Liquid Saturation Density from Predictive Correlations Based on the Corresponding States Principle. Part 1: Results for 30 Families of Fluids

Angel Mulero,*,† Isidro Cachadiña,† and M. Isabel Parra‡

Departamento de Física and Departamento de Matemáticas, Universidad de Extremadura, Avenida de Elvas s/n, 06071 Badajoz, Spain

Nine empirical correlations for the calculation of the liquid saturation density of pure fluids are studied for their accuracy and applicability. All of them are based on the corresponding states principle, and we have included very recent proposals. The first model requires only the knowledge of critical parameters, the following seven need the critical parameters and acentric factor as inputs, and the last requires the Lennard-Jones molecular parameters and the acentric factor as input data. As a reference, we take the numerical values for the liquid saturation density accepted by the DIPPR project for 552 fluids, grouped into 30 families. Recommendations are given for the use of each model and for the choice of the adequate model for each family of fluids, including for particular fluids.

Introduction

The saturated liquid density for pure substances is an important property used, for example, as a first step in the calculation of the compressed liquid density[1−5] or as an input for an equation of state.[6] As is well-known,[7−9] the currently used classical equations of state are insufficiently precise for the calculation of liquid densities, and the results must be improved by using a volume translation. On the other hand, there are many accurate empirical correlations giving this property, which are usually applied for design purposes. These correlations are mainly based on (i) the use of appropriate adjustable parameters for each substance;[10] (ii) the use of the corresponding states principle, with critical parameters and acentric factor as input data; and (iii) group contribution methods.[5] These three methods can be combined, and there are proposals that include constant physical properties and at least one adjustable parameter.[11−19]

We here focus attention on the correlations based on the corresponding states principle. These are both predictive (i.e., they do not contain adjustable coefficients for each fluid) and easy to use. By carefully going through the scientific literature, we have found nine empirical correlations that comply with these requirements. In addition to the well-known classical models, it is interesting to test the accuracy of three recent proposals. One is due to Queimada et al.,[20] who used both a first-order and a second-order corresponding states principle to calculate the liquid density (and the vapor pressure and viscosity) of *n*-alkanes. They used specific correlations for reference fluids, and then an interpolation of first or second order in the acentric factor was made. The average absolute deviation for the reduced liquid density (calculated at different temperatures) was 0.65% for the first-order model and 0.44% for the second-order model. No comparison with other methods was made, and no application to other fluids was considered. The second and most recent model that uses the corresponding states principle and involves no adjustable coefficients was proposed by Mchaweh et al.[21] It is based on an earlier proposal of Nasrifar and Moshfeghian.[15] The main difference is that whereas the latter involves three

adjustable coefficients for each fluid, the former uses the Soave−Redlich−Kwong equation of state temperature-dependent term and, hence, no adjustable coefficients. In both cases, however, at least one adjustable coefficient is required for each fluid to significantly improve the accuracy. For the purpose of comparison with other predictive models, we shall use Mchaweh et al.'s model but without including that adjustable coefficient. Mchaweh et al.[21] have shown that this predictive proposal reproduces experimental data for fluids of different kinds with an average absolute deviation of 1.74%.

Finally, the third proposal is a new kind of correlation for the vapor−liquid properties of nonpolar fluids,[22,23] based on the application of the molecular version of the corresponding states principle and then on the use of the Lennard-Jones molecular parameters and the acentric factor as input data. In particular, for the saturated liquid density the correlation model is a cubic function of the molecular reduced temperature and a quadratic function of the acentric factor. The model was designed to reproduce the saturated liquid density of 42 nonpolar substances as given by the correlation functions proposed by the DIPPR project,[24,25] which are specific for each substance. Even though the proposed function does not include the critical temperature as input, so that there is no imposition of the physical condition giving the critical density at the critical temperature, the deviation for a given temperature was found to be less than 3% for 36 of these substances, and the overall mean deviation was only[22] 1.5%. No comparison with other methods was made, and the extrapolative potential of the model was not studied.

There have been studies of the accuracy and applicability of these models for different kinds of fluids, generally in the temperature range where experimental data are available, and there are recommendations for the use of one or another method.[1,2,5] Nasrifar and Moshfeghian[16] evaluated 14 empirical correlations applied to 15 pure refrigerants over a wide temperature range. Also Nasrifar et al.[17] compared the accuracy of four correlations that include adjustable parameters for 87 fluids of different kinds, and of 10 correlations for 104 nonpolar fluids (see their Table 4). Obviously, the correlations that include adjustable parameters are more accurate than those without them. Nevertheless, the disadvantage is the need for experimental data to evaluate these adjustable parameters and, hence, a relative lack of predictability. There has until now been no broader study including a large number of fluids and all the proposed

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* To whom correspondence should be addressed. Fax: 34-924289651. E-mail: mulero@unex.es.
† Departamento de Física.
‡ Departamento de Matemáticas.

correlations based on the corresponding states principle, making comparisons with the same source of data.

The aim of this present work is to describe such a wide study of the accuracy and applicability of nine predictive correlations, three of them proposed recently, based on the corresponding states principle. In none of the cases is any adjustable parameter used; that is, all the models are predictive once certain constant physical properties are known for each fluid. As a reference, we took the liquid saturation values accepted by the DIPPR project[10] for 552 fluids grouped into 30 families (see Tables 2 and 3).

Predictive Correlation Models

We shall first briefly describe the correlations we used. The simplest expression is that proposed by Rackett:[26]

$$\rho = [V_c Z_c^{(1-T_r)^{2/7}}]^{-1} \tag{1}$$

where $T_r = T/T_c$ and then the input parameters are the critical volume, V_c, critical compressibility factor, Z_c, and critical temperature, T_c. Poling et al.[5] indicate that, while eq 1 is remarkably accurate for many substances, it overestimates the saturated density when $Z_c < 0.22$. It has been the starting point for the development of other equations for correlating saturated liquid densities.

Thus, Yamada and Gunn[27] (YG) changed the value of Z_c in eq 1 to a linear expression including the acentric factor, ω, as follows:

$$\rho = [V_c(0.290\ 56 - 0.087\ 75\omega)^{(1-T_r)^{2/7}}]^{-1} \tag{2}$$

Poling et al.[5] report a mean deviation of 2.6% for eq 2 with respect to the values given in Appendix A (section B) of their book for a liquid temperature of 255 substances with $\omega < 0.4$, this being an improvement over the Rackett model.

Another correlation is that proposed by Reid et al.,[1] which we shall call the RRPS correlation. It is based on a proposal of Riedel[28] and requires the same inputs as the previous case (T_c, V_c, and ω) but does not include the temperature in the exponent:

$$\rho = \frac{1}{V_c}(1 + 0.85(1 - T_r) + (1.6916 + 0.984\omega)(1 - T_r)^{1/3}) \tag{3}$$

Nasrifar and Moshfeghian,[16] in a test of the accuracy of eq 3 for 15 pure refrigerants over a wide temperature range, find an average deviation of 1.1%.

The next method we tested was that proposed by Bhirud.[29] This is a Lee−Kesler type calculation, valid for $T_r < 0.98$ (tables are available for higher temperatures). Following Reid et al.,[2] for 752 data points for hydrocarbons with T_r between 0.3 and 1, the mean deviation is 0.8%. For 15 refrigerants over different temperature ranges, it is 2.3%.[16] The analytical expression is notably more complicated than the previous case:

$$\ln \frac{P_c}{\rho RT} = \ln V^{(0)} + \omega \ln V^{(1)} \tag{4}$$

where P_c is the critical pressure and the terms of the sum are[2]

$$\ln V^{(0)} = 1.396\ 44 - 24.076T_r + 102.615T_r^2 - 255.719T_r^3 + 355.805T_r^4 - 256.671T_r^5 + 75.1088T_r^6 \tag{5}$$

and

$$\ln V^{(1)} = 13.4412 - 135.7437T_r + 533.380T_r^2 - 1091.453T_r^3 + 1231.43T_r^4 - 728.227T_r^5 + 176.737T_r^6 \tag{6}$$

Another model based on the corresponding states principle is the so-called COSTALD (corresponding state liquid density) correlation.[30,31] It contains eight fixed constants and is valid for $0.25 < T_r < 0.95$. The acentric factor from the Soave equation of state and a volumetric parameter (near V_c) are needed as inputs. They have been tabulated by Hankinson and Thomson[30] and by Reid et al.[2] Nevertheless, Poling et al.[5] found that these values can be replaced by the usual values of the acentric factor and the critical volume, ω and V_c, with only a slight loss in accuracy. The resulting mean deviation for 225 substances with $\omega < 0.4$ is[5] 2.56% at a fixed liquid temperature for each fluid, an accuracy of the same order as that of the YG[27] method, eq 2. The COSTALD expression we used is

$$\rho^{-1} = V_c V^{(0)}[1 - \omega V^{(1)}] \tag{7}$$

with

$$V^{(0)} = 1 - 1.5281(1 - T_r)^{1/3} + 1.4390(1 - T_r)^{2/3} - 0.8144(1 - T_r) + 0.190\ 45(1 - T_r)^{4/3} \tag{8}$$

$$V^{(1)} = (-0.296\ 123 + 0.386\ 914T_r - 0.042\ 725\ 8T_r^2 - 0.048\ 064\ 5T_r^3)/(T_r - 1.000\ 01) \tag{9}$$

As can be seen, the inputs needed are T_c, V_c, and ω. The COSTALD correlation has frequently been used successfully.[3,4,16,32] In particular, Nasrifar and Moshfeghian[16] show that for 15 pure refrigerants this expression is better than 14 other expressions over a wide temperature range. Nevertheless, the analytical expression of eqs 7−9 is somewhat less straightforward than eq 3, although for $\omega < 0.4$, they deviate very little in results. [5]

As indicated above, one recent proposal is due to Queimada et al.,[20] and it is based on the use of the correlations proposed by the DIPPR project for two or three reference fluids, and then the first- or the second-order corresponding states theory is applied by interpolating with the acentric factor. The model is defined only for n-alkanes, from methane to n-hexatriacontane. The first-order model, which we shall denote as QSMC1, can be written as follows:

$$\rho_r = \rho_{r1} + \frac{\omega - \omega_1}{\omega_2 - \omega_1}(\rho_{r2} - \rho_{r1}) \tag{10}$$

where ρ_r is the reduced liquid density with respect to the critical value (ρ/ρ_c) and where the subscripts "1" and "2" correspond to the reference fluids chosen: butane and n-dodecane ($C_{12}H_{26}$). Values for the density of these fluids were calculated using the DIPPR correlations,[10,20] and values for their acentric factors are[10] $\omega_1 = 1.154\ 78 \times 10^{-2}$ and $\omega_2 = 0.576\ 385$, respectively. Following Queimada et al.,[20] the absolute average percentage deviation (AAD) of the QSMC1 model, eq 9, with respect to the DIPPR specific models for n-alkanes is only 0.65%.

The analytical expression for the second-order model, which we shall denote as QSMC2, is[20]

$$\rho_r = \rho_{r1} + \frac{\omega - \omega_1}{\omega_2 - \omega_1}(\rho_{r2} - \rho_{r1}) + D(\omega - \omega_1)(\omega - \omega_2) \tag{11}$$

with

$$D = \frac{[(\rho_{r3} - \rho_{r1})/(\omega_3 - \omega_1)] - [(\rho_{r2} - \rho_{r1})/(\omega_2 - \omega_1)]}{\omega_3 - \omega_2}$$

$$(12)$$

Subscripts 1−3 correspond to methane, *n*-pentadecane ($C_{15}H_{32}$), and *n*-hexacosane ($C_{26}H_{54}$), respectively. The new AAD was 0.44%. As indicated above, the application to other fluids was not considered and comparison with other methods was not made.

The most recent model for the saturation liquid density that uses the corresponding states principle and involves no adjustable coefficients for each fluid was proposed by Mchaweh et al.[21] This model is based on an earlier proposal of Nasrifar and Moshfeghian.[15] The main difference is that whereas the latter involves three adjustable coefficients for each fluid, the former uses the Soave−Redlich−Kwong equation-of-state temperature-dependent term and, hence, no adjustable coefficients. In both cases, however, an adjustable coefficient is required for each fluid to significantly improve the accuracy of the models. For the purpose of comparison with other predictive models, we shall use Mchaweh et al.'s model but without including that adjustable coefficient, with the critical temperature and density and the acentric factor being the required inputs. Following their notation, we denote this model the simplified-Nasrifar−Moshfeghian-0 (SNM0) correlation. Its analytical expression is

$$\rho_L(T) = \rho_C(1 + 1.169\tau^{1/3} + 1.818\tau^{2/3} - 2.658\tau +$$
$$2.161\tau^{4/3}) \quad (13)$$

where τ is a temperature-dependent variable defined by

$$\tau = 1 - (T/T_C)/[1 + m(1 - \sqrt{T/T_C})]^2 \quad (14)$$

with *m* being defined as in the Soave−Redlich−Kwong equation of state:

$$m = 0.480 + 1.574\omega - 0.176\omega^2 \quad (15)$$

Mchaweh et al.[21] used the SNM0 model, eqs 13−15, to predict the saturated liquid density of a great number of fluids of different classes. They showed that the SNM0 model gives practically the same overall accuracy as the original Nasrifar−Moshfeghian[15] model. The AAD for the fluids considered (including paraffins, cyclic paraffins, halogenated paraffins, olefins and cyclic olefins, aromatics, ethers, alcohols, and others) was 1.74%, with the maximum AAD being 2.86%, which was obtained for halogenated paraffins. Obviously, when an adjustable parameter is used the deviations are clearly smaller.

The last model we tested is based on the statistical mechanics or molecular version of the corresponding states principle. The reference data are the saturation densities for a Lennard-Jones fluid.[22] Then, for real fluids, one adds a perturbation term[22] which includes the acentric factor to take into account the deviation of real molecules from the Lennard-Jones model's spherical shape. The final analytical expression for the saturated liquid density, which we called the FMC expression, is[22]

$$\rho N_a \sigma^3 = \sum_{i=0}^{2} b_i (kT/\epsilon)^i + \omega \sum_{i=3}^{6} b_i (kT/\epsilon)^{i-3} + \omega^2 \sum_{i=7}^{9} b_i (kT/\epsilon)^{i-7}$$
$$(16)$$

where ϵ is the Lennard-Jones parameter giving the well depth of the intermolecular potential (and, hence, indicates the strength of the attractive forces), σ is the molecular distance at which the Lennard-Jones potential is zero (and, hence, indicates the

Table 1. Coefficients for the FMC Model,[22] Equation 16

i	b_i	*i*	b_i	*i*	b_i
0	0.877 283	4	−6.590 789	8	11.059 883
1	0.704 621	5	3.538 686	9	−5.551 122
2	−0.681 397	6	−0.377 065		
3	5.039 774	7	−1.802 264		

mean size of the molecules), *k* is Boltzmann's constant, and N_a is Avogadro's number. The values of the parameters b_i, which were obtained by fitting DIPPR values[24] for 42 fluids at different temperatures,[22] are given in Table 1. Appropriate values for ϵ and σ were obtained by Cuadros et al.[33] for 64 nonpolar fluids, following a new procedure designed by them. The basic idea of the procedure is to compare results for the pressure obtained from molecular simulation with those given by simple equations of state. We here applied that method to obtain values of ϵ and σ for all the fluids considered in the present work (data are available upon request). For the fluids where previous values of these parameters existed, only slight differences were found. As most of these substances were not considered in the fitting procedure of this model, the goodness of the present results is indicative of its potential for extrapolation.

Results

In this work, we used the Rackett, YG, RRPS, Bhirud, COSTALD, QSMC1, QSMC2, SNM0, and FMC models to calculate the liquid saturation density for 552 fluids, grouped into 30 families. No adjustable parameters were used, and values for the critical properties and acentric factor were those given by the DIPPR project. For the molecular model, the values of the parameter of the Lennard-Jones potential were obtained using the method given by Cuadros et al.[33] All the models require three input parameters, except the Bhirud model which requires four.

We calculated the percentage deviation (PD), in absolute value, of the values obtained from each correlation from those accepted by the DIPPR project for each fluid at every temperature. We also calculated the AAD for each fluid (within the range where data are available) and the mean value of the absolute PD (MAPD) for a family of fluids (i.e., by taking into account the number of available data for a family, not the number of fluids for each family). MAPDs for every family of fluids and every model are listed in two separate tables (Tables 2 and 3) to make it easier for the reader.

We must note that sometimes one finds two similar accepted values for the same or very similar temperatures. Moreover, for some fluids the number and the range of data available may be limited, whereas for other fluids one can find different data from several sources. Also, one has to keep in mind that when the temperature is close to the critical point, the liquid saturation density is low, so that the PDs of the models will be large even though the absolute deviations may generally be small.

Although the DIPPR (2003) project gives data for 558 fluids, we have eliminated the data for 6 of them. For these fluids we found very large deviations between the DIPPR data and those predicted by all the models used here. These fluids will be identified in the following subsections.

Also, we revised all the accepted DIPPR data and found erroneous values for some fluids. These erroneous values (which clearly do not agree with all the other accepted values for the same fluid) are clearly mistakes and were also eliminated from our analysis. These values are available upon request.

Finally, we remark that although most of the data included in the DIPPR database are experimental, there are some that were predicted using specific models.

Table 2. MAPDs of the Calculated Liquid Saturation Densities for Several Families of Fluids with Respect to the DIPPR[10] Data when Using Correlations[a–c]

family of fluids	N	ND	R	YG	RRPS	B	COSTALD	FMC	QSMC1	QSMC2	SNM0
n-alkanes	32	804	8.1	8.6	7.1	5.2	7.7	2.6	**2.1**	*1.3*	1.7
methylalkanes	17	591	2.9	**2.0**	**2.3**	**1.7**	**1.9**	**1.8**	**1.3**	1.9	*1.3*
dimethylalkanes	21	629	3.1	**2.4**	2.9	**2.4**	**2.3**	3.0	**1.6**	1.7	*1.5*
other alkanes	25	499	5.0	4.1	4.5	3.3	3.9	**3.1**	2.4	*2.1*	2.3
cycloalkanes	6	257	**0.9**	*0.6*	1.0	1.3	*0.6*	1.7	**0.9**	1.4	0.7
multiring cycloalkanes	3	55	**1.4**	1.7	2.3	2.9	**1.6**	2.8	*1.2*	1.3	1.5
alkylcyclopentanes	11	186	**1.9**	1.6	**2.0**	**1.9**	**1.5**	2.1	*1.1*	1.6	1.3
alkylcyclohexanes	16	189	5.1	**3.2**	3.4	4.5	**3.1**	4.4	*2.3*	2.9	**2.3**
1-alkenes	20	613	4.2	4.1	3.6	3.4	3.7	**2.1**	*1.2*	1.9	1.3
2,3,4-alkenes	18	170	**1.7**	**1.1**	*1.0*	1.3	**1.1**	1.5	1.2	2.5	1.3
methylalkenes	20	172	2.8	**1.8**	**1.8**	2.2	**1.8**	2.4	*1.4*	2.1	1.5
ethyl & higher alkenes	11	129	3.3	**2.6**	3.2	3.6	**2.6**	3.6	**2.2**	*1.8*	**2.2**
cycloalkenes	9	102	1.6	**0.7**	**0.9**	1.6	**0.7**	**1.5**	*0.5*	1.6	**0.6**
dialkenes	26	385	**2.6**	1.9	1.7	4.8	1.9	5.3	*1.6*	2.9	**1.8**
alkynes	18	281	**2.8**	2.5	2.7	5.0	2.3	4.6	*1.8*	2.4	*1.8*
n-alkylbenzenes	19	879	6.3	5.5	4.7	3.7	5.2	**2.7**	**2.6**	2.8	*2.2*
other alkylbenzenes	43	967	**1.5**	**1.3**	*1.1*	1.9	**1.3**	2.9	2.5	3.2	2.5
other monoaromatics	16	156	3.7	*0.9*	**1.1**	4.3	**1.0**	5.5	**1.9**	2.6	2.1
naphthalenes	16	287	**3.3**	**2.5**	*2.4*	2.8	**2.5**	2.9	4.0	4.3	4.6
other condensed rings	2	32	8.0	**1.3**	*1.1*	13.2	1.8	14.2	5.5	5.9	4.9
diphenyl/polyaromatics	12	128	5.8	**3.3**	**3.1**	10.7	**3.0**	9.9	**3.1**	3.7	*2.8*
terpenes	6	75	8.1	5.2	5.9	**1.8**	5.0	*1.1*	2.8	2.4	2.5
other hydrocarbon rings	15	174	5.0	*1.9*	2.1	4.9	*1.9*	5.1	2.9	3.3	3.0

[a] The numbers in italics represent the lowest MAPDs, and the numbers in bold show MAPDs that are similar (±1%) to the lowest one. [b] R = Rackett[26], eq 1; YG = Yamada and Gunn,[27] eq 2; RRPS = Reid et al.,[1] eq 3; B = Bhirud,[29] eqs 4−6; COSTALD,[30−31] eqs 7−9; QSMC1 = Queimada et al.,[20] eq 10; QSMC2 = Queimada et al.,[20] eq 11; SNM0 = Mchaweh et al.,[21] eqs 13−15; FMC = Faúndez et al.[22], eq 16. [c] N = number of fluids, ND = number of data.
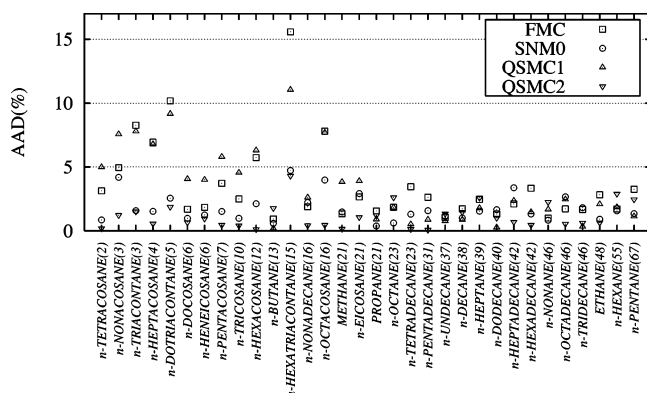
Figure 1. AAD (%) for the liquid saturation density of *n*-alkanes obtained using different correlations (see caption to Table 1). The number of available data points for each fluid is given in parentheses.

1. Results for Alkanes, Alkenes, Aromatics, and Some Other Hydrocarbons. Table 2 presents the results for 382 fluids grouped into 23 families. As it can be seen, the recent models give the best results for *n*-alkanes. This is an expected result. In particular, the QSMC1 and QSMC2 models were constructed[20] by using data for *n*-alkanes and using two or three *n*-alkanes as references. Obviously, the QSMC2 model is more accurate than the QSMC1 model for this family of fluids. Nevertheless, as is shown in Figure 1, significant differences are found for some fluids between the AADs obtained with these two models. The QSMC1 and QSMC2 models were tested by Queimada et al.[20] to reproduce data of alkanes at fixed temperatures, whereas our comparison is made with respect to the accepted data. Hence, the deviations given here differ from those published by Queimada et al.[20] Thus, their MAPDs for *n*-alkanes (0.65 and 0.44%) are clearly lower than those given in Table 2.

As observed in Table 2 and Figure 1, the SNM0 and QSMC2 models give practically the same values for the MAPD and AADs. Considering that the SNM0 model is perhaps simpler and gives better results than the QSMC1 model (specifically constructed for *n*-alkanes), the former seems to be the more appropriate and straightforward predictive model for *n*-alkanes.

As expected, most of the models, and especially the classical ones, are adequate for light *n*-alkanes but not for heavy *n*-alkanes. This is clearly shown in Figure 1, where one can see that the greatest deviations are found for *n*-hexatriacontane ($C_{36}H_{74}$).

As expected, the results for the FMC model are greatly influenced by the inadequate prediction for data near the critical point. In any case, it has to be taken into account that it is the only model not including the critical temperature as input and that despite this the MAPD is only 2.64%. Indeed, only for *n*-hexatriacontane is the AAD given by the FMC model greater than 11% (see Figure 1).

All the models give low MAPDs for methylalkanes and dimethylalkanes, with the lowest values being obtained by using the three most recent models (QSMC1, QSMC2, and SNM0). Despite the Bhirud and FMC models giving adequate results for most of the fluids, the former must not be applied at very low temperatures, and neither model must be applied at very high temperatures (T_r near 1).

For 25 other alkanes (including such substances as[10] 3-ethylheptane, squalane, or 2,2,4,4,6,8,8-heptamethylnonane) we found that, contrary to the results obtained with the preceding families, even the best models are incapable of predicting data with MAPDs below 2.2%. The worst results are obtained for squalane, for which none of the models reproduce the trend of the data adequately. In this case, the adequate location of the critical point must be taken into account before applying any of the models.

In a general sense, all the models work very adequately for cycloalkanes, multiring cycloalkanes, and alkylcyclopentanes. Surprisingly, for cycloalkanes the QSMC2 model gives a greater MAPD than that obtained with QSMC1. We note also that the obtained MAPDs for the FMC model are influenced by the poor results obtained for data near the critical point. We also note that the Bhirud model does not behave adequately for low
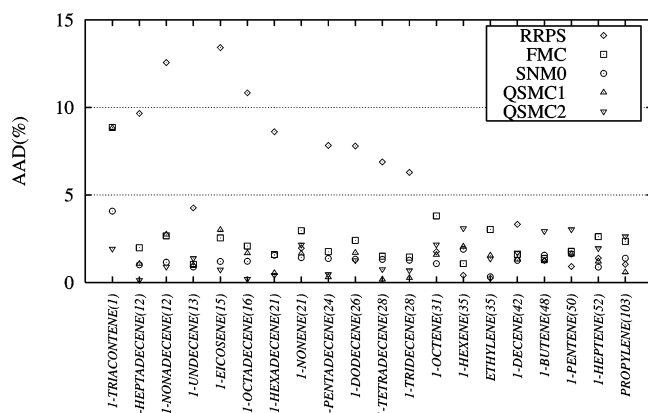
Figure 2. AAD (%) for the liquid saturation density of 1-alkenes obtained using different correlations (see caption to Table 1). The number of available data points for each fluid is given in parentheses.
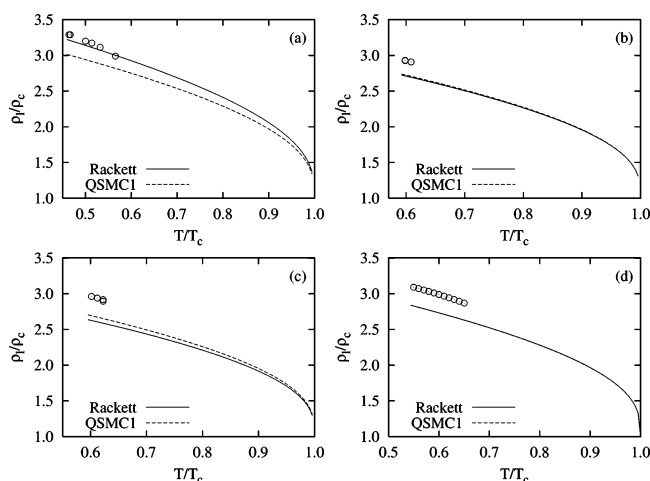
Figure 3. Reduced density versus reduced temperature for four dialkenes: (a) dicyclopentadiene; (b) 3-methyl-1,2-butadiene; (c) 1,4-pentadiene; (d) and 2,3-pentadiene. Points are DIPPR data, and lines are values given using the Rackett and QSMC1 correlations.

temperatures when applied to ethylcyclopentane and methylcyclopentane.

The QSMC1 and SNM0 models give the better results for alkylcyclohexanes. When these two models are used, the highest AADs are found for four fluids (*trans*-1,3-dimethylcyclohexane, *cis*-1,4-dimethylcyclohexane, *cis*-1,2-dimethylcyclohexane, *trans*-1,2-dimethylcyclohexane) for which only three data points at low temperatures are available. More data for these fluids or more accurate values for their critical properties are needed to confirm the lack of validity of the selected models. For other fluids with only one, two, or three data points the models work better.

The QSMC1 and SNM0 models are very adequate for both 1-alkenes and 2,3,4-alkenes, giving very similar MAPDs. The greatest deviations for most of models are found for 1-triacontene (see Figure 2, where the AAD obtained for this fluid by the RRPS model is not shown), for which only one datum point is available.

In Figure 2, the RRPS model is included as representative of the behavior of the classical models. As can be seen, the high MAPDs found for the classical models are due to the poor results obtained for 10 of the 20 1-alkanes selected. Obviously, for these fluids the classical models should not be used. One observes from Table 2 and Figure 2 that the FMC model is a good alternative to the most recent models.

For 2,3,4-alkenes all the models are accurate, with RRPS giving the lowest MAPD and, surprisingly, QSMC2 the highest.

For cycloalkenes it has to be taken into account that 46 of the 102 data points used are for the same fluid (cyclohexene) for which all the models are very accurate and that the highest reduced temperature for which data are available is 0.67 (also for cyclohexene).

Large MAPDs are found when the Bhirud or the FMC models are used for dialkenes. These high values are due to the poor behavior of these models for some particular fluids; that is, they work adequately for some other fluids of this family. As can be seen in Table 2, all the other models give MAPDs lower than 3%. Nevertheless, as can be seen in Figure 3, for dicyclopentadiene only the Rackett model gives a low AAD, and moreover there are three fluids for which no model predicts adequately the liquid densities. In Figure 3 the prediction given by the QSMC1 model is representative of the behavior of all the other models for these fluids.

For alkynes QSMC1 and SNM0 are the models giving the lowest MAPDs, whereas the Bhirud and FMC models give the largest ones. The Rackett model must be used with caution because it gives excellent results for some fluids (e.g., vinylacetylene and 2-pentyne) but inadequate results for others (e.g., 3-methyl-1-butyne).

For *n*-alkylbenzenes the four most recent models give a significant improvement with respect to the "classical" ones. For some fluids (such as benzene and toluene) all the models behave similarly and give good accuracies. For most of the others (such as *n*-hexadecylbenzene, *n*-octadecylbenzene, and *n*-hexylbenzene), however, a clear difference in accuracy between the classical models and recent models is found.

Although the classical models seem not to be completely adequate for *n*-alkylbenzenes, we found surprisingly that for other alkylbenzenes these classical models give smaller MAPDs than the recent models. In any case, the MAPDs for the latter are below 3.3%. For those fluids for which data are available near the critical point (*p*-xylene, *m*-xylene, *o*-xylene, 1,2,4,5-tetramethylbenzene, and cumene) all the models except Bhirud and FMC can be used. On the other hand, for *o*-diethylbenzene and 3-ethyl-*o*-xylene no model can predict with accuracy (AADs and PDs greater than 4%) the data reported by the DIPPR project.

As in the preceding cases, for other monoaromatics we found that some classical models (YG, RRPS, and COSTALD) are significantly more accurate than the most recent models. In any case, QSMC1 and SNM0 give MAPDs below 2.2% and PDs below 9.7%. In particular, we found that only for *p*-methylstyrene all the models clearly disagree (AADs > 6.8%) with the three DIPPR accepted data points. Moreover, large discrepancies between the values predicted by each model are found when only one or two data points are available; that is, for these fluids the appropriate model must be chosen individually.

For naphthalenes the YG, RRPS, Bhirud, COSTALD, and FMC models are the only ones giving MAPDs below 3%. For some fluids the choice of one or another of these models leads to clearly different results. Thus, for example, the Bhirud and FMC models are the only ones that reproduce the three available data points for 2,7-dimethylphthalene. Other examples are shown in Figure 4. Thus, in Figure 4a one can see that the RRPS model is inadequate for 1,2,3,4-tetrahydronaphthalene, with the Bhirud or FMC models clearly being more appropriate (except very near the critical point). Nevertheless, for some other fluids such as 1-phenylnaphthalene, shown in Figure 4b, RRPS works very accurately. SNM0 (and similarly QSMC1 and QSMC2) seem
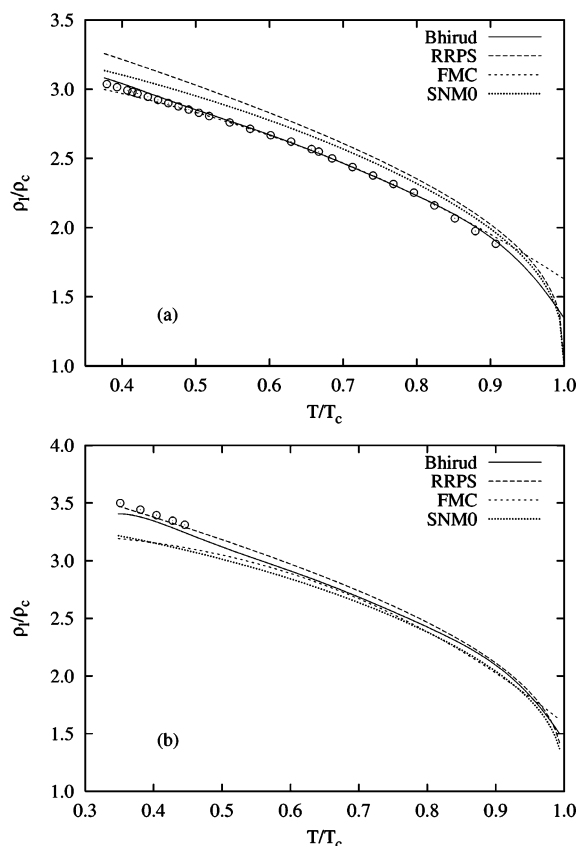
Figure 4. Reduced density versus reduced temperature for two naphthalenes: (a) 1,2,3,4-tetrahydronaphthalene and (b) 1-phenylnaphthalene. Points are DIPPR data, and lines are values given using different correlations.

not to be very adequate for these two fluids (see Figure 4) and some other fluids of this kind. In some other cases, nevertheless, they behave similarly to the classical models.

Data for three other condensed rings were taken from the DIPPR database. For the only polar substance, acenaphthene, we found that all the models give AADs greater than 14.5%. It was, thus, not considered in the calculation of the MAPDs given in Table 2, where we can see that for the other two fluids (anthracene and phenanthrene), large differences are found between the accuracy of the models.

The results in Table 2 show that both the Bhirud and the FMC models are inadequate for most of the diphenyl/polyaromatics substances included in this study. All the other models can be used, in a general sense, with SNM0 giving the smallest MAPD. Nevertheless, all the models must be used with caution for diphenylacetylene, because PDs greater than 4% are always found.

The FMC model is very adequate for terpenes. This is due to the fact that most of the data are for low temperatures. The FMC model can be used to predict data at higher temperatures but not near the critical point.

In summary, our results show that both the SNM0 and QSMC1 models are very adequate to predict the liquid saturation densities of most of the selected fluids included in Table 2, with only some exceptions such as the disagreement found for the data used for acenaphthene, for which all the other models also clearly disagree, and for some naphthalenes. The results obtained with the SNM0 and QSMC1 models clearly improve those obtained with the classical Rackett, YG, RRPS, Bhirud, and COSTALD models for n-alkanes (especially for the heavier n-alkanes), alkylcyclohexanes, 1-alkenes, and n-alkylbenzenes and perhaps less clearly for dimethylalkanes, other alkanes, and

alkynes. For other alkylbenzenes, other monoaromatics, naphthalenes, other condensed rings, and other hydrocarbon rings, however, that improvement is not found. Indeed, for these families and some others the classical models give good results, with YG, RRPS, and COSTALD providing the best results.

The QSMC1 and QSMC2 models were constructed by using data only for n-alkanes, but as we have shown here, they can be applied to more families of fluids. QSMC2, being clearly less straightforward than QSMC1, gives at most similar or even sometimes poorer accuracy than QSMC1, and its use is only justified for some heavier n-alkanes.

Despite the poor results obtained using the Rackett model for some fluids, this very simple model predicts the selected data with MAPDs less than 4% for 14 of the 23 selected families.

The high deviations obtained using the Bhirud model for some fluids are generally due to its poor behavior for low temperatures (i.e., near the triple point) and/or high temperatures (i.e., near the critical point). The use of this model can only be recommended if one requires small deviations for terpenes.

The results for the FMC model are influenced by the fact that this model does not include the critical temperature and density as input. It can, therefore, not be applied for any fluid near the critical point. This model is especially accurate for terpenes at temperatures near the triple point. It is not very accurate, in a general sense, for alkylcyclohexanes, dialkenes, alkynes, other monoaromatics, other condensed rings, diphenyl/aromatics, and other hydrocarbon rings.

From a practical point of view, the SNM0 model is straightforward (it contains only seven coefficients and three input parameters), so we recommend the use of this model for most of the families of fluids listed in Table 2.

Finally, we would remark that for some fluids (such as squalane, 1,4-pentadiene, o-diethylbenzene, 3-ethyl-o-xylene, p-methylstyrene, diphenylacetylene, and acenaphthene), none of the models agree with the data accepted by the DIPPR project. The use of specific models (with adjustable coefficients for each) should be considered. Perhaps the value of their critical properties and acentric factors, as well as the source of the data, should also be carefully revised.

2. Results for Aldehydes, Ketones, and Alcohols. The results for 170 fluids grouped into 7 families of aldehydes, ketones, and alcohols are presented in Table 3. Although the highest reduced temperature for which data are available is 0.705, Table 3 shows that both the Bhirud and the FMC models are inadequate for aldehydes. The Rackett model also gives a clearly high MAPD. Nevertheless, it is the only model that gives small AADs for some fluids for which only one or two data points are available (formaldehyde, glutaraldehyde, glyxoal, and methacrolein). All the other models behave similarly, with SNM0 and QSMC1 being the ones giving the smallest MAPDs. In any case, these two models must be used with caution in predicting densities for some fluids when few data are available.

The Rackett, Bhirud, and FMC models give the greatest MAPDs for ketones. An exception is 3-pentanone, for which only the Bhirud and FMC models predict values near those accepted by the DIPPR project. As can be seen in Figure 5, for some of them the recent models give the smallest AADs, whereas for others the classical models agree better with the available data. Finally, we note that for acetylacetone none of the models agree with the available data.
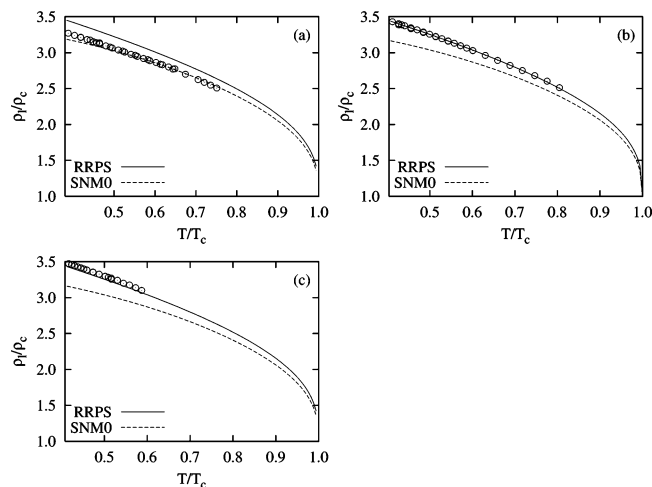
As is seen from Table 3, the use of the most recent models clearly improves the prediction of the saturation densities of n-alcohols with respect to the accuracy given by the classical

Table 3. MAPDs of the Calculated Liquid Saturation Densities for Several Families of Fluids with Respect to the DIPPR[10] Data when Using Correlations[a]
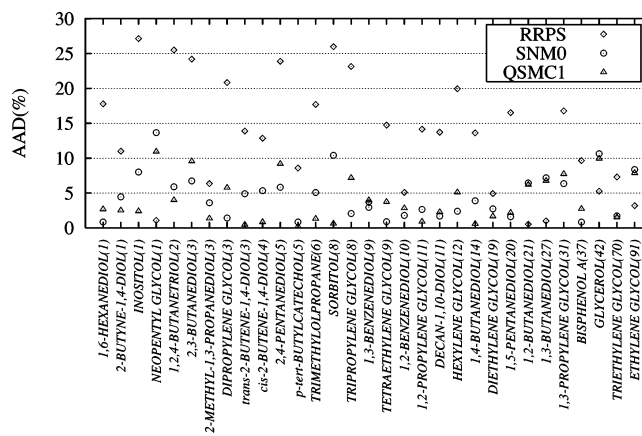
family of fluids	N	ND	R	YG	RRPS	B	COSTALD	FMC	QSMC1	QSMC2	SNM0
aldehydes	29	185	5.0	**3.0**	**2.9**	9.9	**2.9**	9.4	*2.7*	3.2	2.5
ketones	33	500	6.8	**2.5**	**2.7**	6.3	*2.4*	6.9	3.1	3.3	3.1
n-alcohols	20	668	7.3	8.3	7.9	10.7	7.5	7.6	**3.0**	*2.8*	2.8
cycloaliphatic alcohols	9	75	2.6	8.3	7.9	17.1	7.5	14.2	**1.9**	*1.5*	1.9
aromatic alcohols	21	165	5.9	8.8	7.9	20.7	8.0	16.1	*3.3*	3.5	3.7
other aliphatic alcohols	27	603	3.9	4.3	4.3	12.6	3.6	10.1	**2.1**	2.6	*1.5*
polyols	31	488	10.4	12.8	8.9	28.8	11.2	19.6	*4.9*	6.5	**5.0**

[a] See footnotes to Table 2 for the meanings of each column. The numbers in italics represent the lowest MAPDs, and the numbers in bold show MAPDs that are similar (±1%) to the lowest one.
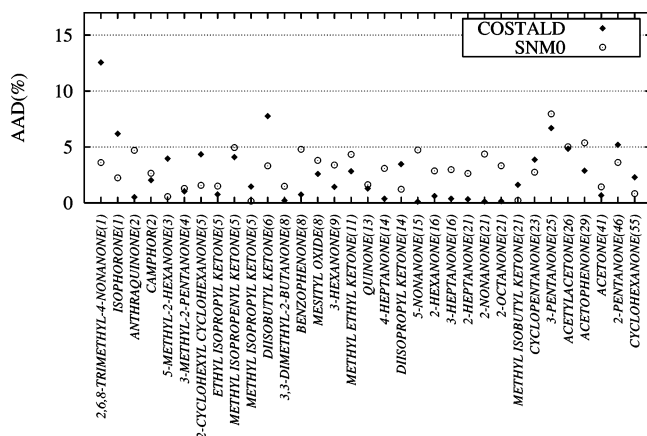
Figure 5. AAD (%) for the liquid saturation density of ketones obtained using the COSTALD and SNM0 correlations. The number of available data points for each fluid is given in parentheses.

Figure 7. AAD (%) for the liquid saturation density of polyols obtained using the RRPS, SNM0, and QSMC1 correlations. The number of available data points for each fluid is given in parentheses.

Figure 6. Reduced density versus reduced temperature for three n-alcohols: (a) 1-octanol; (b) 1-decanol; and (c) 1-undecanol. Points are DIPPR data, and lines are values given using the RRPS and SNM0 correlations.

models. A clear example is shown in Figure 6a, in which RRPS and SNM0 are representative of the behavior of the classical and recent models, respectively. There are no fluids with only one datum point, and only four fluids have fewer than four data points available. For 1-pentadecanol, 1-heptadecanol, 1-nona-decanol, and 1-eicosanol (four available data points), for 1-hexadecanol (44 available data points), and for 1-octadecanol (37 available data points), all the models give PDs greater than 4%. As it is shown in Figure 6b,c, for 1-decanol and 1-unde-canol, respectively, the classical models agree with the data better than the most recent models.

For cycloaliphatic alcohols the recent QSMC1, QSMC2, and SNM0 models clearly improve the results obtained using the

classical models. Nevertheless, for some fluids of this family the Rackett model predicts the available data better than the recent models (L-menthol is a clear example).

We found that for five aromatic alcohols (phenol, o-cresol, p-cresol, 3,5-xylenol, and o-ethylphenol) none of the selected models can be used with accuracy, so they were not considered in our analysis. Results for another 21 aromatic alcohols are given in Table 3. For these fluids the recent models clearly work better than the classical ones with only three exceptions: benzyl alcohol, p-cumylphenol, and 2,5-xylenol. The simple Rackett method is the only classical model giving a MAPD below 6% and, in particular, is the only model predicting the DIPPR accepted data for 2,5-xylenol.

For other aliphatic alcohols the SNM0 model gives the smallest MAPD, with QSMC1 being a good alternative. The Bhirud and FMC models are clearly inadequate for most of these fluids. The other classical models give more heterogeneous results; that is, for some fluids they even improve the results obtained with the recent models (as in the case of 2-nonanol, 2-octanol, and 3-methyl-3-pentanol), but for some other fluids (generally with a low number of available data), they clearly disagree with the data used here.

As can be seen in Figure 7, only for the five polyols does the classical model work better than the recent ones. In particular, for 2,4-pentanediol the Rackett or the QSMC2 models agree better than those shown in Figure 7. For 1,3-propylene glycol all the models give AADs greater than 6.3% (see Figure 7). Finally, for glycerol (Figure 8) and ethylene glycol some models give low AADs, although the trend of the data is not adequately reproduced.

In summary, for the families of fluids listed in Table 3, we found that, in a general sense, the recent QSMC1, QSMC2, and SNM0 models improve the predictions of the liquid saturation densities obtained with the classical models for n-alcohols,
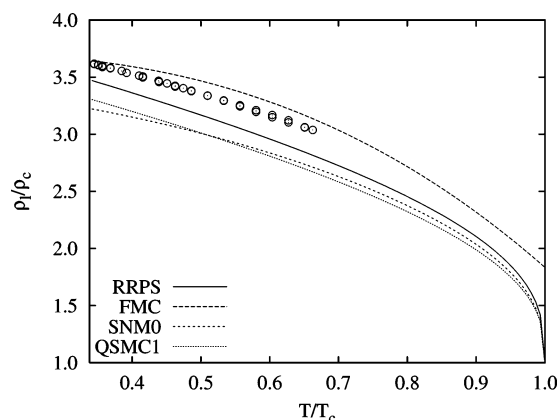
Figure 8. Reduced density versus reduced temperature for glycerol. Points are DIPPR data and lines are values given using different correlations.

cycloaliphatic alcohols, most aromatic alcohols, other aliphatic alcohols, and polyols. Obviously this is just a general rule with some particular exceptions for certain fluids of these families. Thus, we have found that, for some fluids (such as ethanol, methanol, and 1-propanol), although the recent models predict clearly better the behavior of the density near the triple point, they can give large deviations near the critical point where the classical models seem to be more adequate.

For aldehydes and ketones we found that the classical YG, COSTALD, and RRPS models work as well as the most recent models. Moreover, results found for polyols indicate that the models must be carefully chosen for some fluids of this family, because heterogeneous results are found. We also found that none of the analyzed models agree with the data accepted by the DIPPR project for acetylacetone, 1,3-propylene glycol, and the five aromatic alcohols (these last were not included in Table 3).

The Bhirud and FMC models are not very adequate in a general sense, although they can be the only models predicting the available data for some fluids near the triple point. The Rackett model can give very good results for some fluids but also very poor results for others; that is, it does not behave homogeneously.

The behavior of the models proposed by Queimada et al. is excellent if one takes into account that they were constructed using data for *n*-alkanes as reference fluids. The SNM0 model seems straightforward, and we recommend its use, always bearing in mind the aforementioned exceptions.

Conclusions

We have checked the validity of nine predictive empirical correlations, based on the corresponding states principle, for the calculation of the liquid saturation density of 552 pure fluids grouped into 30 families. As a reference, we took the data accepted by the DIPPR project. For six fluids (squalane, 1,4-pentadiene, *o*-diethylbenzene, 3-ethyl-*o*-xylene, *p*-methylstyrene, diphenylacetylene, and acenaphthene), we found great or even very great disagreement between these data and those obtained using all the models selected. That lack of agreement could be due to the need to use more specific correlations or perhaps to unidentified mistakes in the DIPPR accepted data for the saturation liquid density, the critical properties, and the acentric factor for those substances.

Our results show that the recent SNM0, QSMC1, and QSMC2 models are very adequate to predict the liquid saturation densities of most of the fluids selected, with only a few exceptions. In particular, the results obtained with these recent models clearly improve those obtained with the classical models for *n*-alkanes (especially for the heavier *n*-alkanes), alkylcyclohexanes, 1-alkenes, *n*-alkylbenzenes, *n*-alcohols, cycloaliphatic alcohols, aromatic alcohols, other aliphatic alcohols, and polyols. There was perhaps a less clear improvement for dimethylalkanes, other alkanes, and alkynes. On the other hand, for other alkylbenzenes, other monoaromatics, naphthalenes, other condensed rings, and other hydrocarbon rings the classical YG, COSTALD, and RRPS models gave the best results. There were also some other families of fluids (such as cycloalkanes, 2,3,4-alkenes, dialkenes, diphenyl/polyaromatics, aldehydes, ketones, and some others) for which the choice of one of the aforementioned classical or recent models had no influence on the general results.

Obviously all the above conclusions are general rules with some particular exceptions for particular fluids of those families. Thus, for example, the results found for polyols indicate that the models must be carefully chosen for some fluids of this family, because some of the results were very heterogeneous.

The Rackett model does not behave homogeneously. Despite the poor results obtained for some fluids, this very simple model predicts the data analyzed with MAPDs less than 4% for 16 of the 30 families selected.

The Bhirud and FMC models are not very adequate in a general sense. The large deviations obtained using the Bhirud model for some fluids are generally due to its poor behavior for low temperatures (i.e., near the triple point) and/or high temperatures (i.e., near the critical point). The use of this model can only be recommended if one requires small deviations for terpenes. The results for the FMC model are influenced by the fact that this model does not include the critical temperature and density as input. It cannot, therefore, be applied for any fluid near the critical point, but it is especially accurate for terpenes at temperatures near the triple point. Despite the above comments, these two models are the only ones predicting the available data for some fluids far from the critical point.

The QSMC1 and QSMC2 models were constructed using data only for *n*-alkanes, but as we have shown here, they can be applied to more families of fluids. QSMC2, being less straightforward than QSMC1, gives generally poorer accuracy than QSMC1, and its use is only justified for some heavier *n*-alkanes.

From a practical point of view, the SNM0 model is straightforward (it contains only seven coefficients and three input parameters) and gives a MAPD less than or equal to 5% for all the families included in Tables 2 and 3. We recommend the use of this model for most of the families of fluids considered in this work. Perhaps new coefficients could be obtained to improve the results for some families of fluids such as naphthalenes, other condensed rings, and polyols.

The study of the behavior of those nine models for other families of fluids is in progress.

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