

# A New Hard Sphere Cubic Equation of State for Predicting Fluids' Properties and Vapor-Liquid Phase Equilibrium Calculations

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In this study, a new cubic hard sphere equation of state (EOS) was developed from standard classical thermodynamics. The new equation is applied to calculate properties of fluids and vapor-liquid phase equilibrium calculations. The derived equation is a simplified expression of the hard sphere equation which yields satisfactory agreement with the molecular simulation of hard molecule data. The EOS is written in a cubic form by combining the derived repulsive hard spheres with Redlich-Kwong (RK) empirical attractive term. Satisfactory calculated results for the saturated properties of pure fluids for temperature ranges from 303 to 523 K and pressure ranges from 50 to 5000 psi are obtained. Simplicity and generality of this equation combined with reasonable accuracy makes it a useable EOS for almost all areas of equipment design for separation processes and production operations including refinery and petroleum reservoir industries. The accuracy of the predicted properties from the developed EOS are greater than of other commonly used two parameter cubic equations of state, RK and Peng-Robinson (PR).

**Keywords** equation of state, liquids, phase equilibrium, thermodynamics properties, vapor pressure

## 1. Introduction

An accurate equation of state (EOS) is a powerful tool for describing the thermodynamic properties of fluids in the equipment design for separation processes, and for petroleum, chemical and material processing industries. Equations of state have been utilized for the estimation of properties and phase equilibria of fluids. Numerous theoretical and semi-empirical equations of state have been reported in the literature. Among these equations, cubic equations of state draw more attention due to their simplicity and accuracy and are widely used in the petroleum, process design, and chemical industries.

The first cubic EOS consisting of a repulsive or unperturbed term and an attractive or perturbed term was the van der Waals (vdW)<sup>[1]</sup>:

$$Z = \frac{Pv}{RT} = \frac{v}{v-b} - \frac{a}{RTv} \quad (\text{Eq 1})$$

Many attempts have been made to modify the vdW equation to produce an EOS with greater accuracy while retaining the cubic form. Numerous different cubic equations of state

have been proposed to improve the attractive term of vdW equation for the computation thermodynamic properties and phase equilibria calculation. One of the most successful and well-known improvement of the vdW EOS is the two parameter empirical equation proposed by Redlich-Kwong (RK).<sup>[2]</sup> There have been numerous efforts to improve the RK EOS by modifying the volume function and by changing the alpha function of RK formulation, among these, Soave (SRK)<sup>[3]</sup> and Peng-Robinson (PR)<sup>[4]</sup> equations are two of the modifications of the RK equation in wide use due to their simplicity and generality as well as reasonable accuracy.

The major shortcoming of a vdW type EOS, as in the RK, SRK, and PR is the vdW excluded-volume expression for the repulsive term,  $Z_{\text{rep}} = v/(v-b)$ . This term is valid for a dilute gas but breaks down at high densities ( $v > 0.1$ ) and hence the predicted densities of the saturated liquids by the equations of state with the vdW repulsive term, differ considerably from experimental values.<sup>[5-9]</sup>

Although numerous equations of state have been published, investigations are in progress to develop a new EOS for all fluids in wide ranges of temperatures and pressures.<sup>[10-12]</sup> In the present work we have developed a cubic equation by replacing the repulsive term in the RK equation with a new hard sphere equation which is derived from standard classical thermodynamics. The applicability of the new equation for calculating and predicting vapor-liquid equilibrium and properties of real fluids is evaluated.

## 2. Theory and Formulation

The inaccurate volumetric prediction of vdW type equations of state may be improved by replacing the

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Nomenclature	
AAD	Average absolute deviation
BIAS	Bias
RMS	Root mean square
$a$	Attractive parameter
$b$	Repulsive parameter
$d$	Error
$f$	Fugacity
$K$	Boltzmann's constant
$m, n$	Constants in Eq 28 and 29
$n$	Number of points
$N$	Number of molecules
$P$	Pressure
$Q$	Partition function
$R$	Universal gas constant
$T$	Absolute temperature
$v$	Molar volume
$V$	Total volume
$Z$	Compressibility factor
Greeks	
$\alpha, \beta$	Dimensionless functions
$\varepsilon, \gamma, \lambda$	Constants in Eq 12
$\eta$	Packing fraction
$\rho$	Density
$\omega$	Acentric factor
Scripts	
att	Attraction
cal	Calculated property
exp	Experimental
rep	Repulsion
c	Critical property
f	Free
hs	Hard sphere
l	Liquid
r	Reduced property
tr	Translational
v	Vapor

repulsive forces of vdW with an exact and accurate hard sphere equation. Based on the concept of perturbation theory of statistical mechanics, semi-empirical equations of state express the compressibility factor as the sum of two terms as follows:<sup>[13-16]</sup>

$$Z = Z_{\text{rep}} + Z_{\text{att}} = \left(\frac{Pv}{RT}\right)_{\text{hs}} + \left(\frac{Pv}{RT}\right)_{\text{att}} \quad (\text{Eq 2})$$

where  $Z_{\text{rep}}$  and  $Z_{\text{att}}$  are repulsive and attractive terms, respectively. The repulsive compressibility factor is considered as the unperturbed term and expressed by the hard sphere equation and the attractive compressibility is the perturbed term in the perturbation theory.

## 2.1 Hard Sphere Compressibility Factor, $Z_{\text{hs}}$

Since the properties of hard spheres provide the theoretical basis for many equations of state for real fluids, but such a model also serves as a reference system in statistical mechanical theories of liquid such as in the perturbation approach where there has been considerable interest in developing more accurate hard-sphere equations to improve predictions at high density.<sup>[9]</sup> The justification for such work is that a highly accurate representation of hard-sphere interactions might improve the prediction of real fluids.

Several of the most common equations of state for hard sphere molecules as a function of packing factor,  $\eta = b/4v$ , obtained from the molecular dynamic calculations of hard-sphere fluids reported in the literature are listed in Table 1 and numerous reviews on hard sphere equations are available.<sup>[7,15,17,20,21]</sup> These equations can replace the repulsive term in the equations of state to increase the accuracy of the prediction of properties of fluids. However, these equations are rather complicated for practical use and by replacing the repulsive term of vdW type cubic EOS, the resulting equation is not going to be in the cubic EOS form.

In this study, we developed a simple form of an EOS for hard spheres. When this equation is combined with an appropriate and accurate attractive term, the results will be a cubic EOS.

The compressibility factor for hard spheres in Eq 2 is defined as:

$$Z_{\text{hs}} = \left(\frac{Pv}{RT}\right)_{\text{hs}} \quad (\text{Eq 3})$$

From the standard classical thermodynamics, the pressure contribution of hard sphere molecules is given by

$$P_{\text{hs}} = KT \left(\frac{\partial \ln Q_{\text{tr}}}{\partial V}\right)_{N,T} \quad (\text{Eq 4})$$

where the partition function due to translation of molecules of real fluids is:<sup>[21]</sup>

$$Q_{\text{tr}} = \frac{1}{N!} (V_f)^N \quad (\text{Eq 5})$$

**Table 1 Different form of hard sphere equations of state**

Author	Equation
Carnahan and Starling <sup>[15]</sup>	$Z = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3}$
Khoshkbarchi and Vera <sup>[17]</sup>	$Z = \frac{1-0.04\zeta-0.4\zeta^2-1.25\zeta^3+0.18\zeta^4+1.42\zeta^{12}}{(1-\zeta)^3}$ where $\zeta = \frac{\eta}{0.74}$
Percus et al. <sup>[18]</sup>	$Z = \frac{1+\eta+\eta^2}{(1-\eta)^3}$
Thiele <sup>[19]</sup>	$Z = \frac{1+\eta+\eta^2-3\eta^3}{(1-\eta)^3}$
Boublik <sup>[20]</sup>	$Z = \frac{1+\eta+\eta^2-\frac{2}{3}(\eta^3+\eta^4)}{(1-\eta)^3}$

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By inserting Eq 4 into Eq 3, then  $Z_{hs}$  follows

$$Z_{hs} = V \left[ \frac{\partial \ln \left( \frac{V_f}{V} \right)}{\partial V} \right]_{N,T} \quad (\text{Eq 6})$$

We define the following relation for the free volume of molecule  $V_f$ :

$$\frac{V_f}{V} = \left( \frac{V - nb}{V} \right)^m \quad (\text{Eq 7})$$

where  $n$  and  $m$  are constant parameters. From Eq 6 and Eq 7 the hard sphere EOS is:

$$Z_{hs} = \frac{v + (nm - n)b}{v - nb} \quad (\text{Eq 8})$$

Several hard sphere equations of state similar to Eq 8 are reported in the literature. None of the equations are accurate enough to replace  $Z_{hs}$  in a cubic EOS. Scott and Henderson<sup>[22]</sup> introduced the following equation for the repulsive term in pure fluid equations of state:

$$Z_{hs} = \frac{v + 0.5b}{v - 0.5b} \quad (\text{Eq 9})$$

Similarly, Kim et al.<sup>[23]</sup> proposed another equation for the repulsive term:

$$Z_{hs} = \frac{v + 0.77b}{v - 0.42b} \quad (\text{Eq 10})$$

Table 2 shows values of  $n$  and  $m$  for different hard sphere equations.

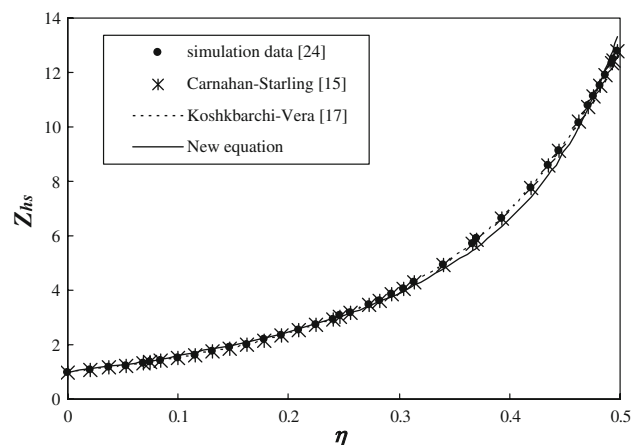
The values of  $n$  and  $m$  in Eq 8 are obtained by using molecular simulation for the hard sphere compressibility factor. New molecular simulation data are reported for the compressibility factors of hard spheres covering the isotropic liquid, meta-stable fluid, and solid ranges of density.<sup>[24]</sup> These data provide a comprehensive set of values for the development of hard-sphere equations of state. In particular, they represent a substantial increase in the data available at high isotropic liquid densities. By using these data and a genetic algorithm, the values of  $n = 0.401$  and  $m = 3.1246$  are obtained. Therefore, the new hard sphere EOS is:

$$Z_{hs} = \frac{v + 0.852b}{v - 0.401b} \quad (\text{Eq 11})$$

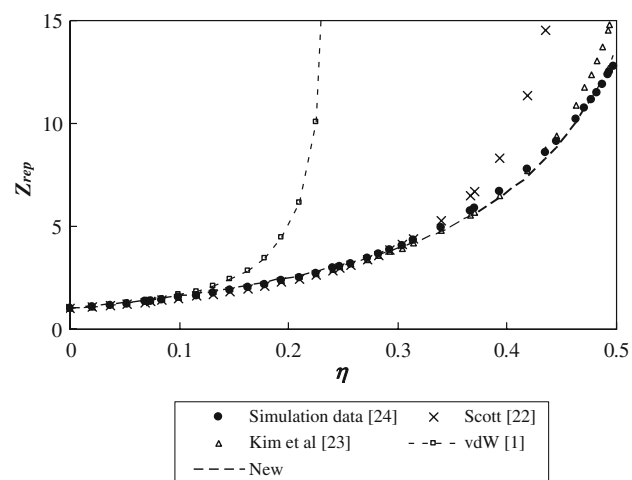
This EOS model is based on the molecular dynamic calculations of hard-sphere fluids and it is a simplified expression of the hard sphere equation which yields satisfactory agreement with the molecular simulation data

**Table 2 Value of constants in different repulsive term of EOS**

Equation of state	$m$	$n$
vdW type <sup>[1-4]</sup>	1	1
Scott and Henderson <sup>[22]</sup>	2	0.5
Kim et al. <sup>[23]</sup>	2.833	0.42
Equation 11	3.1246	0.401



**Fig. 1** Compressibility factors of hard-sphere as function of packing fraction



**Fig. 2** Comparison of repulsive term of equations of state

of hard sphere molecules. Figure 1 shows reproducing simulation data for several hard sphere equations. Comparison of this equation, Eq 11, with other similar forms of equations, reveals greater accuracy (Fig. 2) and closer agreement with simulation data. This equation predicts properties isotropic liquids and has proven to be the best analytical form in existence.

Equation 11 can replace  $Z_{hs} = (Pv/RT)_{hs}$  in Eq 2. Then an accurate attractive term is needed to be combined with Eq 11 to form a cubic EOS.

### 2.2 Attractive Term, $Z_{att}$

By including a suitable term for the attractive term in Eq 2 and combining with Eq 11 as the repulsive term, the total EOS can be formed. The general form of the attractive term is expressed as:

$$Z_{att} = \frac{av/RT}{T^\epsilon(v + \gamma b)(v + \lambda b)} \quad (\text{Eq 12})$$

where  $a$  can be considered as a measure of the intermolecular attraction force,  $b$  is related to size of the hard spheres, and  $\varepsilon$ ,  $\gamma$ ,  $\lambda$  are arbitrary values. This general form can be reduced to the attractive term of Redlich-Kwong EOS by selecting  $\varepsilon = 0.5$ ,  $\gamma = 1$ , and  $\lambda = 0$ .

Many modifications have been made in the literature to improve the attractive term of EOS. One of the most successful modifications was the two-parameter empirical equation proposed by Redlich and Kwong. In view of the remarkable success of the empirical Redlich-Kwong equation and due to the fact that using the attractive part of the PR equation, the total EOS will not be a cubic one, it may appear promising to use the form of the attractive part of the RK EOS:

$$Z_{\text{att}} = \frac{a}{RT^{1.5}(v+b)} \quad (\text{Eq 13})$$

### 2.3 Total Cubic Equation of State

Equations 11 and 13 are combined as the repulsive and attractive compressibility factors respectively in the manner of Eq 2 and the new two-constant cubic EOS is suggested as:

$$Z = \frac{v + 0.852b}{v - 0.401b} - \frac{a}{RT^{1.5}(v+b)} \quad (\text{Eq 14})$$

The simplicity of Eq 14 makes it very attractive. It contains only two parameters and remains a cubic equation in terms of volume.

The constants  $a$  and  $b$  of Eq 14 are related to critical properties of pure fluids by applying the two conditions at the critical point to Eq 14, the first and second derivations of pressure respect to volume be zero,

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = 0 \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = 0 \quad (\text{Eq 15})$$

Expressions for  $a$  and  $b$  at the critical point in terms of the critical properties are:

$$a(T_c) = 0.49281 \frac{R^2 T_c^{2.5}}{P_c} \quad (\text{Eq 16})$$

$$b(T_c) = 0.10577 \frac{RT_c}{P_c} \quad (\text{Eq 17})$$

$$Z_c = 0.312 \quad (\text{Eq 18})$$

The experimental values of hydrocarbon critical compressibility factors lie between 0.24 and 0.3.<sup>[25]</sup> The new EOS predicts the critical compressibility factor close to those realistic values.

At temperatures other than the critical,  $a$  and  $b$  are considered as a function of acentric factor and reduced temperature to improve the prediction of vapor pressures for pure substances while  $b$  is usually treated as temperature dependent. These parameters are related to volume and pressure of molecules and thus they play an effective role in

prediction of liquid densities and calculation phase behavior of heavy gas and liquid systems. In this paper, dimensionless scaling factors are used to describe the temperature dependence of  $a$  and  $b$  parameters which are:

$$a(T) = a(T_c)\alpha(T_r, \omega) \quad (\text{Eq 19})$$

$$b(T) = b(T_c)\beta(T_r, \omega) \quad (\text{Eq 20})$$

where  $\alpha(T_r, \omega)$  and  $\beta(T_r, \omega)$  are the dimensionless function of reduced temperature and acentric factor and equal unity at the critical temperature.

$$\alpha(T_r, \omega) = \beta(T_r, \omega) = 1 \quad @ \quad T_r = 1 \quad (\text{Eq 21})$$

Procedure for evaluating  $\alpha(T_r, \omega)$  and  $\beta(T_r, \omega)$  is described in vapor-liquid equilibrium (VLE) section.

Equation 14 with respect to compressibility factor  $Z$  is:

$$Z^3 + [0.599B - 1]Z^2 + [A - 1.852B - 0.401B^2]Z - [0.852B^2 + 0.401AB] = 0 \quad (\text{Eq 22})$$

where

$$A = \frac{aP}{R^2 T^{2.5}} \quad \text{and} \quad B = \frac{bP}{RT} \quad (\text{Eq 23})$$

### 2.4 Vapor Liquid Equilibrium (VLE) Calculation

For a pure substance at a given temperature, a single value of pressure exists which satisfies the equilibrium condition:

$$f^l = f^v \quad (\text{Eq 24})$$

where  $f^l$  and  $f^v$  are fugacity of a pure component at liquid and vapor phase equilibrium. The fugacity can be obtained from the thermodynamic relationship:

$$\ln\left(\frac{f}{P}\right) = \frac{1}{RT} \int_v^\infty \left(P - \frac{RT}{v}\right) dv - \ln Z + RT(Z - 1) \quad (\text{Eq 25})$$

Substituting Eq 14 into Eq 25 can be summarized as:

$$\ln\left(\frac{f}{P}\right) = Z - 1 - \ln Z - \left(\frac{1.253}{0.401}\right) \ln\left(1 - \frac{0.401B}{Z}\right) - \frac{A}{B} \ln\left(1 + \frac{B}{Z}\right) \quad (\text{Eq 26})$$

The compressibility factor ( $Z$ ) to be used in Eq 26 is the solution of Eq 22 which yields one or three roots depending upon the number of phases in the system. In the two phase region, the smallest positive root will be taken for the compressibility factor of the liquid phase while the largest one will be considered to that of the vapor phase.

For each value of  $\alpha(T_r, \omega)$  and  $\beta(T_r, \omega)$ , vapor pressure can be found by solving Eq 22 and Eq 26 by a trial and error method such that the equilibrium condition Eq 24 is satisfied. The right value of  $\alpha$  and  $\beta$  at each temperature was

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determined by using the literature vapor pressure and liquid density values,<sup>[26]</sup> such that the following objective function is minimized:

$$\Omega = \sum_{i=1}^n \left( w_P \frac{|P_{\text{cal},i}^v - P_{\text{exp},i}^v|}{P_{\text{exp},i}^v} \right) + w_d \left( \frac{|\rho_{\text{cal},i}^l - \rho_{\text{exp},i}^l|}{\rho_{\text{exp},i}^l} \right) \quad (\text{Eq 27})$$

where  $n$  is number of point,  $\rho^l$  is saturated liquid density,  $w_P = 0.8$  and  $w_d = 0.2$ .

The above procedure is applied to methane,  $n$ -pentane,  $n$ -heptane, and  $n$ -octane using vapor pressure and saturated liquid density data to the critical point and set of  $\alpha$  and  $\beta$  values are obtained for each substance and at each temperature. In order to obtain a relationship between  $\alpha$  and  $T_r$  also  $\beta$  and  $T_r$ , the values of  $\alpha_i(T)$  and  $\beta_i(T)$  are plotted against  $(1 - T_r^{2/3})$  and  $(1 - T_r)$ , respectively (Fig. 3 and 4).

Separate curves are obtained showing similar trends and they are fitted to following forms using least square method as all curves pass through the same point: ( $\alpha = \beta = T_r = 1$ ):

$$\alpha = m_1(1 - T_r^{2/3})^3 + m_2(1 - T_r^{2/3})^2 + m_3(1 - T_r^{2/3}) + 1 \quad (\text{Eq 28})$$

$$\beta = n_1(1 - T_r)^3 + n_2(1 - T_r)^2 + n_3(1 - T_r) + 1 \quad (\text{Eq 29})$$

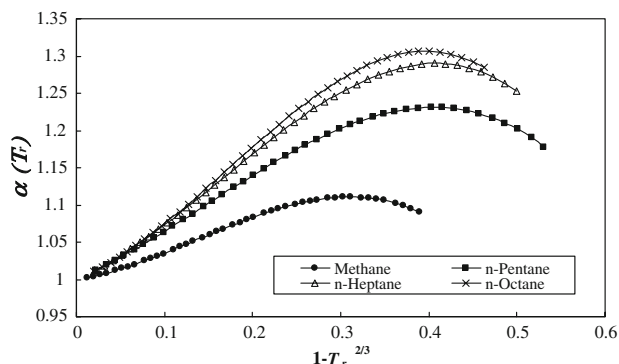


Fig. 3 Relationship between  $\alpha$  and reduced temperature

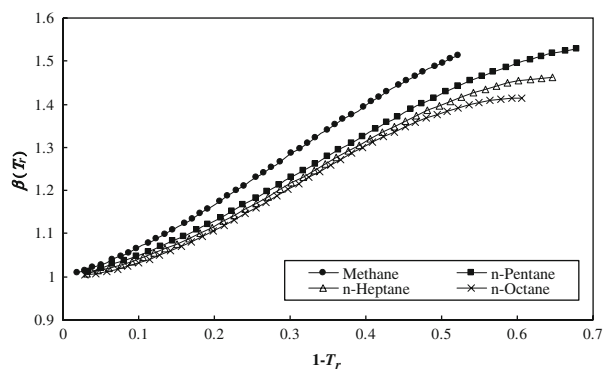


Fig. 4 Relationship between  $\beta$  and reduced temperature

where  $m_1, m_2, m_3, n_1, n_2,$  and  $n_3$  are constant characteristic of each component and therefore they are correlated against their acentric factors. The resulting equations which are calculated using least square method are as follows:

$$m_1 = -77\omega^2 + 28.169\omega - 5.8512 \quad (\text{Eq 30})$$

$$m_2 = 40.706\omega^2 - 13.548\omega + 2.4342 \quad (\text{Eq 31})$$

$$m_3 = -5.4358\omega^2 + 2.9646\omega + 0.1483 \quad (\text{Eq 32})$$

$$n_1 = -40.84\omega^2 + 14.82\omega - 3.0313 \quad (\text{Eq 33})$$

$$n_2 = 29.606\omega^2 - 10.216\omega - 2.6395 \quad (\text{Eq 34})$$

$$n_3 = -5.0725\omega^2 + 1.009\omega + 0.4334 \quad (\text{Eq 35})$$

## 3. Comparisons and Results

The validity of this model is demonstrated by comparing the model results to the experimental and calculated results for the most common pure hydrocarbons. Vapor pressures, saturated liquid, and vapor densities of a number of hydrocarbons are calculated and compared with experimental data. The comparison is intended to show that in engineering calculations, more accurate results can usually be obtained with the new equation than with the RK, SRK, and PR equations.

### 3.1 Vapor Pressures

To provide the objective quantitative measure of the relative accuracy of the new EOS, the average absolute deviation (AAD) is calculated based on following relation:

$$\text{AAD} = \frac{1}{n} \sum_{i=1}^n |d_i| \quad (\text{Eq 36})$$

where the  $d_i$  is the error (either absolute or relative) and  $n$  is the number of data points.

The summary of the prediction results of saturated vapor pressure of 23 pure substances by four equations of state is listed in Table 3.

The relative errors and the value of the grand average indicate the new EOS can predict the saturated vapor pressure more accurately than the RK, SRK, and PR equations.

### 3.2 Saturated Liquid Densities

Comparison of saturated liquid density prediction results for 24 pure substances by four equations of state is listed in Table 4-6 based on absolute and relative errors. In this case, the bias (BIAS) and the root mean square (RMS) are also calculated as following:

**Table 3 Comparison of vapor pressures (experimental data from<sup>[9]</sup>)**

Component	No. of data	Range of $T_r$	%AAD $P^v$			
			RK	SRK	PR	Eq 11
CH <sub>4</sub>	45	0.4776-0.9971	14.604	2.0383	0.6751	0.5606
C <sub>2</sub> H <sub>6</sub>	17	0.4912-0.9823	6.5662	1.5651	0.5133	0.3388
C <sub>3</sub> H <sub>8</sub>	43	0.2621-0.981	24.5452	2.0827	8.0675	1.6077
<i>n</i> -C <sub>4</sub> H <sub>10</sub>	13	0.5013-0.7601	51.1981	1.2371	0.9677	0.7547
<i>i</i> -C <sub>4</sub> H <sub>10</sub>	14	0.5223-0.9143	37.6403	1.3474	1.1355	1.1155
<i>n</i> -C <sub>5</sub> H <sub>12</sub>	42	0.3214-0.9663	103.4636	1.772	6.7789	1.0552
<i>i</i> -C <sub>5</sub> H <sub>12</sub>	29	0.3756-0.9831	63.8789	2.6719	4.2491	1.8536
<i>n</i> -C <sub>6</sub> H <sub>14</sub>	42	0.3624-0.9691	156.7558	2.6326	3.6816	1.7304
<i>n</i> -C <sub>7</sub> H <sub>16</sub>	42	0.3536-0.9682	291.1889	1.6297	6.2356	0.9163
<i>i</i> -C <sub>7</sub> H <sub>16</sub>	43	0.5147-0.9767	91.083	1.0067	1.0596	0.9967
<i>n</i> -C <sub>8</sub> H <sub>18</sub>	42	0.3938-0.9704	342.3332	1.2454	5.1349	0.9434
<i>n</i> -C <sub>9</sub> H <sub>20</sub>	18	0.4254-0.7110	683.8391	3.4387	7.7567	1.6059
<i>n</i> -C <sub>10</sub> H <sub>22</sub>	19	0.4250-0.7157	977.8057	4.5686	8.8708	2.7513
<i>n</i> -C <sub>12</sub> H <sub>26</sub>	22	0.4144-0.7330	2517.8	7.1608	15.58	4.002
<i>n</i> -C <sub>13</sub> H <sub>28</sub>	16	0.5067-0.7430	822.21	3.9523	3.4572	3.6146
<i>n</i> -C <sub>15</sub> H <sub>32</sub>	14	0.5818-0.7648	522.2	7.3607	1.7173	6.4501
<i>n</i> -C <sub>16</sub> H <sub>34</sub>	10	0.6387-0.7628	377.4	9.0438	4.4463	8.9482
<i>n</i> -C <sub>17</sub> H <sub>36</sub>	15	0.5892-0.7797	639.76	2.3071	5.7141	1.6049
<i>n</i> -C <sub>18</sub> H <sub>38</sub>	13	0.6041-0.7641	670.44	1.732	9.3726	3.2968
<i>n</i> -C <sub>19</sub> H <sub>40</sub>	12	0.6093-0.754	763.75	5.8329	14.872	7.8216
<i>n</i> -C <sub>20</sub> H <sub>42</sub>	11	0.6104-0.7394	784.14	15.174	5.5224	12.263
C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>	39	0.5285-0.9855	41.822	7.2726	5.9575	5.5196
H <sub>2</sub>	20	0.4514-0.9630	43.420	5.6170	3.81929	3.9313
Grand Avg.	581		435.99	4.03	5.433	3.2036

**Table 4 Comparison of saturated liquid densities based on absolute and relative AAD (experimental data from<sup>[9]</sup>)**

Component	No. of data	Range of $T_r$	AAD				% AAD			
			RK	SRK	PR	Eq 11	RK	SRK	PR	Eq 11
CH <sub>4</sub>	45	0.4776-0.9971	0.00091	0.00092	0.00215	0.00024	4.819	4.950	8.967	1.425
C <sub>2</sub> H <sub>6</sub>	17	0.4912-0.9823	0.00138	0.00126	0.00108	0.00036	9.492	8.671	6.648	2.816
C <sub>3</sub> H <sub>8</sub>	43	0.2621-0.981	0.00109	0.00095	0.00069	0.00015	9.187	7.941	5.376	1.491
<i>n</i> -C <sub>4</sub> H <sub>10</sub>	13	0.5013-0.7601	0.00096	0.00073	0.00052	0.00009	9.308	7.085	5.005	0.877
<i>i</i> -C <sub>4</sub> H <sub>10</sub>	14	0.5223-0.9143	0.00087	0.00066	0.00056	0.00015	9.090	6.862	5.629	1.536
<i>n</i> -C <sub>5</sub> H <sub>12</sub>	42	0.3214-0.9663	0.00110	0.00089	0.00020	0.00011	13.719	10.98	2.623	1.519
<i>i</i> -C <sub>5</sub> H <sub>12</sub>	29	0.3756-0.9831	0.00105	0.00085	0.00025	0.00014	13.652	11.065	3.491	2.140
<i>n</i> -C <sub>6</sub> H <sub>14</sub>	42	0.3624-0.9691	0.00108	0.00084	0.00014	0.00010	15.916	12.417	2.368	1.708
<i>n</i> -C <sub>7</sub> H <sub>16</sub>	42	0.3536-0.9682	0.00108	0.00085	0.00018	0.00008	18.177	14.225	3.215	1.634
<i>i</i> -C <sub>7</sub> H <sub>16</sub>	43	0.5147-0.9767	0.00097	0.00072	0.00014	0.00013	17.617	13.207	2.924	2.679
<i>n</i> -C <sub>8</sub> H <sub>18</sub>	42	0.3938-0.9704	0.00105	0.00081	0.00023	0.00007	20.166	15.567	4.700	1.706
<i>n</i> -C <sub>9</sub> H <sub>20</sub>	18	0.4254-0.7110	0.00103	0.00081	0.00024	0.00003	19.400	15.204	4.514	0.597
<i>n</i> -C <sub>10</sub> H <sub>22</sub>	19	0.4250-0.7157	0.00099	0.00078	0.00028	0.00004	20.802	16.26	5.728	0.902
<i>n</i> -C <sub>12</sub> H <sub>26</sub>	22	0.4144-0.7330	0.00097	0.00077	0.00037	0.00008	24.229	19.137	9.018	1.871
<i>n</i> -C <sub>13</sub> H <sub>28</sub>	16	0.5067-0.7430	0.00087	0.00065	0.00028	0.00005	24.350	18.177	7.820	1.496
<i>n</i> -C <sub>15</sub> H <sub>32</sub>	14	0.5818-0.7648	0.00079	0.00058	0.00027	0.00006	26.744	19.388	9.123	2.123
<i>n</i> -C <sub>16</sub> H <sub>34</sub>	10	0.6387-0.7628	0.00078	0.00056	0.00028	0.00006	28.570	20.615	10.46	2.460
<i>n</i> -C <sub>17</sub> H <sub>36</sub>	15	0.5892-0.7797	0.00080	0.00060	0.00035	0.00007	30.630	23.005	13.22	2.800
<i>n</i> -C <sub>18</sub> H <sub>38</sub>	13	0.6041-0.7641	0.00068	0.00049	0.00024	0.00009	27.830	19.704	9.53	3.991
<i>n</i> -C <sub>19</sub> H <sub>40</sub>	12	0.6093-0.754	0.00071	0.00053	0.00030	0.00006	30.553	22.597	12.82	2.442
<i>n</i> -C <sub>20</sub> H <sub>42</sub>	11	0.6104-0.7394	0.00077	0.00059	0.00039	0.00009	34.489	26.64	17.45	4.083

Table 4 continued

Component	No. of data	Range of $T_r$	AAD				% AAD			
			RK	SRK	PR	Eq 11	RK	SRK	PR	Eq 11
C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>	7	0.5285-0.5982	0.00098	0.00074	0.00082	0.00027	7.610	5.666	6.36	2.056
Ethanol	35	0.4494-0.9787	0.00406	0.00283	0.00135	0.00065	29.521	20.398	10.09	4.853
H <sub>2</sub>	21	0.4213-0.9630	0.00491	0.00300	0.00640	0.00097	14.273	8.899	18.75	3.034
Grand Avg.	585		0.00125	0.00093	0.00074	0.00017	19.17	14.53	7.74	2.18

Table 5 Comparison of saturated liquid densities based on absolute and relative BIAS (experimental data from <sup>[9]</sup>)

Component	No. of data	BIAS				% BIAS			
		RK	SRK	PR	Eq 11	RK	SRK	PR	Eq 11
CH <sub>4</sub>	45	-0.00068	-0.00092	0.00190	-0.00021	-4.00	-4.93	7.25	-1.27
C <sub>2</sub> H <sub>6</sub>	17	-0.00138	-0.00126	0.00067	-0.00036	-9.49	-8.67	3.13	-2.82
C <sub>3</sub> H <sub>8</sub>	43	-0.00109	-0.00095	0.00056	-0.00004	-9.19	-7.94	3.77	-0.64
<i>n</i> -C <sub>4</sub> H <sub>10</sub>	13	-0.00096	-0.00073	0.00052	0.00009	-9.31	-7.09	5.00	0.87
<i>i</i> -C <sub>4</sub> H <sub>10</sub>	14	-0.00087	-0.00066	0.00054	0.00012	-9.09	-6.86	5.34	1.15
<i>n</i> -C <sub>5</sub> H <sub>12</sub>	42	-0.00110	-0.00089	0.00007	-0.00005	-13.72	-10.98	0.44	-0.81
<i>i</i> -C <sub>5</sub> H <sub>12</sub>	29	-0.00105	-0.00085	0.00008	-0.00011	-13.65	-11.07	0.36	-1.73
<i>n</i> -C <sub>6</sub> H <sub>14</sub>	42	-0.00108	-0.00084	-0.00005	-0.00003	-15.92	-12.42	-1.15	-0.69
<i>n</i> -C <sub>7</sub> H <sub>16</sub>	42	-0.00108	-0.00085	-0.00018	-0.00004	-18.18	-14.23	-3.21	-0.95
<i>i</i> -C <sub>7</sub> H <sub>16</sub>	43	-0.00097	-0.00072	-0.00007	-0.00001	-17.62	-13.21	-1.88	-0.61
<i>n</i> -C <sub>8</sub> H <sub>18</sub>	42	-0.00105	-0.00081	-0.00023	-0.00003	-20.17	-15.57	-4.70	-0.93
<i>n</i> -C <sub>9</sub> H <sub>20</sub>	18	-0.00103	-0.00081	-0.00024	0.00002	-19.40	-15.20	-4.51	0.32
<i>n</i> -C <sub>10</sub> H <sub>22</sub>	19	-0.00100	-0.00078	-0.00028	0.00004	-20.80	-16.26	-5.73	0.77
<i>n</i> -C <sub>12</sub> H <sub>26</sub>	22	-0.00097	-0.00077	-0.00037	0.00005	-24.23	-19.14	-9.02	1.11
<i>n</i> -C <sub>13</sub> H <sub>28</sub>	16	-0.00087	-0.00065	-0.00028	0.00005	-24.35	-18.18	-7.82	1.50
<i>n</i> -C <sub>15</sub> H <sub>32</sub>	14	-0.00080	-0.00058	-0.00027	0.00006	-26.74	-19.39	-9.12	2.02
<i>n</i> -C <sub>16</sub> H <sub>34</sub>	10	-0.00078	-0.00056	-0.00029	0.00005	-28.57	-20.62	-10.46	2.05
<i>n</i> -C <sub>17</sub> H <sub>36</sub>	15	-0.00080	-0.00060	-0.00035	-0.00002	-30.63	-23.01	-13.22	-0.54
<i>n</i> -C <sub>18</sub> H <sub>38</sub>	13	-0.00068	-0.00049	-0.00024	0.00009	-27.83	-19.70	-9.53	3.99
<i>n</i> -C <sub>19</sub> H <sub>40</sub>	12	-0.00071	-0.00053	-0.00030	0.00001	-30.55	-22.60	-12.82	0.54
<i>n</i> -C <sub>20</sub> H <sub>42</sub>	11	-0.00077	-0.00059	-0.00039	-0.00009	-34.49	-26.64	-17.45	-3.75
C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>	7	-0.00099	-0.00074	0.00082	0.00027	-7.61	-5.67	6.36	2.06
Ethanol	35	-0.00406	-0.00283	-0.00135	0.00030	-29.52	-20.40	-10.09	1.56
H <sub>2</sub>	21	-0.00477	-0.00221	0.00640	0.00096	13.67	5.75	18.75	3.00
Grand Avg.	585	-0.00083	-0.00072	0.00028	0.00005	-17.97	-13.92	-2.93	0.26

$$\text{BIAS} = \frac{1}{n} \sum_{i=1}^n d_i \quad (\text{Eq 37})$$

$$\text{RMS} = \frac{1}{n} \sum_{i=1}^n d_i^2 \quad (\text{Eq 38})$$

These results indicate that the proposed equation significantly improves the prediction of saturated liquid densities of pure substances.

### 3.3 Saturated Vapor Densities

To compare saturated vapor density prediction results, relative errors (AAD, BIAS, and RMS) are considered for

10 pure substances. As indicated in Table 7 and 8 saturated vapor densities are predicted more accurately by the new EOS compared with the other four equations.

As an example of the use of new equation to predict the vapor pressure and the saturated liquid and vapor densities, Fig. 5-8 are plotted for propane and compared with the PR equation. As indicated in these figures, there is excellent agreement of calculated data with experimental data.

Table 9 compares experimental and predicted molar density of *n*-C<sub>9</sub> at 325.13 K and high pressures and Table 10 compares molar density of *n*-C<sub>13</sub> at 5000 bar and high temperatures.

These results indicate the exceptional capability of the new equation in predicting molar density at high pressures and temperatures.

**Table 6 Comparison of saturated liquid densities based on absolute and relative RMS (experimental data from [9])**

Component	No. of data	RMS $\times 10^6$				% RMS			
		RK	SRK	PR	Eq 11	RK	SRK	PR	Eq 11
CH <sub>4</sub>	45	1.460	1.563	5.851	0.216	0.0085	0.0090	0.0233	0.0015
C <sub>2</sub> H <sub>6</sub>	17	2.308	1.923	1.421	0.332	0.0169	0.0142	0.0086	0.0028
C <sub>3</sub> H <sub>8</sub>	43	1.257	0.966	0.543	0.065	0.0111	0.0084	0.0042	0.0008
<i>n</i> -C <sub>4</sub> H <sub>10</sub>	13	0.920	0.535	0.274	0.010	0.0090	0.0052	0.0026	0.0001
<i>i</i> -C <sub>4</sub> H <sub>10</sub>	14	0.773	0.443	0.338	0.024	0.0082	0.0047	0.0033	0.0003
<i>n</i> -C <sub>5</sub> H <sub>12</sub>	42	1.225	0.808	0.056	0.026	0.0154	0.0100	0.0008	0.0004
<i>i</i> -C <sub>5</sub> H <sub>12</sub>	29	1.106	0.736	0.087	0.049	0.0147	0.0098	0.0013	0.0009
<i>n</i> -C <sub>6</sub> H <sub>14</sub>	42	1.163	0.724	0.038	0.024	0.0173	0.0107	0.0007	0.0005
<i>n</i> -C <sub>7</sub> H <sub>16</sub>	42	1.175	0.740	0.052	0.018	0.0197	0.0122	0.0010	0.0004
<i>i</i> -C <sub>7</sub> H <sub>16</sub>	43	0.936	0.526	0.043	0.033	0.0172	0.0098	0.0010	0.0008
<i>n</i> -C <sub>8</sub> H <sub>18</sub>	42	1.097	0.668	0.067	0.015	0.0210	0.0127	0.0014	0.0004
<i>n</i> -C <sub>9</sub> H <sub>20</sub>	18	1.061	0.665	0.066	0.002	0.0199	0.0124	0.0012	0.0000
<i>n</i> -C <sub>10</sub> H <sub>22</sub>	19	0.997	0.622	0.085	0.004	0.0207	0.0128	0.0017	0.0001
<i>n</i> -C <sub>12</sub> H <sub>26</sub>	22	0.951	0.607	0.144	0.016	0.0236	0.0149	0.0035	0.0004
<i>n</i> -C <sub>13</sub> H <sub>28</sub>	16	0.754	0.426	0.082	0.004	0.0211	0.0119	0.0023	0.0001
<i>n</i> -C <sub>15</sub> H <sub>32</sub>	14	0.634	0.336	0.076	0.007	0.0213	0.0112	0.0025	0.0003
<i>n</i> -C <sub>16</sub> H <sub>34</sub>	10	0.604	0.316	0.082	0.007	0.0222	0.0116	0.0030	0.0003
<i>n</i> -C <sub>17</sub> H <sub>36</sub>	15	0.638	0.363	0.121	0.007	0.0244	0.0138	0.0046	0.0003
<i>n</i> -C <sub>18</sub> H <sub>38</sub>	13	0.469	0.237	0.056	0.014	0.0190	0.0096	0.0023	0.0006
<i>n</i> -C <sub>19</sub> H <sub>40</sub>	12	0.511	0.281	0.091	0.004	0.0218	0.0120	0.0039	0.0002
<i>n</i> -C <sub>20</sub> H <sub>42</sub>	11	0.591	0.354	0.153	0.011	0.0265	0.0158	0.0068	0.0005
C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>	7	0.976	0.542	0.681	0.072	0.0075	0.0042	0.0052	0.0006
Ethanol	35	17.046	8.040	1.997	0.535	0.1272	0.0584	0.0157	0.0043
H <sub>2</sub>	21	34.923	13.176	55.864	1.687	0.0983	0.0372	0.1582	0.0050
Grand Avg.	585	3.066	1.483	2.844	0.133	0.025	0.014	0.0108	0.0009

**Table 7 Comparison of saturated vapor densities based on relative AAD (experimental data from [9])**

Component	No. of data	Range of $T_r$	$\rho^v$ % AAD			
			RK	SRK	PR	Eq 11
CH <sub>4</sub>	45	0.4776-0.9971	5.414	2.1652	1.4626	1.9593
C <sub>2</sub> H <sub>6</sub>	17	0.4912-0.9823	6.8977	1.9794	1.5262	1.3904
C <sub>3</sub> H <sub>8</sub>	43	0.2621-0.981	26.2021	4.5937	10.4486	3.7631
<i>n</i> -C <sub>5</sub> H <sub>12</sub>	42	0.3214-0.9663	105.7499	1.6502	7.1354	0.9936
<i>n</i> -C <sub>6</sub> H <sub>14</sub>	42	0.3624-0.9691	159.6299	2.4905	4.1491	1.9997
<i>n</i> -C <sub>7</sub> H <sub>16</sub>	42	0.3536-0.9682	296.8654	2.1761	7.3664	1.6978
<i>i</i> -C <sub>7</sub> H <sub>16</sub>	43	0.5147-0.9767	95.4571	1.22	1.5328	1.3557
<i>n</i> -C <sub>8</sub> H <sub>18</sub>	42	0.3938-0.9704	348.4108	1.4583	5.9075	1.8405
C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>	39	0.5285-0.9855	44.678	7.2603	6.8054	6.2547
C <sub>2</sub> H <sub>2</sub> F <sub>2</sub>	42	0.7661-0.9939	9.6406	6.2796	5.0305	5.6481
Grand Avg.	397		110.9	3.13	5.14	2.7

#### 4. Conclusion

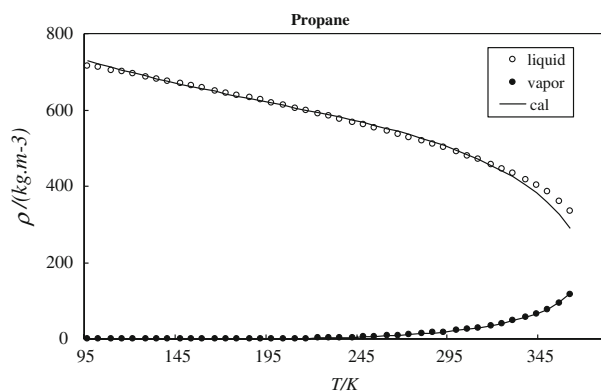
Vapor and liquid phases coexist in almost all areas of production operations including reservoirs and processing plants and therefore an accurate knowledge of fluid properties and phase behavior is essential. In this study, a

new EOS has been developed and has shown the feasibility of improving Eq 14 for representing pure component properties by considering the two parameters temperature and acentric factor dependent. Also the applicability of Eq 14 for calculating and predicting vapor-liquid equilibrium has been evaluated. The results of our study indicate

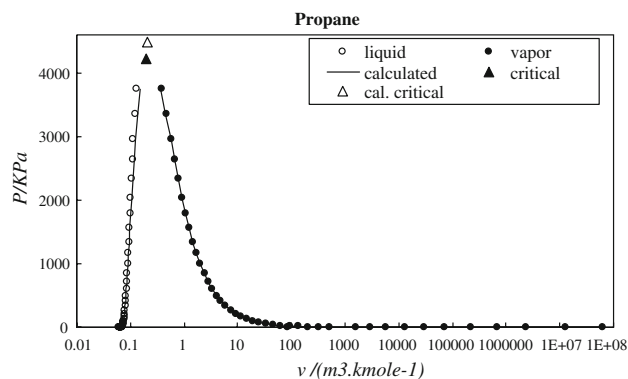


**Table 8 Comparison of saturated vapor densities based on relative BIAS and RMS (experimental data from [9])**

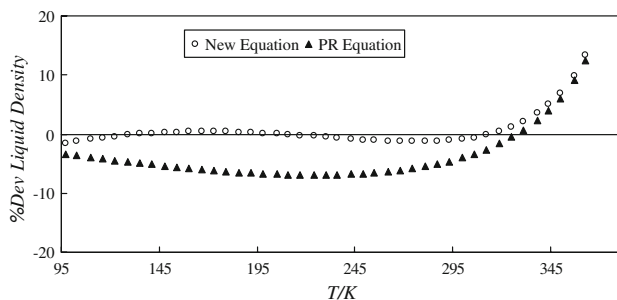
Component	No. of data	% BIAS				% RMS $\times 10^5$			
		RK	SRK	PR	Eq 11	RK	SRK	PR	Eq 11
CH <sub>4</sub>	45	-15.38	-1.58	1.46	1.12	47.93	5.63	15.08	9.28
C <sub>2</sub> H <sub>6</sub>	17	4.53	-1.69	0.62	0.44	29.99	9.34	3.77	3.44
C <sub>3</sub> H <sub>8</sub>	43	6.17	-4.58	5.14	-1.16	50.61	2.62	4.96	3.11
<i>n</i> -C <sub>3</sub> H <sub>12</sub>	42	105.75	-0.56	6.70	-0.38	152.05	0.13	0.74	0.05
<i>n</i> -C <sub>6</sub> H <sub>14</sub>	42	159.63	-2.04	3.16	-1.58	213.12	0.25	1.09	0.13
<i>n</i> -C <sub>7</sub> H <sub>16</sub>	42	296.87	0.62	7.16	0.71	294.42	8.62	13.61	8.60
<i>i</i> -C <sub>7</sub> H <sub>16</sub>	43	95.46	-1.19	0.33	-0.55	277.30	0.38	0.37	0.48
<i>n</i> -C <sub>8</sub> H <sub>18</sub>	42	348.41	-0.29	5.02	-0.35	329.69	4.52	7.48	5.05
C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>	39	43.11	2.94	4.31	4.23	395.25	49.58	58.94	49.73
C <sub>2</sub> H <sub>2</sub> F <sub>2</sub>	42	8.89	-6.28	-5.03	-5.65	101.78	57.12	26.11	36.32
Grand Avg.	397	105.34	-1.47	2.89	-0.32	189.21	13.82	13.22	11.62



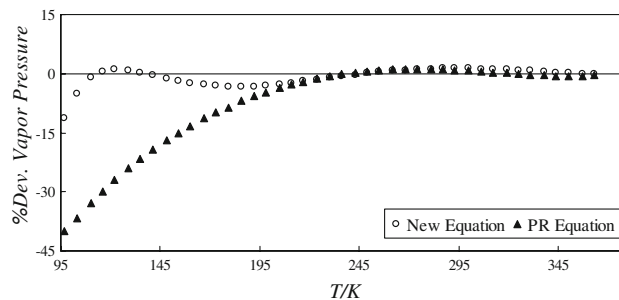
**Fig. 5** Saturated density-temperature curve for propane



**Fig. 7** Pressure-molar volume curve of propane



**Fig. 6** Saturated liquid propane density deviation



**Fig. 8** Propane vapor pressure deviation

that the combination of the new hard sphere compressibility factor and the RK empirical attractive term appears to be superior to all the other vdW type equations, including RK equation for representing pure component properties which are relevant to vapor-liquid equilibrium calculations.

The new equation requires three constants  $T_c$ ,  $P_c$ , and  $\omega$  for the substances to be described. The new EOS is applied

to calculations of vapor pressure and saturated liquid and vapor densities of different pure fluids. Table 9 and 10 show the calculated molar densities for high temperature (303-523 K) and high pressure (50-5000 psi) from the proposed equation, the RK, the PR, and the SRK equations. The comparisons indicate the superiority of the new EOS over similar equations.

**Table 9** Prediction results of molar density of  $n\text{-C}_9$  at 325.17 K by four EOSs at high pressures (experimental data from <sup>[10]</sup>)

Pressure (bar)	Experimental	RK	SRK	PR	Eq 11
50	5.45	4.4424	4.6225	5.1918	5.485
100	5.53	4.5047	4.6609	5.2278	5.5855
200	5.64	4.6022	4.7248	5.2885	5.7555
300	5.74	4.6762	4.7761	5.3382	5.8960
500	5.84	4.7832	4.8545	5.4154	6.1194
1000	6.13	4.9374	4.9758	5.5386	6.4947
1500	6.3	5.0223	5.0467	5.6129	6.7381
2000	6.4	5.0768	5.0937	5.6634	6.9132
3000	6.56	5.1432	5.1528	5.7281	7.1530
5000	6.73	5.2083	5.2126	5.7956	7.4260
%AAD		19.67	18.39	8.93	5.15

**Table 10** Prediction results of molar density of  $n\text{-C}_{13}$  at 5000 bar by four EOSs at high temperatures (experimental data from <sup>[10]</sup>)

T, K	Experimental	RK	SRK	PR	Eq 11
303.15	4.869	3.4720	3.4747	3.8654	5.4216
373.15	4.762	3.4590	3.4616	3.8496	5.1806
423.15	4.705	3.4496	3.4521	3.8380	5.2875
493.15	4.643	3.4365	3.4386	3.8216	5.6692
523.15	4.591	3.4310	3.4327	3.8145	5.8729
%AAD		26.80	26.75	18.56	16.51

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