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# Liquid Saturation Density from Simple Equations of State

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Several simple equations of state, requiring only two input properties, have been studied in order to determine the liquid saturation density of 144 fluids of different kinds. This study includes old and new simple modifications of the van der Waals equation of state, and the Carnahan–Starling–Yelash–Kraska and Carnahan–Starling–Dieterici equations. The new simple modifications of the van der Waals equation give better overall results than some other more complex proposed equations, especially near the critical point. The recent equation proposed by Eslami including the boiling temperature and density as input parameters was also checked, and was found not to reproduce the critical point, but to give excellent results at intermediate or low temperatures. As a reference, the behavior of the well-known Soave–Redlich–Kwong and Peng–Robinson equations, and the more recent expression proposed by Mohsen-Nia et al. that requires three input parameters were also checked. The latter does not improve the accuracy of the Peng–Robinson equation, and very simple van-der-Waals type equations give better overall results.

**KEY WORDS:** equation of state; liquid saturation density; pure fluids; vapor–liquid equilibrium.

## 1. INTRODUCTION

The calculation of saturated densities at vapor–liquid equilibrium (VLE) of pure substances is essential in important practical applications and serves as the basis for the calculation of some other properties such as the surface tension [1–6]. Currently used classical equations of state are

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insufficiently precise for the calculation of liquid saturation densities [7–9], and a volume correction is needed to obtain adequate results [10]. Another alternative is the use of specific coefficients for each fluid in a general cubic equation of state [11, 12]. Also, some crossover equations of state have been proposed based on the simplest classical cases such as the well-known van der Waals equation [13, 14]. Due to the complexity of the required calculations, the use of accurate empirical correlations giving the saturated liquid density is frequently preferred [1, 4, 6, 15–17].

Since the time of van der Waals, a very large number of equations of state (EOSs) have been proposed [8, 18, 19]. There are a few very simple EOSs such as the van der Waals, the Redlich–Kwong [20], and the Fox [21], which can be considered as predictive since they contain only two fixed parameters that are calculated by knowing only the critical properties. They are, in general, not accurate but have served as the basis for the development of more complex empirical equations [8, 11–14, 19]. These empirical EOSs usually give a better description of the fluid properties, but they have the disadvantage of containing a certain number of adjustable parameters. The simplest empirical equations have been obtained by following the van der Waals scheme, i.e., the separation of the contributions of the repulsive and attractive forces as summed terms, and are cubic in volume [8]. Correlations for some of the included coefficients are made, and then new input parameters such as the acentric factor are needed. Well-known examples are the Soave–Redlich–Kwong [22] and the Peng–Robinson [23] EOSs. Valderrama and Alfaro [7] use some of these well-known EOSs to obtain the liquid-phase volumes of several industrially important fluids, and analyze the accuracy of each of them. They give some recommendations about which equation should be used for a given situation [7, 8]. Two of their conclusions are that classical EOSs should not be used, and that a generalized semi-empirical correlation should be always preferred.

Some studies [18, 24–30] have considered the use of simple analytical expressions for EOSs. In particular, Yelash and Kraska [18] focus on possible choices of the analytical expression for the repulsive and attractive contributions, maintaining the cubic form of the EOS. Their results for the liquid saturation density indicate that the use of the Carnahan–Starling EOS for the repulsive part and a modified vdW term for the attractive part leads to a qualitative improvement with respect to other simple (predictive) EOSs. Unfortunately, no numerical results were given.

Eslami [24] proposes a simple equation of state, based on an earlier one proposed by Ihm et al. [31], in which the boiling temperature and density are the only inputs needed. The saturated liquid densities of a great number of compounds were reproduced within a few percent. Unfortunately, those densities were obtained directly from the vapor-pressure data instead of by applying the equilibrium conditions or the Maxwell equal-area construction [24]. It would therefore be interesting to know whether the Eslami EOS is capable of adequately reproducing the liquid saturation density and over what temperature range it is valid. As the Eslami EOS does not include the critical properties as inputs, it would also be interesting to study its behavior near the critical point.

Mohsen-Nia et al. [28] propose a new method to derive the repulsive term of cubic EOSs. By adding a general form for the attractive term, they propose a new cubic, simple EOS (MMM EOS) including only two constants and three input properties. The authors indicate that their proposed equation significantly improves the results for the liquid saturation density with respect to the classical Peng–Robinson (PR) and Soave–Redlich–Kwong (SRK) EOSs, at least for the 35 fluids considered in their work.

In the present work, we shall compare these three EOSs, but using results for a larger number of fluids and wider temperature ranges. In particular, we include here the low-temperature region, i.e., near the triple point, where calculations must be done with particular care [32,33].

Román et al. [30] study the reliability of six families of EOS in reproducing VLE properties. These families are constructed by using the repulsive term proposed by van der Waals or that proposed by Carnahan and Starling [34], and the van der Waals or the Redlich–Kwong attractive terms, and by considering the van der Waals (repulsive-plus-attractive) or the Dieterici (repulsive-times-attractive) schemes. The authors observe that a properly chosen value (different from that used in the classical vdW or RK EOSs) for the exponent in the temperature dependence of the attractive vdW term can significantly improve results for the saturated densities of simple fluids. We shall consider in this present work three different values for that exponent, as will be described in Section 2. In particular, one of these values leads to the well-known Berthelot EOS.

The foregoing equations are based on the original van der Waals idea of summing the contributions of repulsive and attractive interactions. Recently, we have shown that the Carnahan–Starling–Dieterici (CSD) equation proposed by Sadus [25–27] and based on the product of these terms significantly improves the prediction of the saturated liquid densities for simple fluids such as argon and methane [29] when compared with other simple EOSs. Here we extend this study to a greater number of fluids, and compare the results with those given by other EOSs requiring only two input properties. One objective is to determine whether the Dieterici equation can serve as the basis for the development of new simple equations of state improving results for the liquid saturation density. As indicated above, Román et al. [30] have shown that a modified temperature dependence in the attractive term does not improve the results. Hence, we shall study here only the original proposal of Sadus.

The main aim of the present work is to study the validity of the simple equations of state mentioned above, which require only two well-known properties as input and which do not include adjustable coefficients, to determine the liquid saturation density of fluids.

The selected EOSs were those proposed by van der Waals, by Redlich and Kwong [20], by Fox [21] and by Eslami [24], the CSD equation proposed by Sadus [25], one of the expressions proposed by Yelash and Kraska [18], and the slight modification of the vdW EOS proposed by Román et al. [30] which includes the Berthelot EOS as a particular case. Calculations with the PR, the SRK, and the Mohsen-Nia et al. [28] EOSs were made as a reference. Predictions from all these EOSs for the liquid saturation densities will first be compared with the values in DIPPR [35] for 31 fluids over the whole temperature range where data are available. This first comparison is extended to 139 fluids only for the most adequate EOSs and for four different temperature ranges. We should note that 5 out of the 31 initial fluids were not considered in the final list of 139, so that the total number of fluids analyzed is 144. (These fluids belong to very different families including, for example, 14 C–H–multihalogen compounds, 12 C–H–F compounds, 10 *n*-alkanes, 9 methlyalkanes, 9 dimethylalkanes, several aromatic compounds, and some other organic and inorganic compounds. A complete list is available upon request.)

In particular, it would be interesting to know: (i) which simple vdW-type EOS best predicts the saturation liquid density of some fluids; (ii) whether the proposal of Yelash and Kraska [18] clearly improves the prediction of that property; (iii) whether the CSD EOS proposed by Sadus significantly improves the prediction of the liquid saturated density with respect to other simple EOSs based on the vdW (repulsion-plus-attraction) separation of contributions; (iv) what is the accuracy of the Eslami EOS in reproducing the liquid saturation density, and over what temperature range is it valid; and (v) whether the new repulsive term proposed by Mohsen-Nia et al. [28] clearly improves the results obtained with the PR and SRK EOSs.

## 2. SIMPLE EQUATIONS OF STATE

In this section, we shall present briefly the selected EOSs, except for the well-known van der Waals (vdW), Carnahan–Starling–van der Waals (CSvdW), Redlich–Kwong (RK), Soave–Redlich–Kwong (SRK), and Peng–Robinson (PR) equations.

The EOS proposed by Fox is really a slightly modified vdW EOS in which the temperature dependence of the attractive term is modified in a way similar to that done by Redlich and Kwong [20]. Its analytical expression is

$$P = \rho RT/(1 - b\rho) - a\rho^2 T^{-1/2} \tag{1}$$

where $P$, $\rho$, and $T$ are the pressure, molar density and temperature, $R$ is the universal gas constant, and $a$ and $b$ are parameters that can be obtained from the critical properties by applying the critical point constraints

$$a = (9/8)RT_c^{3/2}/\rho_c, \quad b = (3\rho_c)^{-1}, \tag{2}$$

where $T_c$ is the critical temperature and $\rho_c$ is the molar critical density.

Recently, our group [30] has shown that a properly chosen value (different from that used in the classical vdW or RK EOSs) for the exponent in the temperature dependence of the attractive vdW term can significantly improve results for the saturated densities of simple fluids with respect to those obtained with the other simple EOSs studied. Unfortunately, the appropriate exponent seems to be different for each fluid [30]. In any case, in order to be comparable with the other EOSs studied here, we shall consider two different values for that exponent and a larger number of fluids. The vdW-$\beta$ EOS is then very similar to the Fox EOS, Eq. (1), with only the temperature dependence changed:

$$P = \rho RT/(1 - b\rho) - a\rho^2 T^{-\beta} \tag{3}$$

with

$$a = (9/8)RT_c^{1+\beta}/\rho_c; \quad b = (3\rho_c)^{-1}. \tag{4}$$

By using $\beta = 0, 0.5$, and 1, one obtains the vdW, Fox, and Berthelot EOSs, respectively. Following the ideas of Román et al. [30], we shall use two additional values for the parameter $\beta$ (0.7 and 1.5) in Eq. (3), and we will use vdW0.7 and vdW1.5 to denote the resulting expressions.

Yelash and Kraska [18] study the possibility of simple changes in cubic EOSs maintaining a quadratic dependence on the volume for the attractive term. In particular, they investigate the effect of the density dependence of an attractive term by using a generalized quadratic volume dependence, but maintaining the vdW temperature dependence. The generalization is accomplished by introducing two (substance independent) parameters which allow several families of generalized simple cubic EOSs to be considered. Unfortunately, results for the saturation densities of pure fluids were presented only as a figure, and no clear conclusion was given. Nevertheless, from that figure, we selected one of the simplest proposed EOSs giving adequate results for the liquid saturation density of some pure fluids. That proposal includes a CS repulsive term and a vdW type attractive term. We denote this EOS by CSYK. Its analytical form is [18]

$$P = \rho RT Z_{\mathrm{CS}} - a\rho^2/(1-y)^2 \tag{5}$$

where $Z_{\mathrm{CS}}$ is the compressibility factor given by the Carnahan–Starling [34] equation

$$Z_{\mathrm{CS}} = (1 + y + y^2 - y^3)/(1-y)^3, \tag{6}$$

$y$ is the packing fraction ($y = \rho b/4$), and $a$ and $b$ are given by

$$a = 1.574024RT_{\mathrm{c}}/\rho_{\mathrm{c}}; \quad b = 1.07995/\rho_{\mathrm{c}}. \tag{7}$$

Sadus [25–27] proposed the use of a CSD equation based on the product of the CS repulsive term and the Dieterici attractive term. The analytical form of the CSD EOS is then

$$P = \rho RT Z_{\mathrm{CS}} \exp(-a\rho/RT) \tag{8}$$

where $Z_{\mathrm{CS}}$ is given by Eq. (6) and the parameters $a$ and $b$ (needed in the CS expression) are [26,29]

$$a = 3.19960RT_{\mathrm{c}}/\rho_{\mathrm{c}}; \quad b = 1.52528/\rho_{\mathrm{c}}. \tag{9}$$

We have shown [29] that the CSD EOS significantly improves the prediction of the saturated liquid densities for simple fluids such as argon and methane when compared with other simple EOSs. Results for other fluids will be given here.

Eslami [24] uses as a reference the EOS proposed by Ihm et al. [31], and proposes the expression

$$P = \rho RT \left[ 1 - \rho \frac{\alpha - B_2}{1 + 0.11b\rho} + \frac{\alpha\rho}{1 - 0.495b\rho} \right], \tag{10}$$

where $B_2$, i.e., the second virial coefficient, $\alpha$, and $b$ are correlated by Eslami as temperature functions by using the boiling temperature and density ($T_{\mathrm{b}}$ and $\rho_{\mathrm{b}}$) as inputs [24]:

$$\begin{aligned} B_2\rho_{\mathrm{b}} = {} & 1.033 - 3.0069(T_{\mathrm{b}}/T) - 10.588(T_{\mathrm{b}}/T)^2 + 13.096(T_{\mathrm{b}}/T)^3 \\ & -9.8968(T_{\mathrm{b}}/T)^4 \end{aligned} \tag{11}$$

$$a\rho_b = -0.0860\exp[-0.5624(T/T_b)] + 2.3988\{1-\exp[-1.4267(T_b/T)^{1/4}]\} \tag{12}$$

$$\begin{aligned} b\rho_b = &-0.0860[1-0.5624(T/T_b)]\exp[-0.5624(T/T_b)] \\ &+2.3988\{1-[1+0.356675(T_b/T)^{1/4}]\exp[-1.4267(T_b/T)^{1/4}]\}. \end{aligned} \tag{13}$$

As indicated in the Introduction, Eslami [24] did not apply the equilibrium conditions or the Maxwell equal-area construction to obtain the vapor–liquid saturation densities, and no results for these densities were specifically given. As the Eslami EOS does not include the critical properties either as inputs or in the calculation of the included parameters, one expects this EOS to fail near the critical point. Obviously, very good results are expected near the boiling point.

Finally, the proposal of Mohsen-Nia et al. [28] is a cubic EOS in which the temperature dependence for the attractive term is that proposed by Redlich and Kwong [20]:

$$P = \rho RT(1+1.3191b\rho)/(1-b\rho) - a\rho^2 T^{-1/2}/(1+2.6382b\rho) \tag{14}$$

where $a$ and $b$ are functions of the temperature and the acentric factor that are obtained by a fitting procedure. The authors show that their EOS accurately reproduces the liquid saturation densities, clearly improving the results obtained with other cubic EOSs such as the SRK and PR equations, at least for the 35 fluids selected [28].

## 3. RESULTS

We imposed the VLE constraints on the selected EOSs: vdW, RK, Fox (Eq. (1)), Berthelot (Eq. (3) with $\beta=1$), vdW0.7 (Eq. (3) with $\beta=0.7$), vdW1.5 (Eq. (3) with $\beta=1.5$), CSvdW, CSYK (Eq. (5)), CSD (Eq. (8)), Eslami (Eq. (10)), PR, SRK, and MMM (Eq. (14)), and obtained predictions of the liquid saturation density for 31 simple fluids of different kinds (mainly the same as considered in Ref. 28). This preliminary study with only 31 fluids permitted us to adequately choose some of the equations for a wider study, and also showed the advantages or limitations of the selected EOSs.

For the EOSs similar to the vdW, we used the critical temperature and critical volume as inputs. For the RK and CSD EOSs, different density values are obtained according to whether the input parameters are $T_c$ and $\rho_c$ or $T_c$ and $P_c$. This is because the critical compressibility factor has a fixed value for each EOS, which is different from the experimental value for each fluid. Thus, when one uses $P_c$ as input, the critical density obtained does not exactly match the experimental value. In any case, we observed that for the aforementioned EOSs the input of $T_c$ and $P_c$ sometimes leads to better results than the use of $T_c$ and $\rho_c$. We shall denote these options as RK($\rho_c$), RK($P_c$), CSD($\rho_c$), and CSD($P_c$), respectively.

As a reference, we took the results of the more complex (more than two input parameters) SRK, PR, and MMM EOSs (using the critical temperature and pressure as inputs, because the use of $T_c$ and $\rho_c$ generally leads to higher deviations). For all the input properties we used the values in DIPPR [35]. Results for the liquid saturation densities were compared with the values proposed in the DIPPR [35] project. We obtained for each EOS the percentage deviation for each datum, and the mean absolute percentage deviation (APD) for each fluid. The APDs values for most EOSs are listed in Table I, where the temperature range considered is indicated in reduced $T/T_c$ units.

We start our analysis by studying the validity of the simplest EOSs and 31 simple fluids (mainly the same as in Ref. 28). Obviously, the vdW and CSvdW EOSs give the poorest results. The APDs for the 31 selected fluids were always greater than 10% for the vdW EOS. Moreover, the CSvdW EOS gave APDs from 4 to 6% for only three of those fluids, being worse for all the others. The RK($\rho_c$) and RK($P_c$) EOSs always gave APDs greater than 4 and 3.3%, respectively, and for each one of the 31 fluids it was always possible to choose a better simple EOS.

The Fox EOS gave APDs less than 5% only for methane, argon, xenon, oxygen, and nitrogen. Nevertheless, as is shown in Fig. 1, for all those fluids except argon, the Berthelot EOS gave better overall results than the Fox EOS, especially near the critical point. Moreover, the Berthelot EOS gave results better than or similar to the slightly more complex RK equation (not shown in Table I) for these fluids, with only two exceptions (methyl chloride and ethyl chloride, using RK($\rho_c$) in both cases). This EOS improved the results obtained with other simple EOSs for fluorine and carbon tetrafluoride. Finally, it gave similar results to the other simple EOSs for different kinds of fluids, including benzene, acetylene, and hydrogen sulfide (see Table I).

For most of the fluids considered in Table I, it was possible to choose a temperature dependence in the attractive part of the vdW EOSs, i.e., a value for $\beta$ in Eq. (3), different from that commonly used ($\beta = 0, 0.5$, or 1), which leads to a clear improvement in the prediction of the liquid saturation density with respect to the vdW, Fox, Berthelot, and RK EOSs.

**Table I.** Mean Absolute Percentage Deviations (APDs) of the Predicted Saturated Liquid Densities from EOSs Compared to Values Accepted by the DIPPR [35] Project. ($T_{\min}$ and $T_{\max}$ are the minimum and maximum temperatures for which calculations were made. $N$ is the number of experimental data for each fluid.)

| Fluids | $T_{\min}/T_c$ | $T_{\max}/T_c$ | $N$ | Berthelot | vdW0.7 | vdW1.5 | CSYK | CSD($P_c$) | Eslami | SRK | PR | MMM |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Argon | 0.5553 | 0.9943 | 21 | 3.3 | 0.9 | 7.3 | 4.6 | 12.5 | 4.2 | 3.2 | 11.1 | 2.8 |
| Xenon | 0.5569 | 0.9664 | 28 | 1.8 | 1.7 | 5.4 | 3.9 | 8.5 | 4.8 | 4.7 | 8.5 | 3.1 |
| Oxygen | 0.3517 | 0.9833 | 50 | 2.2 | 2.0 | 4.8 | 4.5 | 7.9 | 3.6 | 3.4 | 9.8 | 4.9 |
| Fluorine | 0.3711 | 0.9714 | 10 | 2.0 | 3.2 | 3.8 | 4.1 | 6.4 | 2.9 | 4.1 | 9.5 | 5.1 |
| Nitrogen | 0.5004 | 0.9826 | 59 | 2.3 | 1.2 | 6.4 | 3.4 | 10.7 | 1.3 | 3.6 | 9.6 | 3.2 |
| Chlorine | 0.4127 | 0.9971 | 32 | 3.2 | 5.5 | 3.7 | 3.7 | 2.9 | 6.5 | 12.3 | 7.0 | 8.0 |
| Methane | 0.4759 | 0.9865 | 21 | 2.5 | 1.4 | 6.0 | 4.5 | 9.0 | 4.1 | 4.8 | 9.1 | 3.3 |
| Ethane | 0.2960 | 0.9957 | 48 | 3.2 | 5.0 | 3.3 | 3.8 | 3.9 | 2.0 | 6.7 | 7.4 | 7.6 |
| Propane | 0.2311 | 0.9734 | 21 | 2.5 | 5.4 | 3.8 | 2.3 | 4.0 | 2.0 | 9.2 | 4.9 | 5.6 |
| *n*-Butane | 0.3172 | 0.9409 | 13 | 3.7 | 6.5 | 3.1 | 2.4 | 3.4 | 2.0 | 10.1 | 3.5 | 4.9 |
| *n*-Pentane | 0.3054 | 0.9985 | 67 | 5.4 | 8.1 | 2.9 | 3.9 | 4.5 | 5.4 | 12.7 | 4.3 | 5.5 |
| *n*-Hexane | 0.3805 | 0.9897 | 55 | 6.0 | 8.7 | 2.5 | 4.4 | 6.6 | 4.0 | 13.3 | 3.0 | 4.2 |
| *n*-Heptane | 0.3380 | 0.9907 | 39 | 7.2 | 9.7 | 4.0 | 4.4 | 10.1 | 5.8 | 14.8 | 4.0 | 5.4 |
| *n*-Octane | 0.5858 | 0.9727 | 23 | 5.6 | 8.6 | 1.5 | 5.4 | 9.1 | 5.0 | 15.9 | 4.8 | 4.2 |
| *n*-Nonane | 0.3753 | 0.8967 | 46 | 6.9 | 9.5 | 3.4 | 4.3 | 12.7 | 3.3 | 15.6 | 4.7 | 3.2 |
| *n*-Decane | 0.3942 | 0.9764 | 38 | 6.7 | 9.3 | 3.3 | 4.5 | 14.3 | 6.2 | 17.6 | 7.1 | 4.3 |
| Isobutane | 0.5227 | 0.9259 | 65 | 2.9 | 5.8 | 1.4 | 1.2 | 1.6 | 0.3 | 7.1 | 5.4 | 2.6 |
| Isopentane | 0.3255 | 0.9891 | 60 | 3.4 | 6.1 | 2.7 | 2.4 | 3.1 | 2.7 | 10.1 | 4.6 | 4.7 |
| Ethylene | 0.3654 | 0.9983 | 35 | 2.8 | 4.9 | 2.9 | 3.2 | 3.6 | 1.7 | 6.2 | 7.6 | 6.3 |
| Acetylene | 0.6148 | 0.9833 | 26 | 1.8 | 4.8 | 2.9 | 1.8 | 1.6 | – | 10.6 | 4.3 | 2.8 |
| Propylene | 0.2409 | 0.9975 | 103 | 5.4 | 7.7 | 4.4 | 1.4 | 5.3 | 2.5 | 7.8 | 5.2 | 7.9 |
| 1,3-Butadiene | 0.3864 | 0.9980 | 119 | 3.4 | 6.1 | 2.6 | 1.6 | 2.7 | 1.5 | 10.3 | 3.7 | 3.4 |
| Benzene | 0.4959 | 0.9984 | 123 | 2.8 | 5.8 | 2.4 | 2.2 | 2.1 | 1.8 | 11.7 | 3.7 | 3.3 |
| Toluene | 0.3008 | 0.9990 | 104 | 6.2 | 8.6 | 3.6 | 2.6 | 8.4 | 2.8 | 13.1 | 2.4 | 5.1 |

Table I. (Continued)

| Fluids | $T_{\min}/T_c$ | $T_{\max}/T_c$ | $N$ | Berthelot | vdW0.7 | vdW1.5 | CSYK | CSD($P_c$) | Eslami | SRK | PR | MMM |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Methyl chloride | 0.4215 | 0.9926 | 40 | 7.0 | 9.8 | 3.2 | 6.1 | 3.8 | 2.0 | 14.1 | 3.5 | 6.3 |
| Ethyl chloride | 0.6368 | 0.9192 | 12 | 6.6 | 9.6 | 2.7 | 5.7 | 3.5 | 0.6 | 12.1 | 1.4 | 2.1 |
| Carbon tetrafluoride | 0.4095 | 0.9985 | 23 | 2.6 | 3.8 | 4.3 | 4.0 | 3.7 | 4.3 | 7.6 | 8.7 | 6.2 |
| Carbon dioxide | 0.7119 | 0.9960 | 29 | 3.7 | 6.7 | 2.3 | 4.5 | 1.3 | – | 12.7 | 4.8 | 5.1 |
| Carbon monoxide | 0.5126 | 0.9768 | 31 | 1.9 | 4.9 | 2.4 | 2.2 | 9.8 | 1.3 | 3.5 | 9.7 | 2.8 |
| Sulfur dioxide | 0.5413 | 0.9591 | 30 | 4.8 | 7.8 | 1.5 | 3.7 | 4.1 | 0.8 | 11.9 | 1.6 | 1.9 |
| Hydrogen sulfide | 0.5024 | 0.9905 | 37 | 1.9 | 4.7 | 2.5 | 2.0 | 4.2 | 4.4 | 6.2 | 7.2 | 2.7 |

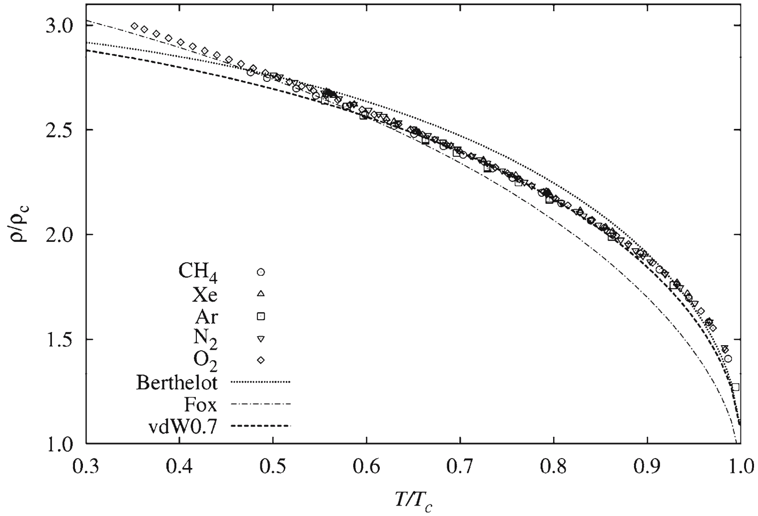

**Fig. 1.** Reduced density vs. reduced temperature for several fluids as predicted from three equations of state (lines) together with accepted DIPPR [35] values (points).

In particular, taking $\beta = 0.7$ as suggested by Román et al. [30], excellent overall results were obtained for the simplest fluids: argon, xenon, oxygen, nitrogen, and methane (Table I, Fig. 1). As indicated above, the Berthelot EOS gave slightly better results for these fluids near the critical point (Fig. 1). Moreover, one can see in Fig. 1 that none of these simple EOSs reproduced the liquid density at low temperatures.

Choosing $\beta = 1.5$, the greatest deviations were for the aforementioned simplest fluids, for which $\beta = 0.7$ was a better choice. As can be seen in Table I, when compared with other vdW-type EOSs, the vdW1.5 equation significantly improved the prediction of the saturated liquid density for a good number of fluids. For most of these fluids the vdW1.5 EOS led to better predictions than those obtained using the SRK, PR, or MMM EOSs, which included three input parameters. Unfortunately, as can be seen in Fig. 2, the vdW1.5 EOS did not give adequate results for some *n*-alkanes at low temperatures.

Finally, we must note that by appropriately choosing $\beta = 0, 0.7$, or 1.5, the saturation liquid density was predicted with APDs less than 4.5% for the fluids in Table I. Other general choices of the $\beta$ value or the use of analytically more complex EOSs such as RK were not needed for those fluids.

Another way of improving the results is the use of the CS EOS for the repulsive part. In particular, it is interesting to test the validity and

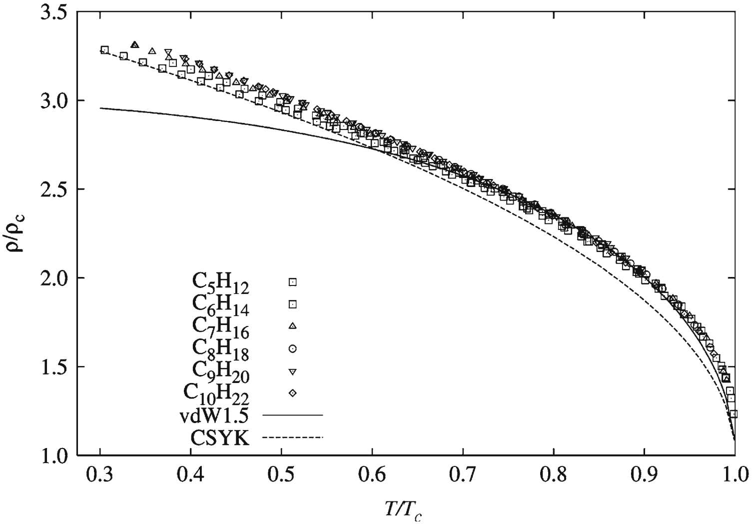

**Fig. 2.** Reduced density vs. reduced temperature for several *n*-alkanes as predicted from two equations of state (lines) together with accepted DIPPR [35] values (points).

accuracy of the CSYK EOS, Eq. (5). As can be seen in Table I, this EOS gave APDs greater than 5% only for *n*-octane, methyl chloride, and ethyl chloride. As can be seen in Fig. 2, the CSYK EOS led to very good results at low temperatures. Nevertheless, near the critical point other simpler EOSs such as vdW1.5 gave clearly better results.

Using the CSD EOS, Eq. (8), different results were obtained by considering the critical density or the critical pressure as inputs. In particular, we found that only 9 out of the 31 fluids had a lower APD obtained using the critical density instead of the critical pressure, and that for some of those nine fluids the difference was not very large. In Table I only the results obtained by using $P_c$ as input are shown. As it can be seen, the CSD($P_c$) EOS significantly improved the overall results obtained with CSYK for only chlorine, methyl chloride, ethyl chloride, and carbon dioxide. Nevertheless, only for carbon dioxide and chlorine did the CSD EOS give a clearly lower APD than that obtained by using other vdW-type EOSs. As can be seen in Fig. 3, this improvement was due only to the excellent behavior of this EOS near the critical point, whereas the CSD equation must be used with caution at low temperatures even for those fluids for which it gives a low APD over the whole temperature range. Figure 3 shows also that the vdW1.5 EOS has very similar behavior for these two fluids.

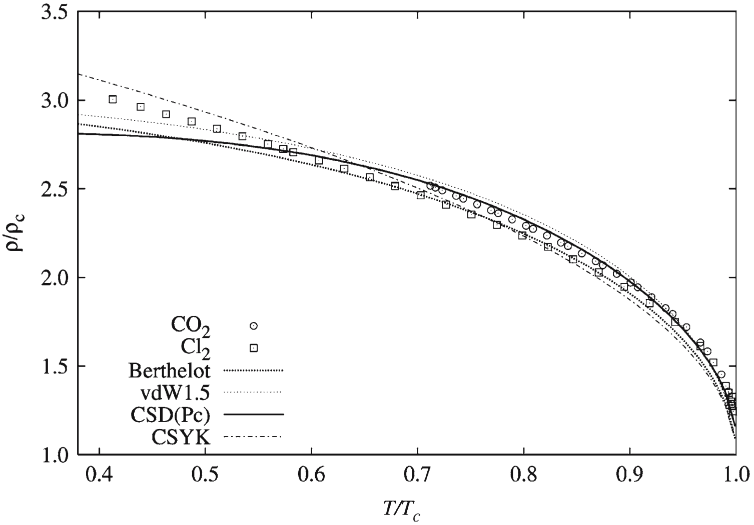

**Fig. 3.** Reduced density vs. reduced temperature for two fluids as predicted from four equations of state (lines) together with accepted DIPPR [35] values (points).

The Eslami EOS, Eq. (10), is the only one requiring the boiling temperature as input, and therefore cannot be applied to carbon dioxide or acetylene. As can be seen in Table I, it reproduced the liquid saturated density with APDs less than or equal to 6.5% for the remaining 29 fluids. Despite this behavior, it did not give adequate values over all the temperature range, and the APDs were greatly influenced by the temperature range in which data exist. In particular, it did not reproduce the critical properties, which were not specifically included in its analytical expression. As is shown in Fig. 4a, very large deviations were found at temperatures near the critical point, even for those fluids for which the Eslami EOS gave a clearly lower APD than all the previously mentioned EOSs. The Eslami EOS gave very good results at intermediate temperatures for most of the fluids. Nevertheless, it deviated at low temperatures, where the calculated density reached a maximum and then clearly decreased. At those very low densities, the CSYK EOS gave clearly better results, with some exceptions such as ethane or ethylene. Clear examples are shown in Fig. 4b. A comparison with a greater number of fluids is needed in order to confirm these and some other previous conclusions.

Table I includes the results obtained by using more complex (more than two input parameters) SRK, PR, and MMM EOSs (always using the critical temperature and pressure as inputs). We note that the APDs are

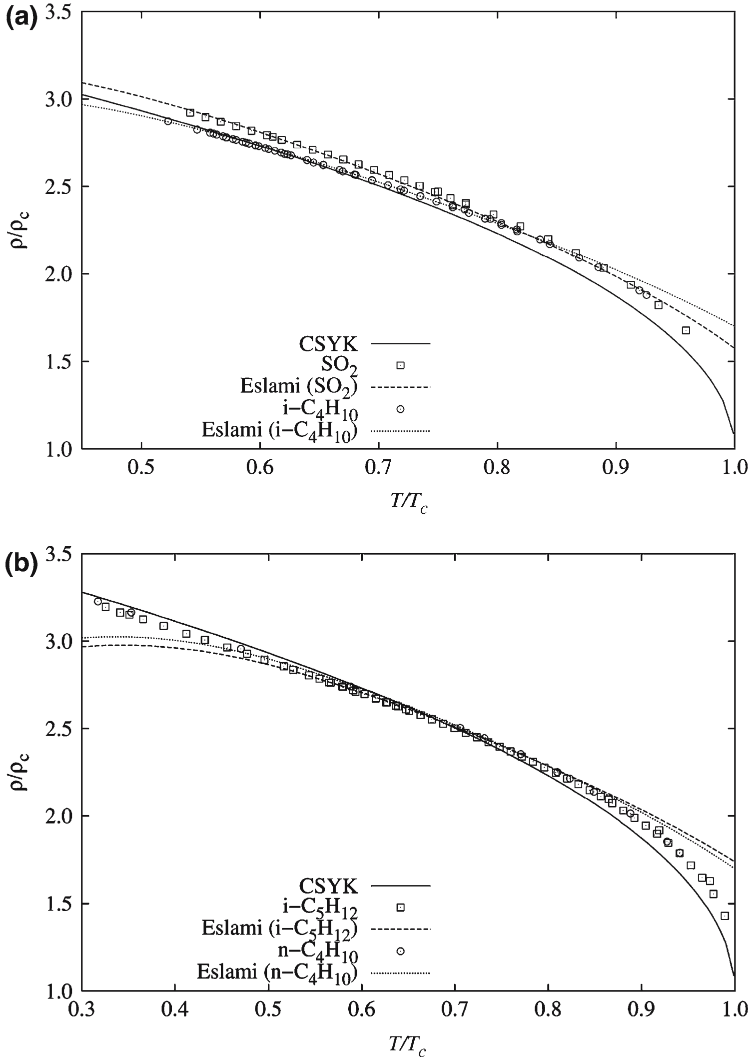

**Fig. 4.** Reduced density vs. reduced temperature for several fluids as predicted from two equations of state (lines) together with accepted DIPPR [35] values (points).

different from those published by Mohsen-Nia et al. [28] because the temperature range and/or the data used are different. Thus, for example, we found a 7.6% deviation for ethane for reduced temperatures from 0.296 to 0.9957, whereas Mohsen-Nia et al. [28] report a 2.11% deviation but for the range from 0.46 to 0.95.

As can be seen in the examples of Fig. 5a,b, we found that, even for those fluids for which the MMM EOS gave a lower APD than the SRK or PR equations, it clearly deviated from the available data at low temperatures. Near the critical point it behaved similarly to the SRK or PR cases (Fig. 5). In any case, one can always find a simple EOS (with only two input parameters) giving overall results equal to or even better than the PR, SRK, and MMM equations (examples are shown in Fig. 5). The only clear exception is ethyl chloride, due to the fact that the temperature range did not include very low or very high temperatures. In summary, these preliminary results, obtained by using practically the same fluids as those used in Ref. 28 but for a wider temperature range, do not confirm the conclusion of Mohsen-Nia et al. about the degree of improvement of the MMM EOS with respect to similar or even simpler EOSs.

In order to confirm the previous findings, we studied liquid saturated density results for some selected EOSs, for a greater number of fluids, and for four different temperature ranges (indicated in Table II). In particular, we chose those fluids with more than four available DIPPR data in each of the first three temperature ranges (low, medium, and high temperature). Because of that, fluorine, propane, *n*-butane, acetylene, and ethyl chloride were not considered, and the total number of fluids included in Table II was 139. The number of data, the mean percentage deviation (PD), and the mean absolute percentage deviation (MAPD) are given for each EOS and each temperature range.

As can be seen, at low temperatures the Eslami and CSYK EOS give the best results. The vdW1.5 EOS is also a good option for a simpler EOS. These three EOSs give better results than the three-parameter equations. At intermediate temperatures the Eslami EOS again gives the best results, and the vdW1.5 shows improved results when compared with CSYK. At high temperatures, i.e., near the critical point, the vdW1.5 EOS clearly gives the best results, with a significant improvement over all the others (see Figs. 2 and 3 as examples of its behavior in this range). Unfortunately, as indicated above, the Eslami EOS does not reproduce the critical point, so that a high MAPD is found at high temperatures. Because of that, the results in Table II indicate that the vdW1.5 EOS gives the best overall results, although it must be used with caution at low temperatures, where the Eslami or CSYK are better choices. Moreover, our results in Table I indicate that the vdW1.5 EOS does not give adequate results for the simplest fluids.

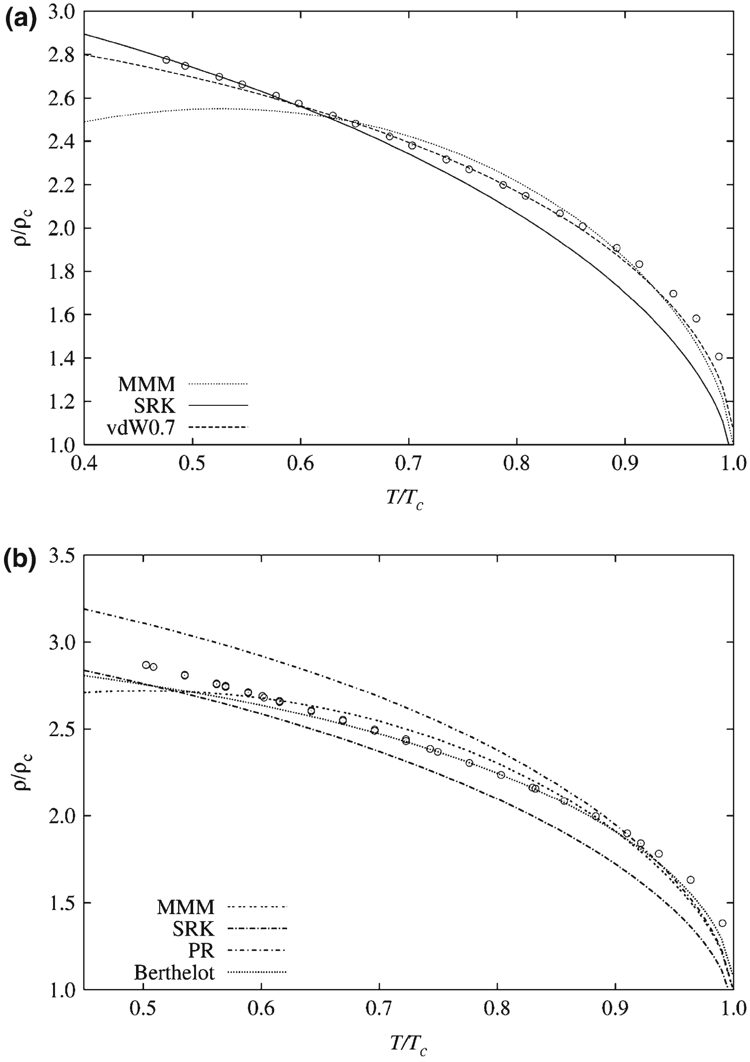

**Fig. 5.** Reduced density vs. reduced temperature for (a) methane and (b) hydrogen sulfide as predicted from equations of state (lines) together with accepted DIPPR [35] values (points).

**Table II.** Results Obtained for 139 Fluids and Some Selected EOSs. (The number of data ($N$), the mean percentage deviations (PD, %), and the mean absolute percentage deviation (MAPD, %), are given for each EOS and each temperature range; $t$ is a reduced temperature, $t = (T - T_t)/(T_c - T_t)$, where $T_t$ is the triple-point temperature.)

| EOS | | Berthelot | | vdW0.7 | | vdW1.5 | | CSYK | | CSD($P_c$) | | Eslami | | SRK | | PR | | MMM | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Range | $N$ | PD | MAPD | PD | MAPD | PD | MAPD | PD | MAPD | PD | MAPD | PD | MAPD | PD | MAPD | PD | MAPD | PD | MAPD |
| $0 \le t \le 0.5$ | 3758 | −6.1 | 6.4 | −8.4 | 8.6 | −3.1 | 4.3 | −1.4 | 2.8 | −8.2 | 9.2 | −1.1 | 1.4 | −11.0 | 11.1 | 0.2 | 5.4 | −1.9 | 5.8 |
| $0.5 < t \le 0.75$ | 2162 | −3.3 | 3.7 | −6.5 | 6.6 | 1.1 | 2.3 | −3.2 | 3.5 | −3.6 | 5.7 | 0.3 | 1.2 | −11.9 | 11.9 | −0.2 | 4.5 | 1.6 | 4.7 |
| $0.75 < t \le 1$ | 1813 | −5.4 | 5.7 | −8.2 | 8.4 | −1.3 | 3.2 | −6.9 | 7.1 | −5.3 | 6.6 | 9.3 | 10.2 | −18.7 | 18.7 | −8.5 | 8.9 | −7.8 | 8.6 |
| $0 \le t \le 1$ | 7784 | −5.2 | 5.5 | −7.9 | 8.0 | −1.5 | 3.5 | −3.2 | 4.0 | −6.3 | 7.7 | 1.7 | 3.4 | −13.1 | 13.1 | −1.9 | 6.0 | −2.4 | 6.2 |

With respect to the CSD EOS, the results in Table II confirm that it should be used with caution at low temperatures (Fig. 3 is a clear example). Although it can give very good results near the critical point for some fluids (Fig. 3), this accuracy cannot be extended to a large number of fluids. In any case, it slightly improves the results obtained with the CSYK EOSs in that high-temperature range.

Finally, with respect to the three-parameter EOSs, our results in Table II confirm that the MMM and PR EOSs have similar accuracy over different temperature ranges, and that a very simple EOS, such as the Berthelot or vdW1.5, give similar or even better overall results.

## 4. CONCLUSIONS

The liquid saturation densities of 144 fluids of different kinds were obtained from several simple equations of state, which require only two input properties. Our study confirmed the idea that it is possible to improve the accuracy of the well-known vdW, CSvdW, Fox, and RK EOSs by using simple modifications of them.

We showed that even the simple and well-known Berthelot EOS gives better or similar overall results than some other more complex EOSs. We also showed that the accuracy of the vdW-type EOSs in predicting the liquid saturation density can be improved by suitably choosing the exponent in the temperature dependence of the attractive term. When the choice is $\beta = 0.7$, as suggested by Román et al. [30], excellent results are obtained for the simplest fluids, especially at intermediate temperatures. The Berthelot EOSs give slightly better results near the critical point, but neither of these two simple EOSs can accurately reproduce the liquid density at low temperatures.

By choosing $\beta = 1.5$, the vdW1.5 EOS leads to very good predictions over the whole temperature range, giving clearly better overall results than other more complex EOSs, including those with three input parameters. Nevertheless, it must be kept in mind that this EOS can give inadequate results for some fluids at low temperatures.

We also checked the use of the CS EOS as the repulsive part in two relatively recent EOSs. We found that the CSYK EOS gives better overall results than other EOSs, although it must be used with caution near the critical point. In this high temperature range, the CSD EOS slightly improves the results obtained with CSYK. At low temperatures, it is the CSD EOS which must be used with caution, whereas the CSYK gives excellent results.

We obtained predicted values for the liquid saturation densities from the Eslami EOS by directly solving the vapor–liquid-equilibrium conditions, which was not done originally by Eslami. We found that the deviations with respect to experimental data greatly depend on the temperature range in which data exist. In particular, we showed that this EOS does not adequately reproduce the critical properties, even for fluids for which it gives a clearly lower APD than all the previously mentioned EOSs. On the other hand, it gives the best results at intermediate temperatures for most studied fluids, although for some fluids it again deviates at very low temperatures.

We included in our study the results obtained by using three EOSs with thee input parameters: SRK, PR, and MMM. We found that, even for those fluids for which the MMM EOS gives a better overall prediction than SRK or PR, it deviates clearly from the available data at high temperatures (near the critical point). In fact, the MMM equation gives practically the same overall results as the PR EOS for all the temperature ranges considered in this work. Therefore, our results do not confirm the conclusion of Mohsen-Nia et al. [28] about the degree of improvement of this equation with respect to PR. Finally, we showed that there are simple van-der-Waals-type EOSs (with only two input parameters) giving overall results equal to or even better than the SRK, PR, and MMM equations (with three input parameters).

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