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LIQUID DENSITY OF PURE ALKANES AND HALOGENATED ALKANES IN A CORRESPONDING STATES FORMAT

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ABSTRACT

The development of a three parameters Corresponding States (CS) model is here proposed aiming at the prediction of the saturated and compressed liquid density of pure fluids pertaining to the two conformal families of alkanes (A) and hydrofluorocarbons (HFC) which are widely used as refrigerants.

Two fluids of the same family are chosen for both their acentric factor value and for the saturated and compressed liquid density dedicated equations availability and, on the basis of the Teja et al. three parameters CS model, the saturated and compressed liquid density of a fluid of interest is obtained in reduced variables. Assuming experimental data of saturated liquid density for several components of each of the two families of fluids an improvement is introduced substituting the acentric factor with a new constant scaling factor. As a final result both the saturated and the compressed liquid models are predictive methods.

The reached prediction accuracy of the proposed method is similar to that of the dedicated equations for all the fluids of a family. The result is particularly satisfactory for the application requirements in refrigeration.

INTRODUCTION

In the study and design of components and systems for refrigeration and heat pumping the prediction of thermodynamic properties of pure refrigerants is required with an high accuracy level over a wide range of pressure and temperature. A very accurate volumetric equation for a pure fluid can be generally obtained from a wide number of precise experimental data regressing over them the parameters of the equation. Each fluid can then be represented only after a long and expensive experimental work.

More often the study of the thermodynamic properties of pure fluids are limited to the components of a same family of compounds, so that the development of accurate thermodynamic models, valid only for the fluids of the same family, looks as a slightly simplifying task.

The utilization of modelling techniques in a corresponding-states format can yield interesting advantages and get a high level of accuracy when utilized inside the same family of fluids, producing new models more accurate than those currently available and with the minimum amount of experimental inputs.

DENSITY MODELS

Saturated Liquid Model

Pitzer and co-workers [1,2] initially proposed to express the compressibility factor $Z$ of a fluid of interest as a first-order perturbation, in form of a power series truncated at the first term, of the compressibility factor $Z^{(0)}$ of a "simple" fluid in the acentric factor of the fluid of interest:

$$Z = Z^{(0)} + \omega \left( \frac{\partial Z^{(0)}}{\partial \omega} \right)$$

(1)

Since it is not possible to represent $\left( \frac{\partial Z^{(0)}}{\partial \omega} \right)$ directly through an EoS, Lee and Kesler [3] proposed to substitute the derivative in eq. (1) with the finite difference between the compressibility factors $Z^{(0)}$ of a "simple" fluid and $Z^{(r)}$ of a reference fluid. Selecting a "simple" fluid having an $\omega$ value very close to zero it comes:
\[
Z(T_r, P_r, \omega) = Z^{(0)}(T_r, P_r) + \frac{\omega}{\omega^{(r)}} \left[ Z^{(r)}(T_r, P_r) - Z^{(0)}(T_r, P_r) \right]
\]

where \( \omega \) and \( \omega^{(r)} \) are respectively the acentric factors of the fluid of interest and of the reference one.

In order to represent the thermodynamic behaviour of fluids of a same family it is more convenient to substitute the "simple" fluid with a second reference one with \( \omega \neq 0 \), allowing both fluids to belong to the family. The first-order perturbation around a reference fluid, according to the original Pitzer proposal, is maintained in this case too transforming it into a linear interpolation between two reference fluids of the family. This model, as a modification of LK model proposed by Teja [4] is formulated as follows:

\[
Z(T_r, P_r, \omega) = Z^{(r_1)}(T_r, P_r) + \frac{\omega - \omega^{(r_1)}}{\omega^{(r_2)} - \omega^{(r_1)}} \left[ Z^{(r_2)}(T_r, P_r) - Z^{(r_1)}(T_r, P_r) \right]
\]

where \( \omega^{(r_1)} \) and \( \omega^{(r_2)} \) are the Pitzer acentric factors of the two reference fluids \( r_1 \) and \( r_2 \). The \( Z \) functions for both reference fluids \( r_1 \) and \( r_2 \) have to be obtained from EoS which are inevitably in the \( P = P(\rho, T) \) or equivalent form. The EoS functions have then to be inverted assuming \( T_r, P_r \) as input variables. Dedicated EoS can be furthermore utilized [5] to increase the accuracy level of the model.

As it is well known the Pitzer acentric factors is defined as:

\[
\omega = -\log_{10}\left[ \frac{P^S}{P^S_{ng}} \right]_{T_r=0.7} - 1.0 = -\log_{10}\left[ \frac{P^S}{P^S_{ng}} \right]_{T_r=0.7}
\]

where \( i \) indicates the fluid of interest and \( ng \) a noble gas (Ar, Kr, Xe). In a graphical representation of \( \log_{10}(P^S) \) vs. \( 1/T_r \) in a \( T_r \) range, for instance from 0.55 to 0.95, quasi-parallel straight lines are obtained so that the temperature dependence can be omitted selecting an arbitrary \( T_r \) value at which to define \( \omega \) as a parameter. For simplifying reasons the \( T_r \) value is assumed to be 0.7, because at that value \( \log_{10}(P^S_{ng}) \) is equal to 1. From eq. (3) it is evident that the model is a linear interpolation of the reference fluids reduced molar densities, at the same \( T_r \) and \( P_r \) of the fluid of interest, with \( \omega \) as the scaling factor. But from eq. (3) the scaling factor for molar densities is based on the vapor pressures; this makes the model not consistent.

It is then proposed to substitute the scaling factor of eq. (3), as defined in eq. (4), with another one, similar in the analytical form, but based on the saturated liquid density. It was verified that reporting \( \log_{10}(\rho^S) \) vs. \( 1/T_r \) for conformal families of fluids as alkanes and halogenated alkanes, straight lines quasi-parallel are obtained here too in a large \( T_r \) range. Assuming randomly a fluid \( j \) of the family as reference the new scaling factor is now defined as:

\[
\delta = -\log_{10}\left[ \frac{\rho^S_j}{\rho^S_{r_1}} \right]_{T_r=0.8}
\]

In the present case no reference is made to the same property of noble gases, but the reference is directly between the interest and the reference fluid property. In this way negative values of \( \delta \) are also possible. The value of 0.8 for \( T_r \) is assumed as mean in the range from 0.55 to 0.95 where the \( \log_{10}(\rho^S) \) lines are practically parallel among them.

For saturated liquid condition the model (3) is here modified as in the following:

\[
\log\rho_{rl}(T_r, \delta) = \log\rho_{rl}^{(r_1)}(T_r) + \frac{\delta}{\delta^{(r_1)}} \left[ \log\rho_{rl}^{(r_2)}(T_r) - \log\rho_{rl}^{(r_1)}(T_r) \right]
\]

If the interest fluid \( j \) is selected so as coincide with the reference one \( r_1 \) the model becomes:
\[
\log \rho_{r,s}(T_r, \delta) = \log \rho_{r,s}^{(r1)}(T_r) + \frac{\delta}{\delta_r} \left[ \log \rho_{r,s}^{(r2)}(T_r) - \log \rho_{r,s}^{(r1)}(T_r) \right]
\]  

(7)

In eq. (7) \(\delta\) and \(\delta_r\) are obtained both from eq. (5) with \(i\) as the interest fluid and \(j\) the reference \(r1\) for the first and \(i\) as the reference \(r1\) and \(j\) the reference \(r2\) for the second one.

The model is then applied to the alkanes family of refrigerants with methane and normal butane as \(r1\) and \(r2\) references. The dedicated equations \(\rho_{r,s}(T_r)\) for both fluids are assumed from [6].

For the halogenated alkanes family the fluids R11 and R152a have been selected as \(r1\) and \(r2\) references, because of their \(\delta\) values which are bracketing those of the other components. For R11 and R152a the saturated liquid equations are from [7] and [8] respectively.

**Compressed Liquid Model**

Moving into the compressed liquid domain the proposed model retains the same structure except that compressed liquid dedicated equations have to replace the saturated liquid ones for the same reference fluids:

\[
\log \rho_{r,s}(T_r, P_r, \delta) = \log \rho_{r,s}^{(r1)}(T_r, P_r) + \frac{\delta}{\delta_r} \left[ \log \rho_{r,s}^{(r2)}(T_r, P_r) - \log \rho_{r,s}^{(r1)}(T_r, P_r) \right]
\]  

(10)

In this case the \(\delta\) values are still obtained through eq. (5), i.e. at saturation, and they are maintained independent from pressure. The values of \(\delta\) and \(\delta_r\) are the same as those in the eq. (7).

The compressed liquid dedicated equations are taken for C1 and \(n-C4\) from [6] while for R11 they come from [7] and for R152a from [9].

**MODELS VALIDATION**

**Saturated Liquid**

The proposed model has been validated for saturated liquid densities both for alkanes and HFC's against conventional and improved existing models and furthermore against experimental data. The models assumed for comparison are the Hankinson, Brobst and Thomson (HBT) [10] for all the fluids and the Iglesias-Silva and Hall (I-SH) [11] for HFC's. In the Fig. 1 the alkanes ethane, propane and iso-butane are studied using experimental data from [14] and the HBT model. The results from the proposed model show a prediction accuracy level and a trend similar to that obtained from HBT. A relevant improvement is obtained by the present model for R32, particularly with respect to HBT as Fig. 2 reports. In Fig. 3 is evident that for R134a the model presents an accuracy comparable with those of the two dedicated density equations from Defibaugh, Moldover (DM) [12] and Tillner-Roth, Baehr (TB) [13], even though in a predictive mode. In Fig. 4 is also presented the relative error for three fluoro-propanes, which are suitable as refrigerant fluids; the comparison is made with dedicated density equations from Defibaugh, Moldover [12]. In the range of validity of these equations, the model performs very well in predicting the densities also of these new refrigerants.

In Table 1 the results obtained for the fluid studied are summarized for the three cited models, the present one and the two for comparison. The AAD in % of the proposed model if significantly better than HBT, and is also better than the I-SH model, which is instead a completely correlative model. It has to be stressed that the I-SH model cannot be applied for fluoro-propanes. In the same Table the \(\delta\) values for each fluid are also reported.
Fig. 1. Saturated liquid density percent deviation of ethane, propane and iso-butane for the proposed model and the HBT model, data from [14].

Fig. 2. Saturated liquid density percent deviation of R32 for the proposed model, the HBT model and the I-SH one, data from [15].

Fig. 3. Saturated liquid density percent deviation for R134a from the proposed model, the EoS's from Defibaugh, Moldover (DM) and Tillner-Roth, Baehr (TB), and data from [16,17,18].

Fig. 4. Saturated liquid density percent deviation for R245ca, R245cb and R236ea from the proposed model, the dedicated density equations from Defibaugh, Moldover [12].

Fig. 5. Compressed liquid density percent deviation for n-pentane from the proposed model and HBT, data from [19].

Fig. 6. Compressed liquid density percent deviation for R134a from the proposed model, HBT and a dedicated EoS [16], data from [17].
Table 1. Saturated liquid density results for the present model, the HBT and the I-SH ones.

<table>
<thead>
<tr>
<th>Fluid</th>
<th>$\delta$</th>
<th>$T_r$ range</th>
<th>$P_r$ range</th>
<th>AAD % this model</th>
<th>AAD % HBT</th>
<th>AAD % I-SH</th>
<th>NPT</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>R22</td>
<td>1.8095E-2</td>
<td>0.51-0.92</td>
<td>0.019</td>
<td>0243</td>
<td>0.096</td>
<td>16</td>
<td>[20]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.71-0.98</td>
<td>0.017</td>
<td>0.323</td>
<td>0.113</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.65-0.92</td>
<td>0.010</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R32</td>
<td>8.3829E-2</td>
<td>0.68-0.94</td>
<td>0.113</td>
<td>2.941</td>
<td>0.141</td>
<td>19</td>
<td>[15]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.72-0.95</td>
<td>0.121</td>
<td>2.842</td>
<td>0.181</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.66-0.99</td>
<td>0.361</td>
<td>3.381</td>
<td>0.717</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R143a</td>
<td>4.9855E-2</td>
<td>0.60-0.95</td>
<td>0.147</td>
<td>1.885</td>
<td>0.301</td>
<td>25</td>
<td>[25]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.64-0.98</td>
<td>0.251</td>
<td>1.261</td>
<td>0.213</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R134a</td>
<td>4.1702E-2</td>
<td>0.65-0.94</td>
<td>0.056</td>
<td>1.378</td>
<td>0.076</td>
<td>13</td>
<td>[16]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.77-0.98</td>
<td>0.076</td>
<td>1.176</td>
<td>0.077</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>0.53-0.96</td>
<td>0.206</td>
<td>1.190</td>
<td>0.260</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>R125</td>
<td>2.0182E-2</td>
<td>0.66-0.98</td>
<td>0.126</td>
<td>0.401</td>
<td>0.093</td>
<td>24</td>
<td>[15]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.67-0.83</td>
<td>0.064</td>
<td>0.781</td>
<td>0.058</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R245ca</td>
<td>2.2306E-2</td>
<td>0.54-0.83</td>
<td>0.225</td>
<td>0.823</td>
<td>-</td>
<td>29*</td>
<td>[27]</td>
<td></td>
</tr>
<tr>
<td>R236ea</td>
<td>1.4622E-2</td>
<td>0.58-0.91</td>
<td>0.071</td>
<td>0.926</td>
<td>-</td>
<td>30*</td>
<td>[28]</td>
<td></td>
</tr>
<tr>
<td>Overall</td>
<td>0.126</td>
<td>1.244</td>
<td>0.175</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Generated data

**Compressed Liquid**

In Figs. 5 and 6 the compressed liquid model is tested for an alkane, n-pentane, and an HFC, R134a. The comparison is here made with the analogous HBT model, assumed as the more utilized and general one for compressed liquid density. For R134a the comparison is also made with the dedicated $EoS$ from [16]. In this case

Table 2. Compressed liquid density results for the present model, for the HBT and the dedicated $EoS$ for alkanes and halogenated alkanes.

<table>
<thead>
<tr>
<th>Fluid</th>
<th>$\delta$</th>
<th>$T_r$ range</th>
<th>$P_r$ range</th>
<th>AAD % this model</th>
<th>AAD % HBT</th>
<th>AAD % d. Eos</th>
<th>NPT</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2</td>
<td>2.1815E-2</td>
<td>0.30-0.92</td>
<td>0.16-7.31</td>
<td>0.293</td>
<td>0.391</td>
<td>0.105</td>
<td>143</td>
<td>[29]</td>
</tr>
<tr>
<td></td>
<td>0.97-1.05</td>
<td>0.87-2.83</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[30]</td>
</tr>
<tr>
<td>C3</td>
<td>3.1451E-2</td>
<td>0.69-0.98</td>
<td>0.12-5.61</td>
<td>0.133</td>
<td>0.198</td>
<td>0.023</td>
<td>84</td>
<td>[31]</td>
</tr>
<tr>
<td></td>
<td>0.83-0.83</td>
<td>16.6-161.6</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[32]</td>
</tr>
<tr>
<td></td>
<td>0.75-0.88</td>
<td>0.26-3.24</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[30]</td>
</tr>
<tr>
<td>iso-C4</td>
<td>3.5737E-2</td>
<td>0.72-0.96</td>
<td>0.47-5.68</td>
<td>0.405</td>
<td>0.698</td>
<td>0.043</td>
<td>81</td>
<td>[33]</td>
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<tr>
<td>n-C5</td>
<td>5.5462E-2</td>
<td>0.66-0.94</td>
<td>0.40-20.45</td>
<td>0.264</td>
<td>0.670</td>
<td>-</td>
<td>120</td>
<td>[19]</td>
</tr>
<tr>
<td>R-22</td>
<td>1.8095E-2</td>
<td>0.46-0.81</td>
<td>0.02-1.61</td>
<td>0.031</td>
<td>0.171</td>
<td>0.056</td>
<td>19</td>
<td>[20]</td>
</tr>
<tr>
<td></td>
<td>0.84-0.97</td>
<td>0.50-2.00</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[34]</td>
</tr>
<tr>
<td></td>
<td>0.74-0.95</td>
<td>0.21-1.25</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[21]</td>
</tr>
<tr>
<td>R-134a</td>
<td>4.1702E-2</td>
<td>0.65-0.97</td>
<td>0.22-3.91</td>
<td>0.351</td>
<td>1.651</td>
<td>0.027</td>
<td>100</td>
<td>[16]</td>
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<tr>
<td></td>
<td>0.48-0.71</td>
<td>0.22-1.13</td>
<td>0.182</td>
<td>1.341</td>
<td>0.075</td>
<td>64</td>
<td></td>
<td>[17]</td>
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<tr>
<td>R-32</td>
<td>8.3829E-2</td>
<td>0.72-0.95</td>
<td>0.57-2.05</td>
<td>0.123</td>
<td>4.604</td>
<td>0.057</td>
<td>108</td>
<td>[23]</td>
</tr>
<tr>
<td></td>
<td>0.71-0.85</td>
<td>0.45-3.46</td>
<td>0.089</td>
<td>4.913</td>
<td>0.178</td>
<td>32</td>
<td></td>
<td>[35]</td>
</tr>
<tr>
<td>R-142b</td>
<td>2.2021E-2</td>
<td>0.71-0.98</td>
<td>0.12-4.33</td>
<td>0.146</td>
<td>0.909</td>
<td>-</td>
<td>35</td>
<td>[36]</td>
</tr>
<tr>
<td>R-125</td>
<td>2.0180E-2</td>
<td>0.82-0.98</td>
<td>0.44-1.73</td>
<td>0.328</td>
<td>0.392</td>
<td>0.032</td>
<td>38</td>
<td>[37]</td>
</tr>
<tr>
<td>R-218</td>
<td>2.0426E-3</td>
<td>0.79-0.91</td>
<td>0.15-5.30</td>
<td>0.812</td>
<td>1.421</td>
<td>0.321</td>
<td>108</td>
<td>[23]</td>
</tr>
<tr>
<td>R-236ea</td>
<td>1.4622E-2</td>
<td>0.58-0.91</td>
<td>0.14-1.85</td>
<td>0.298</td>
<td>0.817</td>
<td>0.004</td>
<td>90</td>
<td>[27]</td>
</tr>
<tr>
<td>R-245ca</td>
<td>2.2306E-2</td>
<td>0.54-0.79</td>
<td>0.25-1.65</td>
<td>0.394</td>
<td>0.865</td>
<td>-</td>
<td>70</td>
<td>[28]</td>
</tr>
<tr>
<td>Overall</td>
<td>0.269</td>
<td>1.217</td>
<td>0.071</td>
<td></td>
<td></td>
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</table>
the present model is superior to the HBT and for R134a is exceeded only by the EoS which, on the other hand, is a completely correlative equation. In Table 2 the analysis results for all the fluids studied are reported showing a same general trend as from the former Figures. Literature do not provide EoS for all the fluids here considered. For those reported for comparison the literature sources are: C2, C3 and iso-C4 [X], R22 [12], R134a [13], R32 [38], R125 [38], R218 [12], R236ea [39].

CONCLUSIONS

The proposed model reaches a high density prediction accuracy, superior to those of the existing models, even though in predictive mode. It is demonstrated to be a simple and suitable tool for the saturated and compressed liquid density calculation of the refrigerant fluids, including the new generation of fluoro-propanes.

REFERENCES