Properties of Refrigerants from Cubic Equations of State

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Vapour - liquid equilibrium, thermodynamic and volumetric properties were predicted for three pure hydrofluorocarbons: difluoromethane (R32), pentafluoroethane (R125) and 1,1,1,2 - tetrafluoroethane (R134a) as well as for binary and ternary mixtures of these refrigerants. Three cubic equations of state GEOS3C, SRK (Soave – Redlich – Kwong) and PR (Peng – Robinson) were used. A wide comparison with literature experimental data was made. For the refrigerant mixtures, classical van der Waals mixing rules without interaction parameters were used. The GEOS3C equation, with three parameters estimated by matching several points on the saturation curve (vapor pressure and corresponding liquid volumes), compares favorably to other equations in literature, being simple enough for applications.

Keywords: equation of state, vapour - liquid equilibrium, volumetric properties, refrigerants

Refrigerants are the working fluids in refrigeration, air-conditioning and heat pumping systems. The development of models for representation and prediction of physical properties and phase equilibria as well as the improvement of current equations of state (EOS) is of particular interest for the refrigeration industry [1, 2].

The difluoromethane (R32), pentafluoroethane (R125) and 1,1,1,2 – tetrafluoroethane (R134a) are environmentally acceptable refrigerants (their ozone depletion potentials are zero) and present a considerable interest in the search for alternative refrigerants. In previous works [3, 4] some properties of pure refrigerants and refrigerator mixtures were calculated by cubic equations of state.

The purpose of this paper is to present the result of simultaneous calculation of vapour – liquid equilibrium, thermodynamic and volumetric properties on R32, R125, and R134a pure fluids as well as on binary and ternary mixtures of these refrigerants. Three cubic equations of state GEOS3C [5, 6], SRK (Soave – Redlich – Kwong) [7] and PR (Peng – Robinson) [8], are used. A wide comparison with recommended literature data [9] and experimental data [10-12] is also made. For the properties of the refrigerant mixtures, classical van der Waals mixing rules without interaction parameters are used.

The GEOS3C equation of state

The GEOS3C equation of state is a general form [3] for the cubic equations of state with two, three and four parameters:

\[ P = \frac{RT}{V-b} - \frac{a(T)}{(V-d)^2+c} \]  

(1)

The GEOS3C equation is based on the GEOS equation [13-15] and uses a new temperature function \( \beta(T) \) expressed as:

\[ \beta(T) = 1 + C_1 y + C_2 y^2 + C_3 y^3 \] for \( T_c \leq 1 \)  

(2)

\[ \beta(T) = 1 + C_1 y \] for \( T_c > 1 \)  

(3)

\[ y = 1 - \frac{T}{T_c} \]  

(4)

The \( C_1, C_2, \) and \( C_3 \) parameters were obtained by matching points on the saturation curve (vapor pressures together with the corresponding liquid volumes). The objective function for parameters estimation and other details are given elsewhere [6].

In this work, the coefficients \( a, b, c, d \) of eqn. (1) were obtained for mixtures of hydrofluorocarbons using the classical van der Waals mixing rules without interaction parameters [4].

Results and discussions

In order to predict accurate values for mixture properties, an equation of state must first be able to properly represent the behavior of pure substances.

The equations of state GEOS3C, SRK and PR were tested firstly to calculate equilibrium and thermodynamic properties for R32, R125 and R134a pure fluids, along the saturation curve. The calculations were compared with data of ASHRAE collection [9]. The values of the GEOS3C parameters \( C_1, C_2, \) and \( C_3 \) together with the critical data andacentric factor for the refrigerants are given in table 1.

The following thermodynamic properties have been calculated together with the saturation pressure and the two phase densities: compressibility factor, \( Z \); enthalpy, \( H \); enthalpy of vaporization, \( \Delta_{vap} H \); entropy, \( S \).

The results of the calculations for R32, R125 and R134a are summarized in tables 2-4.

<table>
<thead>
<tr>
<th>Table 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>VALUES OF CRITICAL DATA, ACENTRIC FACTOR AND C1, C2, C3 PARAMETERS (GEOS3C) FOR R32, R125 AND R134a</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Tc (K)</th>
<th>Pc (MPa)</th>
<th>Vc ( \times 10^4 ) (m$^3$/kg)</th>
<th>( \omega )</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
</tr>
</thead>
<tbody>
<tr>
<td>R32</td>
<td>351.56</td>
<td>5.8579</td>
<td>2.38</td>
<td>0.2710</td>
<td>0.2276</td>
<td>1.1183</td>
<td>-1.7895</td>
</tr>
<tr>
<td>R125</td>
<td>339.19</td>
<td>3.5950</td>
<td>1.75</td>
<td>0.3066</td>
<td>0.3408</td>
<td>0.2642</td>
<td>0.1559</td>
</tr>
<tr>
<td>R134a</td>
<td>374.18</td>
<td>4.0560</td>
<td>1.95</td>
<td>0.3293</td>
<td>0.3160</td>
<td>0.8256</td>
<td>-0.5629</td>
</tr>
</tbody>
</table>

Values of critical data and acentric factors from [9]

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In these tables, the average absolute deviations for a property \( Y \) are relative (%):

\[
\text{AAD} \% = \frac{\sum_{i=1}^{N} |Y_{i}^{\text{exp}} - Y_{i}^{\text{cal}}|}{N} \times 100
\]  

(5)

excepting for the enthalpy and entropy where the following equation was used:

\[
\text{AAD } H \text{ (or } S) = \frac{\sum_{i=1}^{N} |H_{i}^{\text{exp}} - H_{i}^{\text{cal}}|}{N}
\]  

(6)

In each table the number of data points, the pressure and temperature ranges are indicated, too. The two-phase region properties have been calculated at temperatures from the triple point to the critical point of each substance.

The following observations can be made on the basis of the results for all three pure refrigerants:

- the vapour pressures and saturated volumes are better represented by GEOS3C, compared to the results obtained using the other equations;
- the difference in performance between the all EOSs is less noticeable for the other properties.

The equations SRK and PR can be used with the same temperature function \( \beta(T) \) (2-4) with three parameters. This fact leads to better values for vapour pressures but the values of saturated volumes can not be improved without a translation procedure [6]. The advantage of the GEOS3C equation is that the prediction of liquid volume is improved without any translation by the parameter \( C_1 \) [3].

Examples of calculated properties in comparison with experimental data for R125 are presented in figures 1-4. Figure 1 shows the saturation curve calculated with the GEOS3C, PR and SRK equations.

![Fig. 1. The pressure - volume diagram (saturation curve) for refrigerant R125](image)

Figures 2 and 3 present the deviations in vapour pressure and liquid volume of using all three EOS in the saturation range. Figure 4 shows the pressure - entropy diagram calculated by all three EOS, too. It can be seen that the GEOS3C equation reproduces better the vapour pressure and liquid volume while the entropy is good reproduced by all three EOS.

The capability of all three EOS to reproduce the vapour – liquid equilibrium as well as densities of liquid and gas in the single phase region for the refrigerant binary and ternary mixtures containing R32, R125 and R134a was also tested. The classical van der Waals mixing rules without interaction parameters were used. A large comparison with

**Table 2**

<table>
<thead>
<tr>
<th>AAD (%)</th>
<th>AAD</th>
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<tbody>
<tr>
<td>EOS</td>
<td>( P^a )</td>
</tr>
<tr>
<td>---------</td>
<td>-------</td>
</tr>
<tr>
<td>SRK</td>
<td>2.2</td>
</tr>
<tr>
<td>PR</td>
<td>1.5</td>
</tr>
<tr>
<td>GEOS3C</td>
<td>0.4</td>
</tr>
</tbody>
</table>

**Table 3**

<table>
<thead>
<tr>
<th>AAD (%)</th>
<th>AAD</th>
</tr>
</thead>
<tbody>
<tr>
<td>EOS</td>
<td>( P^a )</td>
</tr>
<tr>
<td>---------</td>
<td>-------</td>
</tr>
<tr>
<td>SRK</td>
<td>1.1</td>
</tr>
<tr>
<td>PR</td>
<td>1.3</td>
</tr>
<tr>
<td>GEOS3C</td>
<td>0.7</td>
</tr>
</tbody>
</table>

**Table 4**

<table>
<thead>
<tr>
<th>AAD (%)</th>
<th>AAD</th>
</tr>
</thead>
<tbody>
<tr>
<td>EOS</td>
<td>( P^a )</td>
</tr>
<tr>
<td>---------</td>
<td>-------</td>
</tr>
<tr>
<td>SRK</td>
<td>1.3</td>
</tr>
<tr>
<td>PR</td>
<td>0.8</td>
</tr>
<tr>
<td>GEOS3C</td>
<td>0.3</td>
</tr>
</tbody>
</table>
experimental data [9-12] was made. The GEOS3C equation predicts better values of the liquid density for all binary and ternary mixtures, in comparison with the PR and SRK equations. For the gaseous phase, all three equations lead to good predictions of the densities.

Some results of the density calculations at different pressures (2 – 185 bar) for the liquid mixture R32 + R134a, in the single phase region, are presented in table 5, together with the temperature, composition and number of data points.

Examples of deviation calculations using the three EOS, for liquid and gas density are presented in figures 5 and 6 at constant temperature and composition for R125 + R134a system. Figure 7 presents the enthalpies predicted by all three EOS for R32 + R134a binary system, along the bubble and the dew curve.

A detail of equilibrium diagram for the refrigerant R407C [R32 (23%) + R125 (25%) + R134a (52%, wt)], saturation curve with three isotherms, is presented in figure 8. The computations were performed with the GEOS3C, SRK and PR equations. It is obvious that the agreement with the experimental data [9, 10] is better for the GEOS3C equation.

### Table 5

<table>
<thead>
<tr>
<th>T [K]</th>
<th>X1</th>
<th>X2</th>
<th>NP</th>
<th>AAD[%]</th>
<th>AAD[%]</th>
<th>AAD[%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>252.92</td>
<td>0.1963</td>
<td>0.8037</td>
<td>430</td>
<td>2.54</td>
<td>2.57</td>
<td>13.59</td>
</tr>
<tr>
<td>252.91</td>
<td>0.4251</td>
<td>0.5749</td>
<td>412</td>
<td>2.5</td>
<td>4.53</td>
<td>15.35</td>
</tr>
<tr>
<td>252.92</td>
<td>0.5259</td>
<td>0.4741</td>
<td>369</td>
<td>2.26</td>
<td>5.4</td>
<td>16.17</td>
</tr>
<tr>
<td>252.91</td>
<td>0.5872</td>
<td>0.4128</td>
<td>381</td>
<td>2.37</td>
<td>6</td>
<td>16.68</td>
</tr>
<tr>
<td>252.91</td>
<td>0.7828</td>
<td>0.2172</td>
<td>394</td>
<td>2.34</td>
<td>8.15</td>
<td>18.62</td>
</tr>
<tr>
<td>272.9</td>
<td>0.2174</td>
<td>0.7826</td>
<td>582</td>
<td>0.84</td>
<td>2.72</td>
<td>13.79</td>
</tr>
<tr>
<td>272.9</td>
<td>0.4057</td>
<td>0.5943</td>
<td>543</td>
<td>0.83</td>
<td>4.36</td>
<td>15.24</td>
</tr>
<tr>
<td>272.9</td>
<td>0.5788</td>
<td>0.4212</td>
<td>520</td>
<td>0.79</td>
<td>5.97</td>
<td>16.69</td>
</tr>
<tr>
<td>272.9</td>
<td>0.7551</td>
<td>0.2449</td>
<td>146</td>
<td>0.65</td>
<td>8.13</td>
<td>18.87</td>
</tr>
</tbody>
</table>

| Average values | 14893 | 1.93 | 6.7  | 17.18 |

Fig. 2. The deviations in vapor pressure on the saturation curve for refrigerant R125

Fig. 3. The deviations in liquid volume on the saturation curve for refrigerant R125

Fig. 4. Pressure – entropy diagram (saturation curve) for refrigerant R125
Conclusion

Vapour-liquid equilibrium, volumetric and thermodynamic properties were predicted for three pure hydrofluorocarbons (R32, R125 and R134a) as well as for binary and ternary mixtures of these substances, using the cubic equations of state, GEOS3C, SRK and PR.

The GEOS3C equation with three parameters obtained by matching points on the saturation curve (vapour pressures together with the corresponding liquid volumes) gives the best results for vapour pressure and liquid volume at saturation. The SRK and PR equations used with the same temperature function with three parameters lead to better values for vapour pressures but the values of saturated volumes can not be improved without a translation procedure. The difference in performance between the three equations is less noticeable for the other thermodynamic properties.

For the binary and ternary refrigerant systems, the GEOS3C equation predicts better values of both liquid and gas densities.

The use of interaction binary parameters in the classical van der Waals mixing rules does not lead to significant improvement in the calculation of the volumetric and thermodynamic properties for the studied binary systems.

Acknowledgements: The authors are grateful to National Council for Scientific Research of Romania, for financial support.

List of symbols

- parameters of GEOS3C equation
- AAD - absolute average deviation
- C1, C2 and C3 - parameters of GEOS3C temperature function
- H - enthalpy
- M - molar mass
- P, Ps - pressure, saturation pressure
- R - universal gas constant
- S - entropy
- T - temperature
- V, VL, VV - molar volume, liquid volume, vapour volume

Greeks

- β - reduced temperature function in GEOS3C equation
- ω - acentric factor

Subscripts

- c - critical property
- r - reduced property

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