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A New Analytical Model for the Prediction of Vapor–Liquid Equilibrium Densities

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A new simple, predictive model for estimating both the vapor and the liquid densities of fluids at the vapor–liquid equilibrium is presented. It is based on the symmetry of the derivatives of the two saturation densities with respect to the temperature, which is a consequence of applying the rectilinear diameter law. No adjustable coefficients are involved, and only two parameters—both with certain physical meaning—have to be calculated for each fluid. The method used for these calculations is straightforward, the required inputs being the critical temperature and density, and the value of the vapor and liquid densities at a reference temperature. The results show that the model is accurate for fluids of different kinds as long as the rectilinear diameter law holds, and that, in general, the accuracy is better than that of the most recent model with no adjustable coefficients.

KEY WORDS: pure fluids; saturation densities; vapor–liquid equilibrium.

1. INTRODUCTION

The calculation of saturated densities of pure substances at vapor–liquid equilibrium is essential for important practical applications, and serves as the basis for calculating other properties [1, 2], such as, for example, the surface tension [3, 4]. There are many accurate empirical correlations giving the saturated liquid-density [1, 2]. The simplest are based on applying the corresponding-states method with the critical parameters and the acentric factor as input data [1, 2, 5–11]. There are also proposals that

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include physical constants corresponding to each substance and at least one adjustable parameter [11–14].

Studies of the accuracy and applicability of these models to different kinds of fluids, generally in the temperature range where experimental data are available, have led to recommendations for the use of various methods [1, 2, 11, 13]. Obviously, correlations that include adjustable parameters are more accurate than those without them. Nevertheless, their disadvantage is the need for experimental data against which to evaluate these adjustable parameters, with the concomitant relative lack of predictability. In any case, it is very important to choose the appropriate model for a given kind of fluid or even for a particular fluid at a particular temperature [1, 2, 15]; i.e., there is no universal model that yields very accurate results for all kinds of fluids. Results for the saturated vapor-density have generally not been studied.

As a step in the search for a more universal model, Okrasinski et al. [16] have proposed an analytical model that reproduces both the vapor and liquid saturation densities at vapor–liquid equilibrium of Lennard-Jones fluids obtained by Lotfi et al. [17] by computer simulation, as well as of those obtained from equations of state [18–21]. The starting point in constructing the model is the use of the rectilinear diameter law and the temperature derivatives of the densities. The result is a simple analytical expression with which these densities can be reproduced for any temperature, even near the critical point [16, 21].

In the present work, we apply the Okrasinski et al. [16] method to real fluids, suitably modifying the procedure to obtain the two parameters in the analytical expression. One of these parameters is related to the slope of the rectilinear-diameter equation, and the other to the location of the critical point [17, 22]. Both parameters thus have physical meaning. Only the critical temperature and density of the fluid and the value of the two densities at a reference temperature are needed as input.

The model is then used to predict equilibrium densities for 29 fluids of different kinds. The results are compared with those in the NIST and DIPPR database [23, 24], the Reynolds' book [25], and also with those given by the most recent predictive correlation due to Mchaweh et al. [11]. The results of the proposed model are not only comparable to or even better than the latter, but are also independent of the fluid under study (which is not the case with other simple models), if the rectilinear-diameter law holds. In particular, it is known that simple fluids and several interatomic model potentials [26] clearly fulfill this law. Nevertheless, deviations have been observed for some fluids (water being a clear example), especially near the critical point (see [27] and references therein).

The paper is organized as follows. First, we describe the proposed model and the Mchaweh et al. [11] correlation. Second, the results are given, and commented on. Finally, the main conclusions are presented.

2. MODEL FOR THE VAPOR–LIQUID SATURATION DENSITIES

The model of Okrasinski et al. [16] for Lennard–Jones fluids has a threefold basis:

(i) The temperature derivatives of both the saturation vapor and the liquid densities are symmetrical with respect to an axis located at a distance from the temperature axis equal to the slope of the rectilinear-diameter equation.

(ii) By reflecting one of the derivatives with respect to that symmetry axis, the two derivatives can be fitted simultaneously.

(iii) Both saturation densities at the critical temperature must be equal to the critical density.

Using the same procedure, we propose here the following analytical expression for the temperature derivative of the vapor-density:

$$\dot{\rho}_{\mathrm{V}}(T) = a + \frac{b}{(T_{\mathrm{C}} - T)^{\alpha}} \tag{1}$$

where T_{C} is the critical temperature, and a, b, and α are coefficients [16]. The derivative for the liquid-density can be obtained from

$$\dot{\rho}_{\mathrm{L}}(T) = 2h - \dot{\rho}_{\mathrm{V}}(T) \tag{2}$$

where h is the slope of the rectilinear diameter, which can be obtained from a knowledge of the critical density and temperature (ρ_{C} and T_{C}) and the saturation densities at a reference temperature ($T_0, \rho_{\mathrm{V0}}, \rho_{\mathrm{L0}}$):

$$h = \frac{\rho_{\mathrm{C}} - (\rho_{\mathrm{V0}} + \rho_{\mathrm{L0}})/2}{T_{\mathrm{C}} - T_0} \tag{3}$$

To obtain the final analytical expression, the derivatives must be integrated, which again requires the same reference data:

$$\begin{aligned} \rho_{\mathrm{V}}(T) &= \rho_{\mathrm{V0}} + \int_{T_0}^{T} \dot{\rho}_{\mathrm{V}}(T)dT \\ \rho_{\mathrm{L}}(T) &= \rho_{\mathrm{L0}} + \int_{T_0}^{T} \dot{\rho}_{\mathrm{L}}(T)dT \end{aligned} \tag{4}$$

Our aim is to apply Eq. (1) to real fluids by establishing a straightforward procedure to fix the values of the coefficients from a knowledge of the critical temperature and density and the two densities at a reference temperature.

The first step is to take into account that the coefficient α is related to the critical exponent of the densities [28, 29], β. We propose the following simple relationship:

$$\alpha = 1 - \beta \tag{5}$$

However, since data are needed for the two densities near the critical point to determine the value of β, the model will not be predictive. We here, therefore, take a fixed value $\beta = 1/3$, which is an average value proposed some time ago by Guggenheim [28, 29]. The value of α is therefore also fixed, $\alpha = 2/3$, for all the fluids studied. Obviously, this means that there will be deviations in the calculation of densities near the critical point for those fluids for which β differs from this value. The advantage of taking a fixed value is that the model is predictive and simple, and, as will be shown below, yields good results for different kinds of fluids.

The coefficient b in Eq. (1) must be related to the slope of the rectilinear diameter. In seeking to establish a simple procedure to estimate this coefficient, we studied its behavior for several fluids in relation to the well-known behavior for Lennard–Jones fluids [17–22]. We observed the following simple relationship:

$$b = k\, T_{\mathrm{C}}^{\alpha - 1} \rho_{\mathrm{C}} \tag{6}$$

with k given by known quantities for the Lennard–Jones fluid:

$$k = -h_{\mathrm{LJ}}\, T_{\mathrm{C-LJ}}^{1-\alpha} \rho_{\mathrm{C-LJ}}^{-1} \tag{7}$$

where $h_{\mathrm{LJ}}, T_{\mathrm{C-LJ}}$, and $\rho_{\mathrm{C-LJ}}$ are values, in reduced units, of the slope of the rectilinear diameter and the critical properties for Lennard–Jones fluids [17, 22]. Thus, by using the Lotfi et al. [17] data ($T_{\mathrm{C-LJ}} = 1.31$ and $\rho_{\mathrm{C-LJ}} = 0.314$) one obtain $h_{\mathrm{LJ}} = -0.18075$. With fixed $\alpha = 2/3$, this gives $k = 0.629885$. If the more recent data of Potoff and Panagiotopoulos [22] are preferred ($T_{\mathrm{C-LJ}} = 1.312$ and $\rho_{\mathrm{C-LJ}} = 0.316$), then $k = 0.626185$. Values for the obtained saturation densities are practically identical, so we have chosen $k = 0.629885$ in our calculations.

Finally, the coefficient a in Eq. (1) is obtained by taking into account that the two densities must be equal to the critical density at the critical temperature, so that

$$a = \frac{\rho_{\mathrm{C}} - \rho_{\mathrm{V0}}}{T_{\mathrm{C}} - T_0} - \frac{b\,(T_{\mathrm{C}} - T_0)^{-\alpha}}{1 - \alpha} \tag{8}$$

The final general expressions for the two saturation densities are

$$\rho_V(T)=\rho_{V0}+a(T-T_0)-\frac{b\left[(T_C-T)^{1-\alpha}-(T_C-T_0)^{1-\alpha}\right]}{1-\alpha} \tag{9a}$$

$$\begin{aligned}\rho_L(T)=\rho_{L0}&+2h(T-T_0)-a(T-T_0)\\&+\frac{b\left[(T_C-T)^{1-\alpha}-(T_C-T_0)^{1-\alpha}\right]}{1-\alpha}\end{aligned} \tag{9b}$$

where T is in K, and the densities are in $\text{mol}\cdot\text{L}^{-1}$.

In summary, for a given fluid, the critical temperature and density and the coexistence densities at a reference temperature are the needed input parameters. Since all the coefficients and properties, except the temperature, are constants for a given fluid, the resulting expression for each fluid is simple, and can be applied straightforwardly. Indeed, for a given fluid and for $\alpha=2/3$, the final expressions are

$$\begin{aligned}\rho_V(T)&=\rho_C-a(T_C-T)-3b(T_C-T)^{1/3}\\\rho_L(T)&=\rho_C+(a-2h)(T_C-T)+3b(T_C-T)^{1/3}\end{aligned} \tag{10}$$

where a, b, and h are obtained from Eqs. (8), (6), and (3), respectively.

Note that the expression for the liquid density given in Eq. (10) is very similar to the model proposed by Reid et al. [1]. A clear difference is that our proposal does not include any coefficient obtained from fits to experimental data.

In order to study the suitability of the proposed model, we compared it with a recent model [11] for the saturated liquid density that uses the corresponding-states principle and involves no adjustable coefficients for a fluid, with the critical temperature and density and the acentric factor being the required inputs. This model was proposed by Mchaweh et al. [11], and is based on an earlier proposal of Nasrifar and Moshfeghian [12]. 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 in order to significantly improve the accuracy of the models. For the purpose of comparison with our predictive model, we shall use Mchaweh et al.'s model but without including that adjustable coefficient.

Following their notation, we denote this model the simplified-Nasrifar-Moshfeghian-0 (SNM0) correlation. Its analytical expression is

$$\rho_L(T) = \rho_C \left(1 + 1.169\tau^{1/3} + 1.818\tau^{2/3} - 2.658\tau + 2.161\tau^{4/3}\right) \tag{11}$$

where τ is a temperature-dependent variable defined by

$$\tau = 1 - (T/T_C)/\left[1 + m(1 - \sqrt{T/T_C})\right]^2 \tag{12}$$

where m is defined as in the Soave–Redlich–Kwong equation of state:

$$m = 0.480 + 1.574\omega - 0.176\omega^2 \tag{13}$$

with ω being the acentric factor.

Mchaweh et al. [11] use the SNM0 model, Eqs. (11–13), to predict the saturated-liquid density of a great number of fluids of different classes. They show that the SNM0 model gives practically the same overall accuracy as the original Nasrifar–Moshfeghian [12] model. Obviously, the deviations are low when an adjustable parameter is used.

The SNM0 model can be therefore compared with that proposed here, Eq. (9), because it is accurate, contains no adjustable coefficients, and needs three input parameters. Obviously, for this model, the rectilinear-diameter law must also be applied to obtain the vapor-density, so that the data at some reference temperature must be also known.

3. RESULTS AND DISCUSSION

We applied the proposed method to obtain the saturated-vapor and -liquid densities for 29 fluids of different kinds, including some of interest as alternative refrigerants. In all cases, and as a first choice, we opted to use as input the saturation densities given for the lowest temperature reported by the NIST database [23], which is practically identical to the triple-point temperature. The other input parameters, such as the critical properties and the acentric factor, were either taken from that database or from the DIPPR database [24]. The model was then applied over the entire temperature range, and the results were compared with those reported by the NIST database [23] for both densities, as well as with the DIPPR [24] data for the liquid density and the Reynolds [25] data for the vapor-density. The data are very similar, although the last two references generally involve a shorter temperature range. Comparison is also made with the values obtained using the SNM0 model, Eqs. (11–13), and the rectilinear-diameter law. The analysis took into account the results for both saturation densities, i.e., we did not focus solely on the liquid saturation density.

For some fluids, our model and SNM0 both gave very good, and qualitatively indistinguishable, results. Examples of these fluids were ethane, butane, pentafluoroethane (R125), carbon monoxide, carbon dioxide, and ethene. The results for the last two fluids are shown in Figs. 1 and 2 by way of illustration. Density–temperature curves and absolute deviation (calculated density minus experimental density) plots with respect to the DIPPR (for the liquid-density) and Reynolds (for the vapor-density) data are shown. As can be seen, our model and SNM0 gave very similar results for the vapor densities. Greater differences are observed for

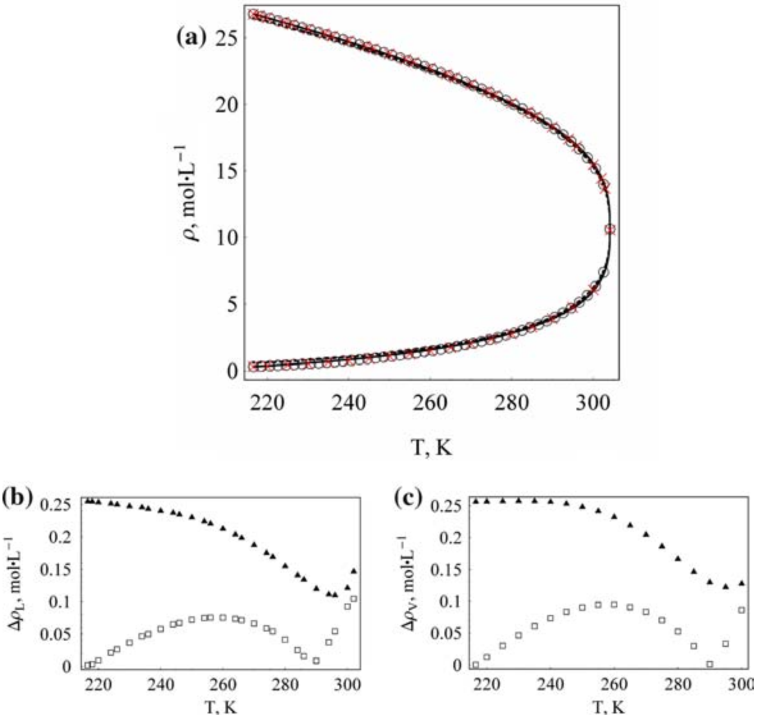

Fig. 1. VLE densities for carbon dioxide. (a) Density–temperature curve: (○) data from NIST [23]; (×) data from DIPPR [24] for the liquid-density and Reynolds [25] for the vapor-density; solid lines are our model, Eq. (9), and dashed lines the SNM0 model [11], Eqs. (11–13). Temperatures are in K and the densities in mol·L^{-1}. (b) Absolute deviations (experimental density minus calculated density) at each temperature with respect to DIPPR data for the liquid-density. (c) Absolute deviations with respect to the Reynolds data for the vapor-density. (Triangles: SNM0 model, squares: our model).

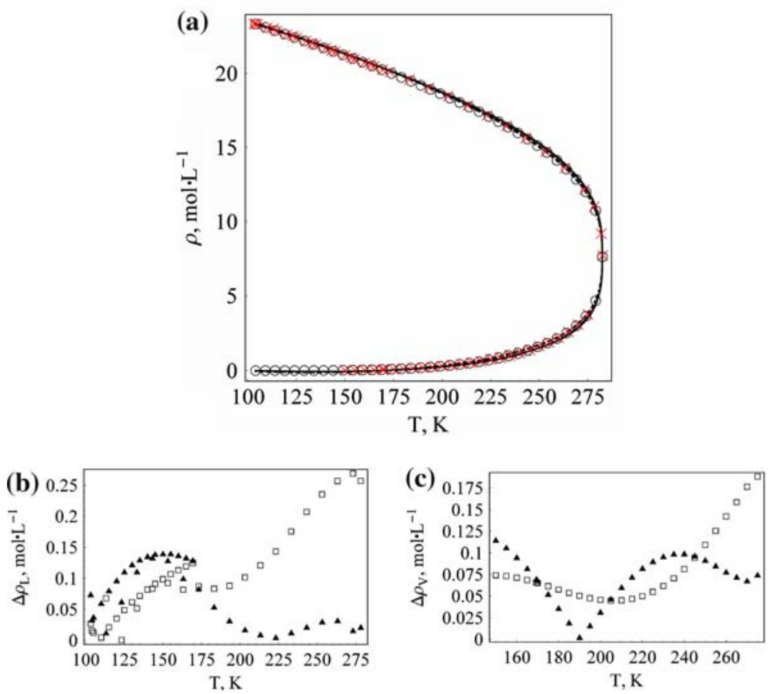

Fig. 2. VLE densities for ethene. Key as in Fig. 1.

the liquid densities, although the deviations are small in both cases. For ethene (Fig. 2), the SNM0 model reproduces the liquid-density better for intermediate and high temperatures.

For the simplest fluids, such as argon, krypton, xenon, neon, oxygen, nitrogen, and methane, the SNM0 model performed better near the critical point, whereas our model was better near the triple point. Examples are shown in Figs. 3 and 4. One observes that, for these fluids at high temperatures, our model overestimated the liquid-density and underestimated the vapor-density. The same was the case with the SNM0 model at low temperatures, where the relative deviations for the vapor-density are extremely high. The more extreme case was found for neon (Fig. 4).

Obviously, the above results are a consequence of the analytical form and the input parameters required for each model. First, the SNM0 includes a more complex temperature dependence which allows it to more adequately represent the behavior of the densities near the critical point. Our model has a pre-set critical exponent, and therefore for some fluids, deviations were found near the critical point, although in no case were

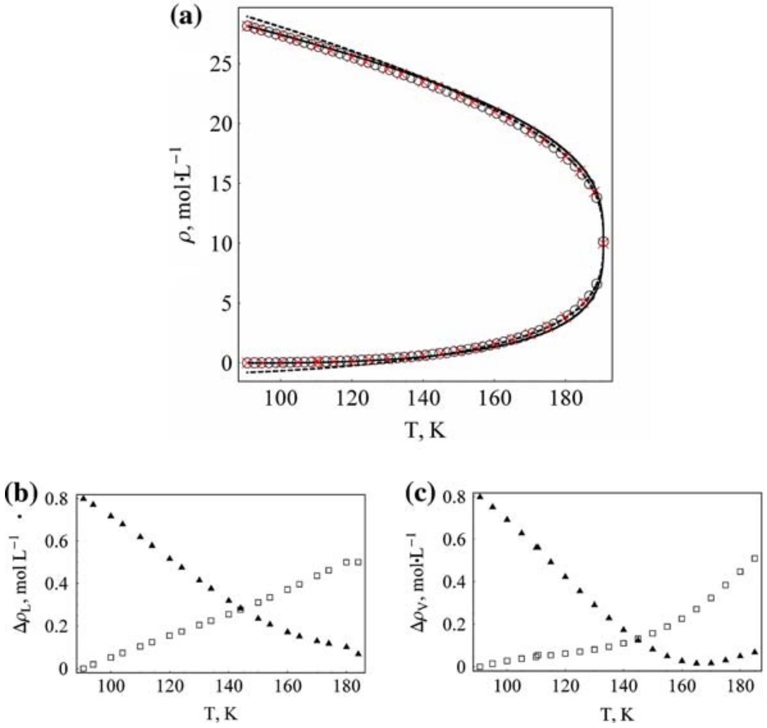

Fig. 3. VLE densities for methane. Key as in Fig. 1.

these deviations large. Second, since our model includes the triple-point data directly as input, its representation is good near this point, whereas the introduction of the triple point data in the SNM0 model is made indirectly through the rectilinear-diameter law.

Another important characteristic of our model is its versatility. Thus, results for a specific class of fluids could be improved by taking specific values of α or β for these fluids. The accuracy of our model near the critical point can be also improved by using a higher reference temperature. Nevertheless, the results would then be poorer at low temperatures. In any case, we do not consider these possibilities here, since the aim of the present work was the construction of a general model.

There are other fluids for which, although the SNM0 model works adequately, our model improved the results at low temperatures and behaved equally as well as SNM0 near the critical temperature. Examples were propane, pentane, hexane (Fig. 5), isobutane, 1-chloro-1,2,2,2-tetrafluoroethane (R124), 2,2-dichloro,1,1,1-trifluoroethane (R123), 1,1,1,

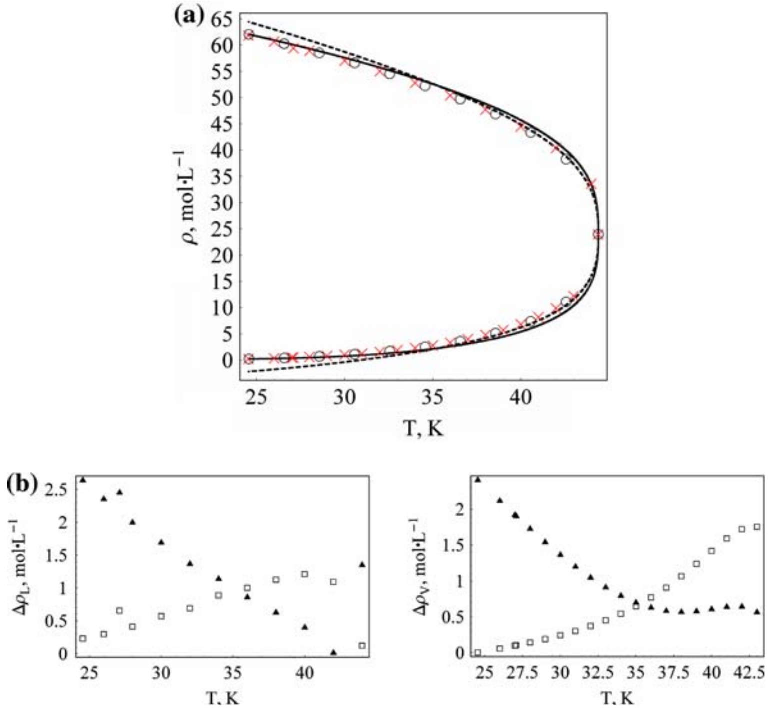

Fig. 4. VLE densities for neon. Key as in Fig. 1.

2-tetrafluoro-ethane (R134a), and chlorodifluo-romethane (R22; Fig. 6). As can be seen in Figs. 5 and 6, for these fluids the SNM0 model clearly underestimates the liquid-density near the triple point. In particular, for the refrigerant R22 the two models gave qualitatively similar results near the critical point, although our model led to smaller deviations with respect to experimental data (Fig. 6).

Finally, we found that our model was a clear improvement over SNM0 for other fluids including heptane, propene, fluorine, nitrogen trifluoride, difluoromethane (R32), 1,1,1-trifluoroethane (R143a), 1,1-difluoroethane (R152a), and ammonia. Four examples are shown in Fig. 7, where only the NIST data are included because the data from the other sources are very similar. One observes that SNM0 worked well only over a narrow temperature range around the critical point. Moreover, SNM0 sometimes overestimated the saturation liquid-density, e.g., for fluorine (Fig. 7b), and at other times underestimated that property, as in the cases of the fluids shown in Fig. 7a, c, and d. One also observes that the greatest deviations

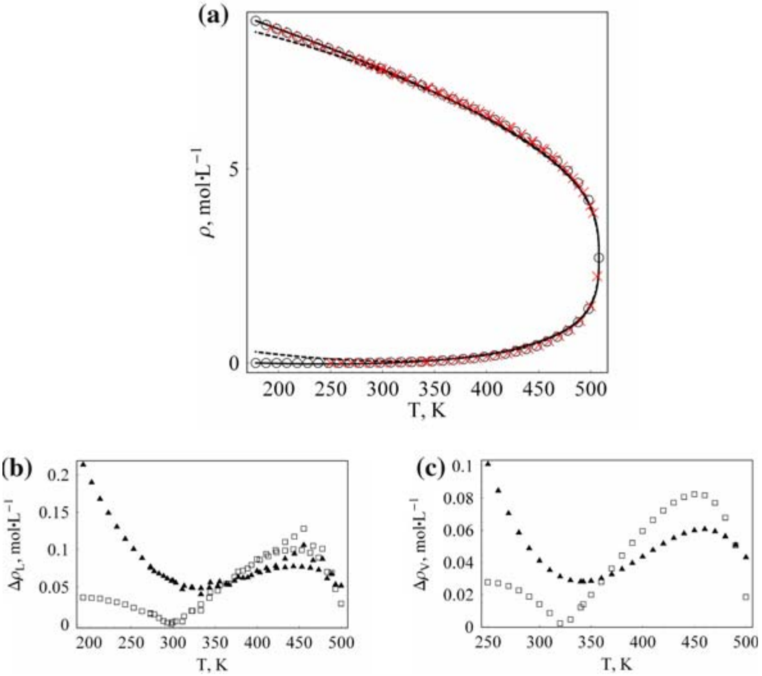

Fig. 5. VLE densities for hexane. Key as in Fig. 1.

given by our model were located at the liquid-density and at high temperatures (not very close to the critical temperature).

In sum, Figs. 1–7 show that the present model performed in a similar way, independently of the substance being considered. For some substances, it deviated near the critical point, and for others at high temperatures. For most of the substances, however, it presented an adequate qualitative behavior over the whole temperature range. This was not the case for the SNM0 model, which sometimes underestimated and at other times overestimated the liquid-density, and moreover seemed to be clearly inadequate for some fluids near the triple temperature.

4. CONCLUSIONS

We have described a new model for predicting both the vapor and liquid densities of fluids at vapor–liquid equilibrium. The model is based on considering the temperature derivatives of the two densities, and applying the rectilinear-diameter law. By fixing the critical exponent at a constant

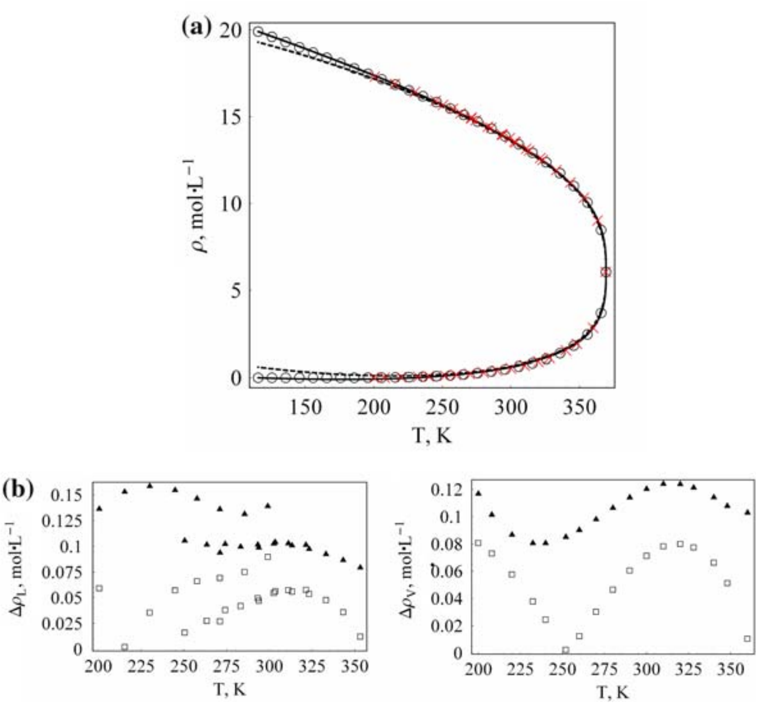

Fig. 6. VLE densities for chlorodifluoromethane (R22). Key as in Fig. 1.

value, the model involves only two parameters for each fluid, both of which have physical meaning. These can be calculated straightforwardly from a knowledge of the critical temperature and density, and of the saturation densities at one reference temperature. The model is therefore both simple and predictive. Results for different kinds of fluids were compared with those obtained with a recent and accurate model that predicts the saturation liquid-density—the SNM0 model proposed by Mchaweh et al. [11] – for which the acentric factor has to be added as an input parameter, and with data taken from the NIST database [23].

For some fluids, the predictions of our model were identical to those of the accurate SNM0 one. In other cases, our model improved the classical results slightly at low temperatures, and yielded equal or slightly poorer results at intermediate temperatures. This was because we chose the lowest temperature as the reference in constructing the model. The results can be improved for any given temperature range by taking an appropriate reference temperature. Also, the results near the critical point can be improved by using a specific substance-dependent value for the critical

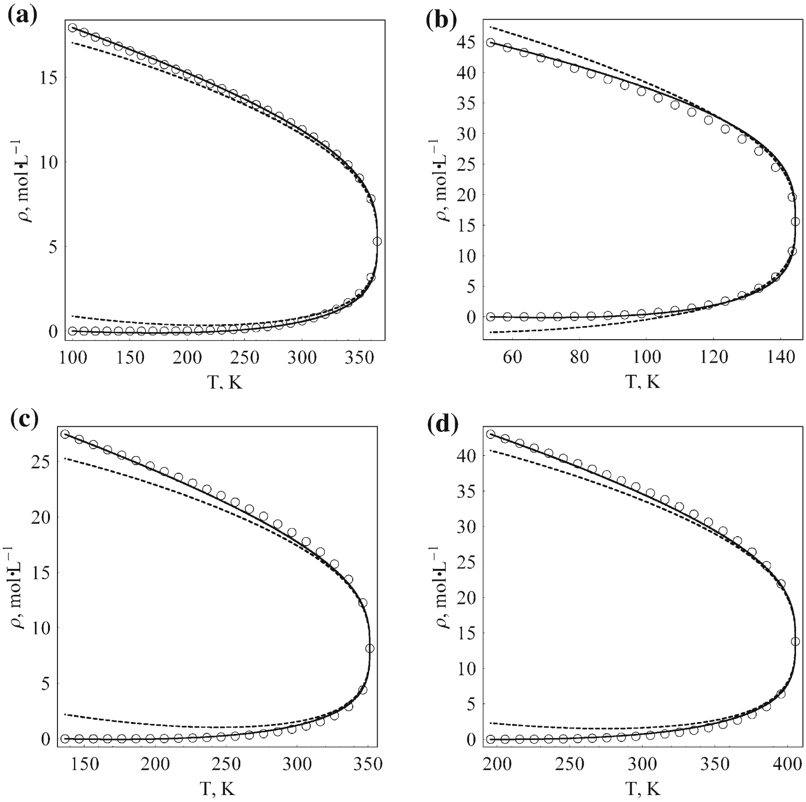

Fig. 7. VLE densities for (a) propene, (b) fluorine, (c) difluoromethane (R32), and (d) ammonia. Key as in Fig. 1.

exponent. The model can thus be adapted to reproduce different kinds of behavior. Indeed, we showed that, even with a fixed reference temperature and critical exponent, the model is adequate (although obviously not perfect) even for those fluids for which SNM0 is less accurate. Obviously, the main limitation of the model is that the linear diameter law must hold for the fluids to which it is applied.

In sum, our model predicts saturation densities with an accuracy that is comparable to or even better than that obtained using a very recent and accurate model. Moreover, the adequacy of the results does not depend on which fluid is being studied (unlike the case with the other simple models), as long as the rectilinear-diameter law holds (which is not the case for water, for example).

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