Thermophysical Properties of Methanol from Cubic Equations of State

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Vapour-liquid equilibrium and thermophysical properties of methanol were predicted, along the saturation curve and in the single-phase region. Five cubic equations of state were used: Soave-Redlich-Kwong (SRK), Peng-Robinson (PR), Schmidt-Wenzel (SW), Freze et al. (C1) and GEOS3C. A wide comparison with NIST recommended data was made. So far GEOS3C, with four optimized parameters, compares favorably to other equations in literature being simple enough for applications.

Keywords: equation of state, vapor-liquid equilibrium, thermophysical properties, methanol

The knowledge of vapour liquid equilibria (VLE) and thermophysical properties of methanol is of importance in many applications, especially in the last time related to its use in production of biodiesel. Among many methods to produce biodiesel, supercritical methanol transesterification [1] has several advantages: no catalyst is used, the reaction rate and the conversion are high, the separation of the products is simple, and the continuous processing in large scale is easily applied. Thus, the study of the mass and heat transfer on supercritical methanol transesterification in a chemical reactor is very important. This study depends strongly upon the thermophysical properties of different components in this reaction system, one of them being methanol [2].

In the classical thermodynamic framework it is possible to develop relations to calculate the Helmholtz and Gibbs energies, enthalpies, entropies, fugacity coefficients and other thermophysical properties of fluids. Such relationships together with equations of states (EOS) can be applied to obtain estimation techniques for thermodynamic property departure functions [3]. Then the real thermodynamic properties are calculated for pure components and mixtures. In our previous works [4-7], thermophysical properties of many pure fluids and mixtures were predicted by cubic equations of state.

In the last two decades, a progress has been made in implementing molecular theories for the development of new generations of thermodynamic models, such as Statistical Association Fluid Theory (SAFT) in equations of state. Most of the SAFT models are not entirely theoretical, because their molecular parameters are obtained by fitting the experimental vapour pressures and other thermodynamic data [8]. On the other hand, cubic equations of state exhibit an overall robustness in predicting various thermophysical properties over a wide range of temperatures and pressures, with the exception of certain phenomena related to heat capacity, sound velocity and Joule-Thomson coefficient [3].

In this work, vapour-liquid equilibrium and thermophysical properties were predicted, along the saturation curve and in the single-phase region for methanol. Five cubic equations of state were used: Soave-Redlich-Kwong (SRK) [9], Peng-Robinson (PR) [10], Schmidt-Wenzel (SW) [11], Freze et al. (C1) [12] and GEOS3C [13]. A wide comparison with recommended NIST (National Institute of Standard and Technology, USA) data [14], considered as pseudo experimental data, was made. So far GEOS3C, with four optimized parameters, compares favorably to other equations in literature, being simple enough for applications.

The GEOS3C equation of state

The GEOS3C equation of state is a general form [4, 15] for the cubic equations of state with two, three and four parameters:

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

The four parameters a, b, c, d for a pure component are expressed by:

\[ \alpha = a \beta^2(T_c); \quad \Omega_a = \Omega_a \frac{RT_c^2}{P_c} \] ; \quad b = \Omega_b \frac{RT_c}{P_c} \] 

\[ \Omega_c = \Omega_c \frac{RT_c^2}{P_c} \] ; \quad d = \Omega_d \frac{RT_c}{P_c} \]

The GEOS3C equation is based on the GEOS equation [15] and uses a new temperature function:

\[ \beta(T) = 1 + C_1 y + C_2 y^2 + C_3 y^3 \quad \text{for } T \leq T_r \] 

\[ \beta(T) = 1 + C_4 y \quad \text{for } T > T_r \] 

\[ y = 1 - \frac{1}{\sqrt{T_r}} \]

The expressions of the parameters \( \Omega_a, \Omega_b, \Omega_c, \Omega_d \) are:

\[ \Omega_a = (1 - B)^2 \] ; \quad \Omega_b = Z_c - B \] ; \quad \Omega_c = (1 - B)^2 (B - 0.25) \] ; \quad \Omega_d = Z_c - 0.5 (1 - B) \] 

\[ B = \frac{1 + C_3}{\alpha_c + C_4} \quad \alpha_c \quad \text{- Riedel’s criterion} \]

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Riedel’s criterion, \( \alpha_c \), is calculated using the acentric factor from the equation:
\[
\alpha_c = 5.808 + 4.93\omega \quad (10)
\]

In our previous papers the \( C_1 \), \( C_2 \), and \( C_3 \) parameters were estimated by constraining the equation of state to reproduce the experimental vapour pressure and liquid volume on the saturation curve. In this work especially for methanol, another approach was used. The \( C_1 \), \( C_2 \), and \( C_3 \) parameters together with the compressibility factor \( Z \), were optimized to reproduce the same experimental data. The modified \( Z \) is slightly different of experimental value, but the vapor pressure and liquid volumes on the saturation curve and on the isotherms are better reproduced.

As pointed out previously [4], the relations (7-9) are general forms for all the cubic equations of state with two, three and four parameters [4, 16]. Our software used in calculations is based on these equations for the reduction of GEOS to different cubic EOS from the literature. This is the meaning of the statement “general cubic equation of state” used for GEOS.

The expressions of the residual departure functions based on GEOS equation [3, 4] may be also used for other cubic equations, which can be converted to the GEOS form. The values of the thermodynamic functions are calculated from:
\[
Y = Y^* + \Delta Y^* \quad (11)
\]

where \( Y^* \) is the ideal gas contribution, and \( \Delta Y^* \) is the residual (departure) function at the same temperature and pressure calculated from the equation of state.

Results and discussions

Five equations of state have been used in this work, to calculate the phase equilibrium and the thermophysical properties for methanol: Soave-Redlich-Kwong (SRK), Peng-Robinson (PR), Schmidt-Wenzel (SW), Freze et al. (C1) and GEOS3C. The investigated PVT range covers single-phase (liquid or gas) and two-phase (liquid-vapor) regions, using recommended NIST data as pseudo experimental values. The calculations were made with the software package PHEQ (Phase Equilibria) developed in our laboratory [17].

The values of the parameters \( C_1 \), \( C_2 \), \( C_3 \) and \( Z \) of the GEOS3C equation for methanol are given in Table 1.

The following thermophysical properties have been predicted: compressibility factor \( (Z) \), enthalpy \( (H) \), enthalpy of vaporization \( (\Delta H_{\text{vap}}) \), entropy \( (S) \), heat capacity at constant pressure \( (C_p) \), heat capacity at constant volume \( (C_v) \), heat capacity ratio \( (C_p/C_v) \), speed of sound \( (W_s) \), fugacity coefficient \( (\phi) \), Joule-Thomson coefficient, \( (\text{JT}) \). No data on these thermophysical properties were regressed in this work. The ideal gas contribution to the thermophysical properties was calculated using the heat capacity function of methanol recommended in [18].

The results of the calculations for VLE and thermophysical properties of methanol are summarized in Tables 2-4. The average absolute deviations (AAD), between calculated values by EOSs and NIST recommended data are given. For each table the number of data points, the pressure and temperature ranges are indicated. The two-phase region properties have been calculated at temperatures from the triple point to the critical point.

The average absolute deviations for a property \( Y \) are relative (%):
\[
\text{AAD} % = \frac{\sum_{i=1}^{N} |Y_{\text{calc}} - Y_{\text{ref}}| \cdot 100}{N} \quad (12)
\]

excepting the enthalpy and entropy where:
\[
\text{AAD} H \text{and} S = \frac{\sum_{i=1}^{N} |H_{\text{calc}} - H_{\text{ref}}|}{N} \quad (13)
\]

The following observations can be made on the basis of the results of the tables 2-4:
- the vapour pressures and saturated volumes are better reproduced by GEOS3C, compared to the results obtained using other equations. The saturated liquid and vapor volumes calculated with the SRK, PR, SW and C1 equations have significant deviations in comparison with NIST recommended data;
- the advantage of the GEOS3C equation is that the liquid volume is improved by the parameter \( C_1 \), without translation [3];
- the GEOS3C equation predicts better results for the enthalpies and the entropies in the both saturated liquid and vapour phase and also for the enthalpy of vaporization.
- the difference in performance between the EOSs is less noticeable for other thermophysical properties on the saturation curve and in the single phase region: heat capacities, speed of sound and Joule Thomson coefficient;
- the AAD% is given in tables 3 and 4 for the JT coefficient in the saturated liquid and also in the single phase region are relatively high, determined by very small values of the JT coefficients;
- the speeds of sound values predicted by GEOS3C have large deviations in comparison with NIST recommended data. The value of \( W_s \) (speed of sound) is depending of both heat capacity ratio and the derivative \( \frac{\partial P}{\partial V} \). [3]. The GEOS3C equation predicts reasonable the heat capacity ratio, but the derivative \( \frac{\partial P}{\partial V} \) has higher deviations relative to NIST equation of state. From this analysis, it results that...

### Table 1

VALUES OF \( C_1, C_2, C_3, Z_c \) (GEOS) PARAMETERS FOR METHANOL OBTAINED IN THE T RANGE: 175.6 – 512.6 K. CRITICAL TEMPERATURE, CRITICAL PRESSURE AND ACENTRIC FACTOR FROM NIST DATABASE [14]

<table>
<thead>
<tr>
<th>Component</th>
<th>( C_1 )</th>
<th>( C_2 )</th>
<th>( C_3 )</th>
<th>( Z_c ) (GEOS)</th>
<th>( Z_c ) (exp.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>0.6860</td>
<td>0.8157</td>
<td>-1.5330</td>
<td>0.2512</td>
<td>0.2173</td>
</tr>
</tbody>
</table>

### Table 2

PVT AND THERMODYNAMIC FUNCTION DEVIATIONS ON THE SATURATION CURVE FOR METHANOL. TEMPERATURE RANGE (K): 175.6–512.6. PRESSURE RANGE (BAR): 0.18 x 10^5 – 81.03. NUMBER OF DATA POINTS: 171

<table>
<thead>
<tr>
<th>EOS</th>
<th>( p^* )</th>
<th>( \nu^* )</th>
<th>( \nu )</th>
<th>( \Delta_{\text{vap}}H )</th>
<th>( H^i ) (kJ/kg)</th>
<th>( H^f ) (kJ/kg)</th>
<th>( S^\text{cv} ) (kJ/kg/K)</th>
<th>( S^\text{cv} ) (kJ/kg/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SRK</td>
<td>20.4</td>
<td>37.1</td>
<td>66.7</td>
<td>10.9</td>
<td>96.7</td>
<td>120</td>
<td>0.30</td>
<td>0.41</td>
</tr>
<tr>
<td>PR</td>
<td>15.6</td>
<td>21.7</td>
<td>37.7</td>
<td>8.6</td>
<td>78.7</td>
<td>93.8</td>
<td>0.24</td>
<td>0.31</td>
</tr>
<tr>
<td>SW</td>
<td>22.0</td>
<td>12.9</td>
<td>129</td>
<td>10.2</td>
<td>99.1</td>
<td>90.2</td>
<td>0.29</td>
<td>0.35</td>
</tr>
<tr>
<td>C1</td>
<td>19.9</td>
<td>6.1</td>
<td>61.3</td>
<td>10.6</td>
<td>85.3</td>
<td>117</td>
<td>0.26</td>
<td>0.39</td>
</tr>
<tr>
<td>GEOS3C</td>
<td>1.7</td>
<td>3.5</td>
<td>2.4</td>
<td>3.5</td>
<td>40.3</td>
<td>59.1</td>
<td>0.11</td>
<td>0.16</td>
</tr>
</tbody>
</table>
the good correlation of vapour pressure and saturated liquid density does not guarantee accurate values of the derivative \( \frac{\partial P}{\partial V} \) in the liquid region.

Examples of calculated properties are presented in the figures 1-12. Figures 1 and 2 show the pressure – density diagrams for methanol.

Points figure NIST data, while the curves are calculated with the GEOS3C and SW equations, for the saturation region and subcritical and supercritical isotherms. Large deviations can be observed in the saturated liquid densities predicted by the SW equation in comparison with NIST recommended data. The same situation is in the single phase region, on the subcritical isotherms. The densities calculated with the GEOS3C equation are in better agreement with the experimental data in comparison with the densities calculated with the SW equation.

The figures 3-5 show the deviations in vapour pressure and saturated liquid and vapour densities for the five EOSs in comparison with NIST recommended data. The very large deviations at low temperatures, given by PR, SRK, SW and C1 EOSs, are determined by their parameters which were optimized only for temperatures higher than the normal boiling point of methanol (337.6 K).

The calculated enthalpies by GEOS3C and SW equations, on the saturation curve and in the single phase region are shown in figure 6 and 7 (points: NIST

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### Table 3

<table>
<thead>
<tr>
<th>EOS</th>
<th>AAD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SRK</td>
<td>51.8</td>
</tr>
<tr>
<td>PR</td>
<td>47.4</td>
</tr>
<tr>
<td>SW</td>
<td>45.6</td>
</tr>
<tr>
<td>C1</td>
<td>25.3</td>
</tr>
<tr>
<td>GEOS3C</td>
<td>14.7</td>
</tr>
</tbody>
</table>

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### Table 4

<table>
<thead>
<tr>
<th>EOS</th>
<th>AAD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SRK</td>
<td>51.8</td>
</tr>
<tr>
<td>PR</td>
<td>47.4</td>
</tr>
<tr>
<td>SW</td>
<td>45.6</td>
</tr>
<tr>
<td>C1</td>
<td>25.3</td>
</tr>
<tr>
<td>GEOS3C</td>
<td>14.7</td>
</tr>
</tbody>
</table>
recommended data). The GEOS3C equation gives better predicted values of enthalpies in the entire range of $T$ and $P$.

The pressure–entropy diagrams of methanol calculated by GEOS3C and C1 equations are presented in figure 8 and 9.

The GEOS3C calculated entropy values are in good agreement with the NIST data. The entropy predictions of C1 equation have higher deviations from the NIST data, especially on the saturation curve.

The heat capacity ($C_p$) prediction from GEOS3C equation, on the saturation curve is shown in the figure 10. The GEOS3C equation predicts correctly an infinite value for isobaric heat capacity at the critical point. As observed, the NIST isobaric heat capacity on the vapor saturation curve shows an unusual behaviour, not proved experimentally. The cubic EOSs predict a different form of this curve. It can be mentioned that the intersection of the
two heat capacity saturated curves given by NIST data is also predicted by GEOS3C equation.

The Joule-Thomson coefficient predictions for methanol from the GEOS3C and SRK equations on the saturation curve are presented in figure 11. Apparently, a satisfactory agreement with NIST data may be remarked in the liquid region for both EOSs, though larger deviations are observed in the AAD% values in table 3.

Figure 12 shows the pressure - speed of sound diagram predicted by SRK equation for methanol, in the entire range of $T$ and $P$. The predicted values are in good agreement with the NIST data only in the vapour region (table 3).

Conclusions

The vapour – liquid equilibrium and the thermophysical properties of methanol were predicted by five equations of state: SRK, PR, SW, C1 and GEOS3C on a wide $PVT$ range, including the entire saturation region. A large comparison with $PVT$ and thermodynamic recommended NIST data was made.

The following thermophysical properties were calculated: compressibility factor, enthalpy, enthalpy of evaporation, entropy, heat capacity at constant pressure, heat capacity at constant volume, heat capacity ratio, speed of sound, fugacity coefficient, Joule-Thomson coefficient. The comparisons with recommended NIST data for these properties were also presented.

The GEOS3C equation gives better the vapour pressure and saturated liquid and vapour volumes than the other cubic equations of state, including the low temperature range.

Regarding the thermophysical properties, the GEOS3C equation predicts better results for the enthalpies and the entropies in the entire $PVT$ range. The speed of sound values predicted for liquid on the saturation curve by GEOS3C have large errors in comparison with NIST recommended data. Joule Thompson coefficient for liquid on the saturation curve and on isotherms is better predicted by GEOS3C equation.

The difference in performance between the five EOSs is less noticeable for other thermophysical properties: the both isochoric and isobaric heat capacities in the entire range of $T$ and $P$, the speed of sound and the Joule-Thompson coefficient for vapour on the saturation curve.

So far, GEOS3C, with four optimized parameters compares favorably to other equations in literature, being simple enough for applications.

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List of symbols

- $a, b, c, d$: parameters in GEOS
- AAD: absolute average deviation
- $B$: dimensionless parameter in GEOS, defined by eq. (7)
- $C_1, C_2, C_3$: parameters in GEOS3C temperature function
- $C_v, C_p$: isochoric and isobaric heat capacities
- $E$: expression based on GEOS, defined by eq. (18)
- $F$: Helmholtz function
- $H$: enthalpy
- $JT$: Joule-Thomson coefficient
- $M$: molar mass
- $P, P_s$: pressure, saturation pressure
- $R$: universal gas constant
- $S$: entropy
- $T$: temperature
- $U$: internal energy
- $V, V_L, V_V$: molar volume, liquid volume, vapor volume
- $W_s$: speed of sound
- $Y$: thermodynamic function (general notation)
- $Z$: compressibility factor

**Greeks**

- $\alpha_c$: Riedel's criterium (parameter in GEOS)
- $\beta$: reduced temperature function in GEOS
- $\varphi$: fugacity coefficient
- $\Omega_a, \Omega_b, \Omega_c, \Omega_d$: parameters of GEOS
- $\omega$: acentric factor

**Subscripts**

- $c$: critical property
- $r$: reduced property

**Superscript**

- $exp$: experimental (NIST recommended) data
- $eos$: calculated values
- $R$: residual (departure) function

**References**


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