a'$:

Now using the second constraint, $\frac{\partial P}{\partial v} = 0$, we have, From ISPT EoS,

$$a = \frac{RTv^*}{2} \left[ (y^{-1} + 2\kappa_1 y^0 + 3\kappa_2 y - 4\kappa_3 y^2)(1 - y)^{-3} + (3y^0 + 3\kappa_1 y + 3\kappa_2 y^2 - 3\kappa_3 y^3)(1 - y)^{-4} \right] \quad (17)$$

From Nezbeda EoS,

$$a = \frac{RTv^*}{2} \left[ (y^{-1} + 2\kappa_1 y^0 + 3\kappa_2 y - (16\kappa_4 - 20\kappa_3) y^2)(1 - y)^{-3} + [3y^0 + 3\kappa_1 y + 3\kappa_2 y^2 + \ldots] \right] \quad (18)$$
From Boublik EoS,
\[ a = \frac{RTv^*}{2} \left[ \frac{1}{(15\kappa_4 - 18\kappa_3)} y^3 \right] (1 - y)^{-4} \left\{ y^{-1} + 2\kappa_1 y^0 + 3\kappa_2 y - (20\kappa_4 - 24\kappa_3) y^2 \right\} (1 - y)^{-3} + \left( 3y^0 + 3 \kappa_1 y + 3 \kappa_2 y^2 \right) \]

where, \( v^* / v = y \), \( \kappa_1 = 3\alpha - 2 \); \( \kappa_2 = 3\alpha^2 - 3\alpha + 1 \); \( \kappa_3 = \alpha^2 \), and \( \kappa_4 = \alpha \).

2.4 Determination of van der Waals parameter \( b \):

The parameter \( v^* \) or \( \beta_v \) is calculated by using the third constraint, \( \frac{\partial^2 P}{\partial v^2} = 0 \), we have,

From ISPT EoS,
\[ \kappa_3 y^5 - 5\kappa_3 y^4 + \kappa_5 y^3 + \kappa_6 y^2 + 5y - 1 = 0 \]
\[ \kappa_5 = 9\alpha^2 + 18\alpha - 7 ; \kappa_3 = \alpha^2 ; \kappa_6 = 19\alpha^2 - 18\alpha + 3 \]

From Nezbeda EoS,
\[ \kappa_7 y^5 + \kappa_8 y^4 + \kappa_9 y^3 + \kappa_{10} y^2 + 5y - 1 = 0 \]
\[ \kappa_7 = -4\alpha + 5\alpha^2 ; \kappa_8 = 20\alpha - 25\alpha^2 ; \]
\[ \kappa_9 = -2 + 68\alpha - 31\alpha^2 ; \kappa_{10} = -1 + 12\alpha + 3\alpha^2 \]

From Boublik EoS,
\[ \kappa_{11} y^5 + \kappa_{12} y^4 + \kappa_{13} y^3 + \kappa_{14} y^2 + 5y - 1 = 0 \]
\[ \kappa_{11} = -5\alpha + 6\alpha^2 ; \kappa_{12} = 25\alpha - 30\alpha^2 ; \kappa_{13} = (3 + 22\alpha^2) ; \]
\[ \kappa_{14} = -7 + 18\alpha + 9\alpha^2 \]

The calculated values of van der Waals parameter \( a, b \) or \( v^* \) are given in A7, Table A8 and Table A9. The values of third virial coefficients \( B_3 \) of linear tangent spheres have been taken from ref. [48]. Equations (14-16) have been used to calculate the nonsphericity parameter \( \alpha \) of hard convex body chain equation of state for three hard linear fluids and is given in Table B2. The \( a \) and \( b \) or \( v^* \) have been calculated using the expressions of ref. [22] and are tabulated in Table B1.

3. Critical properties calculations:
The critical properties calculations in three geometrical model of molecules are given in Tables (1-3) for HCB equations of state (ISPT, Boublik, Nezbeda) and Table 4 for HCB chain equations of state (R J Sadus), respectively.

| Table 1. Predictions of standard deviations of critical properties using ISP EoS in three configurations and their comparisons with existing predictions of EoFs [15]. |
|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| Mixture | \( N \) | \( T^c (K) \) | \( P^c (Mpa) \) | \( \xi \) |
| --- | --- | --- | --- | --- |
| Pentane+ | 5 | 0.3 | 0.3 | 0.10 | --- | 0.999 | 1.001 | 0.993 |
| Hexane | 5 | 0.4 | 0.11 | 1.001 | --- | --- | --- | --- |

| --- | --- | --- | --- | --- | --- | --- |
| HSP | HSP | HSP | HSP | --- | --- | --- |
| --- | --- | --- | --- | --- | --- | --- |
| Mixture       | N   | $T^c$ (K) | $P^c$ (Mpa) | $\xi$ |
|--------------|-----|----------|----------|-------|
|              |     | HLTS     | HCB      | Guggen Heim | HLTS | HCB | Guggen Heim | HLTS | HCB | Guggen Heim |
| Heptane      | 5   | 0.11     | 1.002    |        |       |     |     |       |       |       |     |
| Octane       | 6   | 0.12     | 0.998    |       |       |     |     |       |       |       |     |
| Nonane       | 9   | 0.11     | 0.998    |       |       |     |     |       |       |       |     |
| Decane       | 7   | 0.13     | 0.998    |       |       |     |     |       |       |       |     |
| Undecane     | 5   | 0.12     | 0.998    |       |       |     |     |       |       |       |     |
| Heptane+     | 9   | 0.11     | 0.997    |       |       |     |     |       |       |       |     |
| Octane+      | 9   | 0.12     | 0.998    |       |       |     |     |       |       |       |     |
| Nonane+      | 9   | 0.12     | 0.998    |       |       |     |     |       |       |       |     |
| Hexane+      | 5   | 4.9      | 0.997    |       |       |     |     |       |       |       |     |
| Heptane      | 9   | 0.12     | 0.998    |       |       |     |     |       |       |       |     |
| Octane       | 9   | 0.12     | 0.995    |       |       |     |     |       |       |       |     |
| Nonane       | 9   | 0.12     | 0.993    |       |       |     |     |       |       |       |     |
| Decane       | 9   | 0.12     | 0.997    |       |       |     |     |       |       |       |     |

(Tables and data are continued...)
| Mixture      | N  | \(T^* (K)\) | \(P^* (Mpa)\) | \(\xi\) |
|--------------|----|--------------|---------------|--------|
|              |    | HLTS         | HLTS          | HCB    |
|              |    | HE           | HE            | Guggen |
|              |    | HSP          | HSP           | Guggen |
| Tridecane    | 9  | 2.4          | 2.0           | 1.0    |
|              | 9  | 0.44         | 0.48          | 0.58   |
|              | 9  | 0.24         | 0.912         | 0.957  |
| Hexadecane   | 9  | 5.4          | 5.5           | 6.9    |
|              | 9  | 0.60         | 0.63          | 0.56   |
|              | 9  | 0.898        | 0.892         | 0.968  |
| Cyclohexane+ |    |              |               |        |
| Pentane      | 9  | 0.8          | 1.0           | 0.9    |
|              | 9  | 0.18         | 0.19          | 0.16   |
|              | 9  | 1.003        | 1.002         | 1.000  |
| Hexane       | 9  | 0.8          | 0.3           | 0.7    |
|              | 9  | 0.18         | 0.19          | 0.16   |
|              | 9  | 1.003        | 1.002         | 1.000  |
| Heptane      | 9  | 0.6          | 0.18          |        |
|              | 9  | 0.14         | 0.15          |        |
|              | 9  | 1.005        | 0.995         | 0.994  |
| Octane       | 9  | 0.2          | 0.18          |        |
|              | 9  | 0.14         | 0.15          |        |
|              | 9  | 1.007        | 1.002         | 1.000  |
| Nonane       | 9  | 0.8          | 0.3           | 0.6    |
|              | 9  | 0.24         | 0.23          | 0.25   |
|              | 9  | 0.984        | 0.988         | 1.008  |

Table 2. Predictions of standard deviations of critical properties using NezbedaEoS in three configurations and their comparisons with existing predictions of EoSs [15]

| Mixture      | N  | \(T^* (K)\) | \(P^* (Mpa)\) | \(\xi\) |
|--------------|----|--------------|---------------|--------|
|              |    | HLTS         | HLTS          | HCB    |
|              |    | HE           | HE            | Guggen |
|              |    | HSP          | HSP           | Guggen |
| Pentane+     |    |              |               |        |
| Hexane       | 5  | 0.4          | 0.3           | 0.3    |
|              | 5  | 0.11         | ---           | ---    |
|              | 5  | 1.002        | 1.002         | 1.002  |
| Heptane      | 3  | 0.2          | 0.2           | 0.4    |
|              | 3  | 0.18         | 0.24          | 0.19   |
|              | 3  | 0.999        | 0.999         | 0.988  |
| Octane       | 6  | 0.8          | 1.1           | 0.7    |
|              | 6  | 0.12         | 0.13          |        |
|              | 6  | 0.999        | 0.999         | 0.988  |
| Nonane       | 9  | 0.7          | 0.6           | 0.8    |
|              | 9  | 0.09         | 0.31          | 0.24   |
|              | 9  | 1.012        | 1.014         | 0.996  |
| Decane       | 7  | 1.9          | 2.2           | 2.3    |
|              | 7  | 0.15         | ---           | ---    |
|              | 7  | 1.012        | 1.019         | 0.999  |
| Undecane     | 7  | 2.0          | 2.4           | 2.6    |
|              | 7  | 0.17         | ---           | ---    |
|              | 7  | 1.004        | 1.015         | 0.992  |
| Dodecane     | 6  | 3.4          | 3.6           | 4.1    |
|              | 6  | 0.20         | ---           | ---    |
|              | 6  | 1.001        | 1.004         | 0.978  |
| Tridecane    | 5  | 5.6          | 5.7           | 5.7    |
|              | 5  | 0.19         | ---           | ---    |
|              | 5  | 0.989        | 0.988         | 0.963  |
| Mixture       | $N$ | $T^c (K)$ | $P^c (Mpa)$ | $\xi$ |
|--------------|-----|-----------|------------|-------|
|               | HLTS | HLTS | HCB | Guggen | HLTS | HLTS | HLTS | HCB | Guggen |
|               | HE   | HE   | heim | HE     | HE   | HE   | heim |     |       |
| 5             | 5.7  | 0.18   | 0.987  |
| 5             | 5.8  | 0.18   | 0.988  |
| Hexane+       | Heptane | 9    | 0.1  | 0.4  | 0.12 | 0.12 | 0.10 | 1.003 | 1.001 | 0.994 |
|               | 9    | 0.2   | 0.13 | 1.004 |
|               | 9    | 0.3   | 0.13 | 0.998 |
| Octane       | 9    | 0.2   | 0.12 | 1.001 |
|               | 9    | 0.2   | 0.11 | 1.002 |
| Hexane+       | Heptane | 9    | 0.2  | 0.4  | 0.08 | 0.09 | 0.07 | 0.998 | 1.001 | 0.995 |
|               | 9    | 0.2   | 0.09 | 0.999 |
|               | 9    | 0.3   | 0.08 | 0.997 |
| Benzene+      | Pentane | 5    | 4.9  | 4.7  | 4.7  | ---  | ---  | ---  | 0.994 | 0.993 | 0.981 |
|               | 5    | 4.8   |       |       |       |       |       |       | 0.985 |
|               | 5    | 4.9   |       |       |       |       |       |       | 0.995 |
| Hexane       | 9    | 0.3   | 0.3  | 0.4  | 0.17 | 0.17 | 0.18 | 0.982 | 0.982 | 0.980 |
|               | 9    | 0.4   | 0.18 | 1.001 |
|               | 9    | 0.4   | 0.18 | 0.987 |
| Heptane      | 9    | 0.4   | 0.1  | 0.5  | 0.13 | 0.12 | 0.16 | 0.969 | 0.968 | 0.975 |
|               | 9    | 0.3   | 0.15 | 0.977 |
|               | 9    | 0.3   | 0.15 | 0.972 |
| Octane       | 9    | 0.4   | 0.4  | 0.4  | 0.17 | 0.14 | 0.21 | 0.970 | 0.960 | 0.972 |
|               | 9    | 0.5   | 0.18 | 0.967 |
|               | 9    | 0.4   | 0.17 | 0.978 |
| Nonane       | 9    | 0.4   | 0.5  | 0.7  | 0.21 | 0.17 | 0.26 | 0.955 | 0.951 | 0.968 |
|               | 9    | 0.5   | 0.22 | 0.964 |
|               | 9    | 0.6   | 0.23 | 0.958 |
| Decane       | 9    | 0.8   | 0.8  | 0.7  | 0.30 | 0.26 | 0.36 | 0.949 | 0.941 | 0.963 |
|               | 9    | 0.7   | 0.31 | 0.955 |
|               | 9    | 0.6   | 0.32 | 0.961 |
| Tridecane    | 9    | 2.1   | 2.0  | 1.0  | 0.44 | 0.48 | 0.58 | 0.934 | 0.912 | 0.957 |
|               | 9    | 2.0   | 0.47 | 0.948 |
|               | 9    | 1.8   | 0.46 | 0.957 |
| Hexadecane   | 9    | 5.2   | 5.5  | 6.9  | 0.59 | 0.63 | 0.56 | 0.895 | 0.892 | 0.968 |
|               | 9    | 5.4   | 0.62 | 0.899 |
|               | 9    | 5.6   | 0.63 | 0.878 |
| Cyclohexane+  | Pentane | 9    | 0.9  | 1.0  | 0.9  | ---  | ---  | ---  | 1.022 | 1.023 | 1.010 |
|               | 9    | 0.8   |       |       |       |       |       |       | 1.018 |
|               | 9    | 0.8   |       |       |       |       |       |       | 1.021 |
| Hexane       | 9    | 0.7   | 0.3  | 0.7  | 0.17 | 0.19 | 0.16 | 1.003 | 1.002 | 1.000 |
|               | 9    | 0.6   | 0.16 | 1.005 |
| Heptane      | 9    | 0.7   | 0.2  | 0.3  | 0.15 | 0.15 | 0.16 | 0.994 | 0.995 | 0.994 |
|               | 9    | 0.4   | 0.14 | 0.996 |
|               | 9    | 0.3   | 0.15 | 0.995 |
| Octane       | 9    | 0.4   | 0.6  | 0.5  | 0.18 | 0.19 | 0.21 | 0.991 | 0.992 | 0.994 |
|               | 9    | 0.3   | 0.17 | 0.995 |
|               | 9    | 0.4   | 0.19 | 0.994 |
| Nonane       | 9    | 0.7   | 0.3  | 0.6  | 0.22 | 0.23 | 0.25 | 0.989 | 0.988 | 1.008 |
|               | 9    | 0.6   | 0.23 | 0.987 |
|               | 9    | 0.7   | 0.26 | 0.994 |
### Table 3. Predictions of standard deviations of critical properties using Boublík\(\LaTeX\) EqS in three configurations and their comparisons with existing predictions of EoSs [15].

| Mixture | N | \(T^c\) (K) | \(P^c\) (Mpa) | \(\xi\) |
|---------|---|-------------|---------------|------|
|         |   | HLTS        | HCB           | Guggenheim |
|         |   | HE          | HE            | HE               |
|         |   | HSP         | HSP           | HSP             |
| Pentane+|   |             |               |                  |
| Hexane  | 5 | 0.3         | 0.3           | 0.3             | 0.11 | --- | --- | 1.001 | 1.001 | 0.993 |
|         | 5 | 0.3         | 0.12          | 0.999          |      |
| Heptane | 3 | 0.2         | 0.2           | 0.4             | 0.16 | 0.24 | 0.19 | 0.999 | 0.999 | 0.988 |
|         | 3 | 0.2         | 0.17          | 0.997          |      |
| Octane  | 6 | 0.4         | 1.1           | 0.7             | 0.16 | --- | --- | 0.997 | 0.996 | 0.980 |
|         | 6 | 0.6         | 0.11          | 0.998          |      |
|         | 6 | 0.5         | 0.12          | 0.999          |      |
| Nonane  | 9 | 0.4         | 0.6           | 0.8             | 0.08 | 0.31 | 0.24 | 1.013 | 1.014 | 0.996 |
|         | 9 | 0.5         | 0.12          | 1.012          |      |
| Decane  | 7 | 2.1         | 2.2           | 2.3             | 0.16 | --- | --- | 1.012 | 1.019 | 0.999 |
|         | 7 | 1.7         | 0.17          | 1.011          |      |
|         | 7 | 1.8         | 0.12          | 1.014          |      |
| Undecane| 7 | 2.3         | 2.4           | 2.6             | 0.17 | --- | --- | 1.004 | 1.015 | 0.992 |
|         | 7 | 2.4         | 0.15          | 1.007          |      |
|         | 7 | 2.5         | 0.18          | 1.006          |      |
| Dodecane| 6 | 3.3         | 3.6           | 4.1             | 0.21 | --- | --- | 1.003 | 1.004 | 0.978 |
|         | 6 | 3.6         | 0.21          | 1.005          |      |
|         | 6 | 3.7         | 0.23          | 1.006          |      |
| Tridecane| 5 | 5.6         | 5.7           | 5.7             | 0.18 | --- | --- | 0.988 | 0.988 | 0.963 |
|         | 5 | 5.6         | 0.19          | 0.987          |      |
|         | 5 | 5.7         | 0.19          | 0.977          |      |
| Hexane+ |   |             |               |                  |
| Hexane  | 9 | 0.1         | 0.1           | 0.4             | 0.13 | 0.12 | 0.10 | 1.002 | 1.001 | 0.994 |
|         | 9 | 0.2         | 0.12          | 1.003          |      |
|         | 9 | 0.3         | 0.13          | 1.001          |      |
| Octane  | 9 | 0.2         | 0.2           | 0.4             | 0.13 | 0.14 | 0.11 | 1.002 | 1.005 | 0.996 |
|         | 9 | 0.3         | 0.11          | 1.004          |      |
|         | 9 | 0.2         | 0.12          | 1.002          |      |
| Heptane+|   |             |               |                  |
| Octane  | 9 | 0.1         | 0.1           | 0.4             | 0.08 | 0.09 | 0.07 | 0.997 | 1.001 | 0.995 |
|         | 9 | 0.4         | 0.09          | 0.999          |      |
|         | 9 | 0.3         | 0.07          | 0.996          |      |
| Benzene+|   |             |               |                  |
| Pentane | 5 | 4.8         | 4.7           | 4.7             | 0.17 | 0.17 | 0.18 | 0.983 | 0.982 | 0.980 |
|         | 5 | 5.1         |               | 0.989          |      |
|         | 5 | 4.9         |               | 0.986          |      |
| Hexane  | 9 | 0.3         | 0.3           | 0.4             | 0.17 | 0.17 | 0.18 | 0.983 | 0.982 | 0.980 |
|         | 9 | 0.4         | 0.19          | 0.989          |      |
|         | 9 | 0.5         | 0.18          | 0.983          |      |
| Heptane | 9 | 0.4         | 0.1           | 0.5             | 0.14 | 0.12 | 0.16 | 0.965 | 0.968 | 0.975 |
|         | 9 | 0.2         | 0.15          | 0.974          |      |
|         | 9 | 0.3         | 0.15          | 0.975          |      |
| Octane  | 9 | 0.3         | 0.4           | 0.4             | 0.19 | 0.14 | 0.21 | 0.962 | 0.960 | 0.972 |
|         | 9 | 0.3         | 0.20          | 0.971          |      |
|         | 9 | 0.4         | 0.17          | 0.968          |      |
| Nonane  | 9 | 0.6         | 0.5           | 0.7             | 0.18 | 0.17 | 0.26 | 0.964 | 0.951 | 0.968 |
|         | 9 | 0.5         | 0.22          | 0.964          |      |
|         | 9 | 0.7         | 0.23          | 0.958          |      |
| Decane  | 9 | 0.7         | 0.8           | 0.7             | 0.28 | 0.26 | 0.36 | 0.944 | 0.941 | 0.963 |
Table 4. Predictions of standard deviations using R J SadusEoS, in three configurations and their comparisons with existing predictions of EoSs [15].

| Mixture   | N   | \( T^c(K) \) | \( P^c(Mpa) \) | \( \xi \) |
|-----------|-----|--------------|----------------|---------|
|           |     | HE           | HE             | HE      | HE      | HE      | HE      | HE      |
| Hexane+   |     | HSP          | HSP            | HSP     | HSP     | HSP     | HSP     | HSP     |
| Octane    | 6   | 0.5          | 1.1             | 0.7     | 0.12    | 0.998   | 0.996   | 0.980   |
|           | 6   | 0.5          | 0.13            |         | 0.997   |         |         |         |
|           | 6   | 0.4          | 0.12            |         | 0.998   |         |         |         |
| Decane    | 7   | 2.2          | 2.2             | 2.3     | 0.15    | 1.013   | 1.019   | 0.999   |
|           | 7   | 2.4          | 0.14            |         | 10.14   |         |         |         |
|           | 7   | 2.4          | 0.16            |         | 1.013   |         |         |         |
| Dodecane  | 6   | 3.5          | 3.6             | 4.1     | 0.20    | 1.002   | 1.004   | 0.978   |
|           | 6   | 3.4          | 3.4             |         | 1.003   |         |         |         |
|           | 6   | 3.6          | 0.22            |         | 1.004   |         |         |         |
| Tetradecane | 5   | 5.7          | 5.7             | 5.7     | 0.19    | 0.989   | 0.988   | 0.963   |
|           | 5   | 5.6          | 0.18            |         | 0.976   |         |         |         |
|           | 5   | 5.7          | 0.19            |         | 0.873   |         |         |         |

4. Results and Discussion
The HCB and HCB chain equations of state with different HLTS models have been applied to calculate the critical properties of binary mixtures. The criteria used to compare the predicted and the experimental critical properties is the standard deviation (SD) given as

```plaintext
Mixture N T^c(K) P^c(Mpa) \xi

Hexane+
Octane 6 0.5 1.1 0.7 0.12 0.998 0.996 0.980
6 0.5 0.13 0.997
6 0.4 0.12 0.998
Decane 7 2.2 2.2 2.3 0.15 1.013 1.019 0.999
7 2.4 0.14 10.14
7 2.4 0.16 1.013
Dodecane 6 3.5 3.6 4.1 0.20 1.002 1.004 0.978
6 3.4 0.21 1.003
6 3.6 0.22 1.004
Tetradecane 5 5.7 5.7 5.7 0.19 0.989 0.988 0.963
5 5.6 0.18 0.976
5 5.7 0.19 0.873
```
\[ SD = \left[ \frac{1}{N} \sum (\text{exp. value} - \text{calc. value})^2 \right]^{0.5} \]

where \( N \) is the number of points in a given set of data.

The pure-component properties of the systems studied in this work are listed in Table A1. The values of standard deviations were obtained by adjusting \( \xi \) in equation (8) to optimize the agreement between experimental and theoretical critical temperatures. Values of \( \xi \) are given in Table 1-4. The three molecular models used either for HCB equations of state or HCB chain equation of state can predict accurately the critical properties of binary mixtures. While analyzing the predicted results of critical properties of binary mixtures it is found that in many cases the disagreement is only because of experimental error. While only a few cases results differ with the experimental values. If the mixture considered are of different sizes compounds then the probability of error in the two prescriptions \( a \) and \( \gamma^* \) are somewhat evident. An anomalous appearance of some of the calculated critical properties require performing the experiment again in order to confirm. Tables 1-3 represent SD of temperatures, pressures and adjustable parameters of different mixtures using the van der Waals one fluid mixing rule or the classical mixing rule. In Table 1, for pentane + hydrocarbon mixtures representing any of the three molecular models: the average value of the standard deviations for critical temperature were found to be 2.163K (with a maximum of about 6K) for the HLTS model, 1.887K (with a maximum of about 6K) for the HEs model, and 1.9K (with a maximum of about 6K) for the HSPs model, respectively. For HCB and Guggenheim EoSs, the average value of standard deviations for critical temperature were found to be 2.013K (with a maximum of 6K) and 2.112K (with a maximum of 6K), respectively. The average value of the standard deviations of critical pressure were found to be 0.15Mpa (with a maximum of about 0.2Mpa) for the HLTS model, 0.15Mpa with a maximum of about 0.21Mpa for the HEs model, and 0.149Mpa with a maximum of about 0.22Mpa for the HSP model, respectively. For HCB and Guggenheim EoSs, the average value of standard deviations for critical pressure were found to be 0.275Mpa (with a maximum of 0.3Mpa) and 0.21Mpa (with a maximum of 0.25Mpa), respectively. In the same Table 1, for benzene + hydrocarbon mixtures representing any of the three molecular models: the average value of the standard deviations for critical temperature were found to be 1.925K (with a maximum of about 5.5K) for the HLTS model, 1.925K (with a maximum of about 5.5K) for the HEs model, and 1.875K (with a maximum of about 5.5K) for the HSPs model, respectively. For HCB and Guggenheim EoSs, the average value of standard deviations for critical temperature were found to be 1.788K (with a maximum of about 5K) and 1.913K (with a maximum of about 5K), respectively. The average value of the standard deviations for critical pressure were found to be 0.267Mpa (with a maximum of about 0.6Mpa) for the HLTS model, 0.283Mpa (with a maximum of about 0.6Mpa) for the HEs model, and 0.28Mpa (with a maximum of 0.6Mpa) for the HSPs model, respectively. For HCB and Guggenheim EoSs, the average value of standard deviations for critical pressure were found to be 0.281Mpa (with a maximum of 0.6 Mpa) and 0.33Mpa (with a maximum of 0.6Mpa), respectively. In the same way the average value of standard deviations for critical temperature and critical pressure can also be estimated for all the hydrocarbon binary mixtures in the considered molecular models and equations of state used in this work. The values can be estimated by the tabulated standard deviations critical properties data in Table 2, Table 3.

Table 4 represents SD of temperatures, pressures and adjustable parameters of different hydrocarbon mixtures for hard convex body chain model of molecules. In Table 4, for hexane + hydrocarbon mixtures representing any of the three molecular models: the average value of the standard deviations for critical temperature were found to be 2.975K (with a maximum of about 6K) for HLTS model, 2.975K (with a maximum of about 6K) for the HEs model, and 3.025K (with a maximum of about 6K) for the HSPs model, respectively. The average value of the standard deviations for critical pressure were found to be 0.164Mpa (with a maximum of about 0.2Mpa) for the HLTS model, 0.165Mpa (with a maximum of about 0.21Mpa) for the HEs model, and 0.172 Mpa (with a maximum of about 0.22Mpa) for the HSP model, respectively. For HCB and Guggenheim EoSs, the average
value of standard deviations for critical temperature were found to be 3.15K (with a maximum of 6K) and 3.2K (with a maximum of 6K), respectively.

The average absolute difference in $\xi$ values of pentane + hydrocarbons and benzene + hydrocarbon mixtures when compared from any of the three molecular models to Guggenheim EoS is found to be less than 0.02. It is also observed that there is uncertainty in average absolute difference of $\xi$ values for cyclohexane + alkane mixtures. In spite of the above observations the molecular shape appears to have a little influence on the critical properties.

It is ultimately concluded that there should be a considerable difference in the obtained values of the adjustable parameter $\xi$ from these equations of state. Nevertheless, the obtained $\xi$ values from all these equations of state for the binary mixtures are in good agreement. Christoforakas and Franck [47] concluded that by incorporating molecular shape in the EoS does not remarkably influence the characteristic of predicted critical properties. Mainwaring et. al [17] had also found that an EoS incorporating shape factor does not yield remarkably good prediction of critical properties of binary mixtures as compared to Guggenheim EoS. Therefore, it is clear that the results of critical properties of binary mixtures of any of the linear hard body fluids with the influence of molecular shape do not show noticeable improvement in the predicted result. We know by experience that the $\xi$ values associated with the equations of state cannot influence much in improving the agreement between theory and experiment. Thus, it does not satisfactorily contribute to match the theory with experiment.

Though, the fitting of adjustable parameter to experiment is a best practice in quantifying the interactions between molecules albeit it indicates the inadequacy of the existing combining rules. Thus, both the best combining rules along with the best-fit adjustable parameter is needed to predict the results with the best-close expectancy with the experiment.

5. Conclusions
In this work, critical properties of several binary mixtures have been calculated by using different equations of state. The molecular models were evaluated to yield improved results of the critical properties of binary mixtures. The important conclusion of this work can be a suggestion to seek a best combining rule instead of only developing the most reliable equations of state.

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APPENDICES

Appendix A

Table A1. Input data and determined molecular parameters of the pure fluids in their critical state treated as hard convex bodies (c.f. text). Here, for the given alkanes the values of $S_0$ and $V_0$ is zero (after [15]).

| Compounds | $R_0 \times 10^7$ (nm) | $S_0 \times 10^5$ (nm²) | $V_0 \times 10^5$ (nm³) | $\nu^* \times 10^6$ (m³mol⁻¹) | $T^*$ (K) | $c \times 10^7$ (nm) |
|-----------|------------------------|-------------------------|-------------------------|-------------------------------|----------|---------------------|
| Pentane   | 15.80382               | 0                       | 0                       | 304                           | 469.7    | 3.16081             |
| Hexane    | 18.28388               | 0                       | 0                       | 370                           | 507.5    | 3.25782             |
| Heptane   | 19.79991               | 0                       | 0                       | 432                           | 540.3    | 3.38656             |
| Octane    | 21.45170               | 0                       | 0                       | 492                           | 568.68   | 3.47566             |
| Nonane    | 22.49752               | 0                       | 0                       | 552                           | 594.6    | 3.59951             |
| Decane    | 23.72058               | 0                       | 0                       | 612                           | 617.7    | 3.68784             |
| Undecane  | 24.88136               | 0                       | 0                       | 672                           | 638.2    | 3.77349             |
| Dodecane  | 25.97924               | 0                       | 0                       | 732                           | 658.2    | 3.85416             |
| Tridecane | 27.03285               | 0                       | 0                       | 792                           | 676      | 3.92972             |
| Hexadecane| 29.95892               | 0                       | 0                       | 972                           | 722      | 4.13286             |
| Benzene   | 18.43527               | 21.30711                | 4.3753                  | 259                           | 562.2    | 2.08255             |
| Cyclohexane| 14.13999              | 13.23499                | 2.73687                 | 260                           | 511.7    | 2.63021             |

Table A2. The $\kappa$ coefficients of the equations (2-4)

| Compounds | $\kappa_1$ | $\kappa_2$ | $\kappa_3$ |
|-----------|------------|------------|------------|
| ISPT      | $3\alpha - 2$ | $3\alpha^2 - 3\alpha + 1$ | $-\alpha^2$ |
| Nezbeda   | $3\alpha - 2$ | $\alpha^2 + \alpha - 1$ | $-\alpha(5\alpha - 4)$ |
| Boublik   | $3\alpha - 2$ | $3\alpha^2 - 3\alpha + 1$ | $-\alpha(6\alpha - 5)$ |

Table A3. Calculations of Third Virial Coefficients from equation (12)

| Compounds | $R^* \times 10^7$ (nm) | $S^* \times 10^5$ (nm²) | $V^* \times 10^5$ (nm³) | $\alpha = \frac{R^* S^*}{3V^*}$ | $B_3$ ISPT | $B_3$ Nezbeda | $B_3$ Boublik |
|-----------|------------------------|-------------------------|-------------------------|---------------------------------|------------|---------------|---------------|
| Pentane   | 2.83803                | 81.33965                | 56.00749                | 1.37389                         | 14.9061    | 14.6265       | 14.9061       |
| Hexane    | 3.08390                | 92.90855                | 66.61772                | 1.43365                         | 15.7680    | 15.3919       | 15.7680       |
| Heptane   | 3.26891                | 103.0839                | 77.10671                | 1.45673                         | 16.1066    | 15.6894       | 16.1066       |
| Octane    | 3.44940                | 112.5099                | 86.76949                | 1.48895                         | 16.5846    | 16.1065       | 16.5846       |
| Nonane    | 3.58805                | 121.5036                | 97.04800                | 1.49741                         | 16.7112    | 16.2163       | 16.7112       |
| Decane    | 3.73154                | 130.2039                | 1.6.9122                | 1.51483                         | 16.9731    | 16.4430       | 16.9731       |
| Undecane  | 3.86674                | 138.6234                | 116.7066                | 1.53096                         | 17.2173    | 16.6534       | 17.2173       |
| Dodecane  | 3.99444                | 146.7951                | 126.4545                | 1.54565                         | 17.4410    | 16.8455       | 17.4410       |
| Tridecane | 4.11607                | 154.7462                | 136.1399                | 1.55954                         | 17.6537    | 17.0276       | 17.6537       |
| Hexadecane| 4.45049                | 177.4761                | 164.8902                | 1.59673                         | 18.2290    | 17.5168       | 18.2290       |
| Benzene   | 2.50990                | 73.36629                | 51.31348                | 1.19619                         | 12.4698    | 12.3928       | 12.4698       |
| Cyclohexane| 2.59015               | 81.11383                | 63.66510                | 1.10001                         | 11.2301    | 11.2101       | 11.2301       |
### Table A4. Calculation of nonsphericity \( \alpha \) for Hard Linearly Tangent Spheres (HLTS)

| Hard Linearly Tangent spheres | Nonsphericity \( \alpha \) | ISPT / EoS | NezbedaEoS | Boublik / EoS |
|-------------------------------|--------------------------|-----------|-----------|-------------|
| Pentane                       | 1.33558                  | 1.31689   | 1.33558   |
| Hexane                        | 1.39286                  | 1.36792   | 1.39286   |
| Heptane                       | 1.41524                  | 1.38766   | 1.41524   |
| Octane                        | 1.44671                  | 1.41523   | 1.44671   |
| Nonane                        | 1.45502                  | 1.42247   | 1.45502   |
| Decane                        | 1.47218                  | 1.43740   | 1.47218   |
| Undecane                      | 1.48814                  | 1.451228  | 1.48814   |
| Dodecane                      | 1.50273                  | 1.46382   | 1.50273   |
| Tridecane                     | 1.51658                  | 1.47574   | 1.51658   |
| Hexadecane                    | 1.55390                  | 1.50767   | 1.55390   |
| Benzene                       | 1.17102                  | 1.16575   | 1.17102   |
| Cyclohexane                   | 1.08572                  | 1.08434   | 1.08572   |

### Table A5. Calculations of nonsphericity \( \alpha \) for Hard Ellipsoidal (HE)

| Hard Ellipsoidal Compounds    | Nonsphericity \( \alpha \) | ISPT EoS | NezbedaEoS | Boublik EoS |
|-------------------------------|--------------------------|-----------|-----------|-------------|
| Pentane                       | 1.37994                  | 1.31689   | 1.37994   |
| Hexane                        | 1.44080                  | 1.36792   | 1.44080   |
| Heptane                       | 1.46432                  | 1.38766   | 1.46432   |
| Octane                        | 1.49715                  | 1.41523   | 1.49715   |
| Nonane                        | 1.50577                  | 1.42247   | 1.50577   |
| Decane                        | 1.52353                  | 1.43740   | 1.52353   |
| Undecane                      | 1.53997                  | 1.45122   | 1.53997   |
| Dodecane                      | 1.55495                  | 1.46382   | 1.55495   |
| Tridecane                     | 1.56912                  | 1.47574   | 1.56912   |
| Hexadecane                    | 1.60705                  | 1.50767   | 1.60705   |
| Benzene                       | 1.20542                  | 1.19918   | 1.20542   |
| Cyclohexane                   | 1.10314                  | 1.10148   | 1.10314   |

### Table A6. Calculations of nonsphericity \( \alpha \) for Hard Spherocylinders (HSPs)

| Hard Spherocylinders          | Nonsphericity \( \alpha \) | ISPT EoS | NezbedaEoS | Boublik EoS |
|-------------------------------|--------------------------|-----------|-----------|-------------|
| Pentane                       | 1.39517                  | 1.37715   | 1.39517   |
| Hexane                        | 1.42246                  | 1.43318   | 1.42246   |
| Heptane                       | 1.48874                  | 1.45635   | 1.48874   |
| Octane                        | 1.52567                  | 1.53506   | 1.52567   |
| Nonane                        | 1.53542                  | 1.49723   | 1.53542   |
| Decane                        | 1.55556                  | 1.51475   | 1.55556   |
| Undecane                      | 1.57428                  | 1.53097   | 1.57428   |
| Dodecane                      | 1.59140                  | 1.54575   | 1.59140   |
| Tridecane                     | 1.60764                  | 1.55974   | 1.60764   |
| Hexadecane                    | 1.65138                  | 1.59719   | 1.65138   |
| Benzene                       | 1.20161                  | 1.19541   | 1.20161   |
| Cyclohexane                   | 1.10112                  | 1.09948   | 1.10112   |
### Table A7. Calculations of $a$ and $b$ or $v^*$ for Hard Linearly Tangent Spheres (HLTS)

|          | ISPT EoS [from Eq.(2)] | Nezbeda EoS [from Eq.(3)] | Boulik EoS [from Eq.(4)] | ISPT EoS [from Eq.(2)] | Nezbeda EoS [from Eq.(3)] | Boulik EoS [from Eq.(4)] |
|----------|------------------------|---------------------------|--------------------------|------------------------|---------------------------|--------------------------|
| Pentane  | 33.36696               | 39.28563                  | 34.20750                 | 1.663038               | 1.930149                  | 1.704412                 |
| Hexane   | 39.72748               | 47.24591                  | 40.70961                 | 2.200478               | 2.568440                  | 2.254223                 |
| Heptane  | 46.00080               | 54.91129                  | 47.12411                 | 2.741988               | 3.206813                  | 2.808152                 |
| Octane   | 51.78894               | 62.14322                  | 53.03220                 | 3.298016               | 3.867382                  | 3.376271                 |
| Nonane   | 57.92955               | 69.60650                  | 59.31403                 | 3.872285               | 4.534884                  | 3.963763                 |
| Decane   | 63.82948               | 76.91117                  | 65.34106                 | 4.468045               | 5.250274                  | 4.572649                 |
| Undecane | 69.68748               | 84.18787                  | 71.32391                 | 5.077345               | 5.973784                  | 5.195228                 |
| Dodecane | 75.51632               | 91.44501                  | 77.27609                 | 5.712585               | 6.728770                  | 5.844220                 |
| Tridecane| 81.30684               | 98.67651                  | 83.32067                 | 6.369646               | 7.496562                  | 6.502408                 |
| Hexadecane| 84.31388              | 120.24540                 | 100.72663                | 7.255201               | 8.989119                  | 8.551652                 |
| Benzene  | 30.35251               | 34.77069                  | 31.20650                 | 1.661449               | 1.896320                  | 1.704412                 |
| Cyclohexane| 37.43697             | 42.18126                  | 38.54953                 | 1.922900               | 2.166662                  | 1.979176                 |

### Table A8. Calculations of $a$ and $b$ or $v^*$ for Hard Ellipsoidal (HE)

|          | ISPT EoS [from Eq.(2)] | Nezbeda EoS [from Eq.(3)] | Boulik EoS [from Eq.(4)] | ISPT EoS [from Eq.(2)] | Nezbeda EoS [from Eq.(3)] | Boulik EoS [from Eq.(4)] |
|----------|------------------------|---------------------------|--------------------------|------------------------|---------------------------|--------------------------|
| Pentane  | 33.32714               | 38.92184                  | 32.52716                 | 1.715734               | 1.970252                  | 1.675031                 |
| Hexane   | 39.52798               | 46.78894                  | 38.61277                 | 2.270960               | 2.630130                  | 2.219966                 |
| Heptane  | 45.69893               | 54.37442                  | 44.65529                 | 2.829800               | 3.288002                  | 2.768883                 |
| Octane   | 51.34044               | 61.52956                  | 50.19007                 | 3.403586               | 3.971811                  | 3.328139                 |
| Nonane   | 57.39658               | 68.91799                  | 56.11688                 | 3.996216               | 4.668658                  | 3.908064                 |
| Decane   | 63.17201               | 76.14841                  | 61.77872                 | 4.610987               | 5.399342                  | 4.510291                 |
| Undecane | 68.89966               | 83.35214                  | 72.73722                 | 5.239710               | 6.148549                  | 5.126343                 |
| Dodecane | 74.59437               | 90.53724                  | 72.89728                 | 5.895187               | 6.930930                  | 5.768699                 |
| Tridecane| 80.24602               | 97.69784                  | 78.52020                 | 6.560064               | 7.726430                  | 6.420416                 |
| Hexadecane| 96.97177               | 119.06095                 | 94.39107                 | 8.631092               | 10.21320                  | 8.451218                 |
| Benzene  | 30.74724               | 34.49887                  | 29.92255                 | 1.714206               | 1.941609                  | 1.668447                 |
| Cyclohexane| 38.24524             | 42.00035                  | 37.13548                 | 1.983351               | 2.178100                  | 1.927559                 |
Table A9. Calculations of a and b or \( v^* \) for Hard Spherocylinders (HSPs)

| Compound | ISPT EoS [ from Eq.(2)] | Nezbeda EoS [ from Eq.(3)] | Boublik EoS [ from Eq.(4)] | ISPT EoS [ from Eq.(2)] | Nezbeda EoS [ from Eq.(3)] | Boublik EoS [ from Eq.(4)] |
|----------|------------------------|----------------------------|---------------------------|------------------------|----------------------------|---------------------------|
| Pentane  | 33.41806               | 38.94434                  | 32.61285                  | 1.7145543              | 1.968870                  | 1.673726                  |
| Hexane   | 39.64700               | 46.86047                  | 38.72517                  | 2.2692575              | 2.625278                  | 2.217086                  |
| Heptane  | 45.84092               | 54.46027                  | 44.78949                  | 2.8276208              | 3.281579                  | 2.763479                  |
| Octane   | 51.50676               | 61.08269                  | 50.34745                  | 3.4008708              | 4.006757                  | 3.325147                  |
| Nonane   | 57.58440               | 69.03210                  | 56.29466                  | 3.9930017              | 4.659375                  | 3.904524                  |
| Decane   | 63.38275               | 76.27687                  | 61.97739                  | 4.6072195              | 5.388419                  | 4.506153                  |
| Undecane | 69.13371               | 83.49500                  | 67.61503                  | 5.2353647              | 6.135928                  | 5.121557                  |
| Dodecane | 74.85165               | 90.69480                  | 73.22117                  | 5.8902396              | 6.916503                  | 5.763257                  |
| Tridecane| 80.52644               | 97.86999                  | 87.81623                  | 6.5545008              | 7.710165                  | 6.414301                  |
| Hexadecane| 97.34062              | 119.27753                 | 95.28095                  | 8.6231895              | 10.19108                  | 8.442542                  |
| Benzene  | 30.79820               | 34.52910                  | 29.97024                  | 1.7134649              | 1.912560                  | 1.846672                  |
| Cyclohexane| 38.28024              | 42.02130                  | 37.18610                  | 1.9829609              | 2.112155                  | 1.927108                  |

Appendix B

Table B1. Calculations of a and b or \( v^* \) for HCB Chains [equation(5)]

| Compound   | m | \( v^* \times 10^{-6} \) (m³mol⁻¹) | a (Pa m⁶mol⁻²) |
|------------|---|-------------------------------|----------------|
| Hexane     | 3 | 18.371098                      | 3.712277       |
| Octane     | 4 | 17.955759                      | 3.751434       |
| Decane     | 5 | 17.093537                      | 3.865816       |
| Dodecane   | 6 | 16.376777                      | 4.755120       |
| Tetradecane| 7 | 15.247984                      | 5.37271        |

Table B2. The values of the parameters of HCB Chain equations (5) and \( B_3 \) from (12) [48].

| Compound   | \( B_3 \) | \( m \) | \( S_R \) > \frac{3\alpha + 1}{2.5(1 - 1/m)} | Non-sphericity \( \alpha \) | Nonsphericity \( \alpha \) |
|------------|-----------|--------|----------------------------------|----------------|------------------|
| Hexane     | 24.28     | 3      | 3.2                              | 1.935175       | 2.121555         |
| Octane     | 32.36     | 4      | 3.0                              | 2.415975       | 2.674940         |
| Decane     | 40.66     | 5      | 2.8                              | 2.881445       | 3.215426         |
| Undecane   | 49.49     | 6      | 2.71                             | 3.350023       | 3.755957         |
| Tetradecane| 58.47     | 7      | 2.69                             | 3.802572       | 4.275161         |