New Formulation for the Viscosity of Isobutane

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Outline

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Motivation — Problems with Consistency

Isobutane: EOS, $\eta$, $\lambda$ — inconsistent

- Correlations recommended in REFPROP
  - $\eta$: Vogel et al. (2000)
  - $\lambda$: Perkins (2002)

- Characterization
  - EOS classical including the critical region, an additional parametric crossover EOS not needed
  - $\eta$ not including a critical enhancement, but using an old-fashioned classical MBWR
  - $\lambda$ including a critical enhancement according to a simplified crossover model by Olchowy and Sengers (1988), but again based on an old-fashioned classical MBWR

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## Isobutane — Primary experimental viscosity data

<table>
<thead>
<tr>
<th>Authors</th>
<th>Year</th>
<th>Method</th>
<th>Number of points</th>
<th>$T$ (K)</th>
<th>$\rho$ (kg m(^{-3}))</th>
<th>$\Delta \eta/\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Küchenmeister and Vogel</td>
<td>2015</td>
<td>OD</td>
<td>14</td>
<td>298–627</td>
<td>0</td>
<td>0.3</td>
</tr>
<tr>
<td>Herrmann et al.</td>
<td>2015</td>
<td>VW</td>
<td>9</td>
<td>298–498</td>
<td>0</td>
<td>0.3</td>
</tr>
<tr>
<td>Abe et al.</td>
<td>1979</td>
<td>OD</td>
<td>7(^8)</td>
<td>298–468</td>
<td>1.5–2.4</td>
<td>0.4–1.0</td>
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<tr>
<td>Dunlop</td>
<td>1994</td>
<td>C</td>
<td>1(^8)</td>
<td>298</td>
<td>2.4</td>
<td>0.5</td>
</tr>
<tr>
<td>Gonzalez and Lee</td>
<td>1966</td>
<td>C</td>
<td>47</td>
<td>311–444</td>
<td>11–608</td>
<td>2.5</td>
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<tr>
<td>Agaev and Yusibova</td>
<td>1969</td>
<td>C</td>
<td>452</td>
<td>273–548</td>
<td>1.3–645</td>
<td>4.0</td>
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<tr>
<td>Diller and van Poolen</td>
<td>1985</td>
<td>OQC</td>
<td>141</td>
<td>115–300</td>
<td>548–748</td>
<td>2.5</td>
</tr>
<tr>
<td>Herrmann et al.</td>
<td>2015</td>
<td>VW</td>
<td>567</td>
<td>298–498</td>
<td>1.0–497</td>
<td>0.5</td>
</tr>
</tbody>
</table>

\(^6\) C, capillary; OD, oscillating disk; OQC, oscillating quartz crystal; VW, vibrating wire  
\(^7\) re-evaluated data  
\(^8\) Data virtually not used for developing the new viscosity formulation.
Isobutane — Terms for zero-density viscosity and initial density dependence

- Parts for zero-density viscosity and initial density dependence treated separately
- Using reduced quantities: $\tau = \frac{T_c}{T}$, $\delta = \frac{\rho}{\rho_c}$
- Bank of terms for separate zero-density viscosity correlation:

$$\eta_{0, \text{bank}}(\tau) = \frac{A_{0,PF}}{\tau^{1/2} \left\langle \sum_{j=-2}^{2} \sum_{i=0}^{3} A_{0,ij} (T_c/\tau)^{j/2} \left\{ \exp \left[ \left( \frac{T_c}{\tau} \right)^{1/3} \right] \right\}^i \right\rangle}.$$  Result: $A_{0,00}, A_{0,0-1}, A_{0,10}$.

$\to$ Extrapolation of $\eta_0(\tau)$ down to 0 K and up to 10000 K very reasonable
Rainwater-Friend theory\textsuperscript{9,10} used for separate initial-density dependence of viscosity:

\[
\eta_{1}(\tau) = \eta_{0}(\tau)A_{1,PF}\left[ \sum_{k=0}^{6} A_{1,k}(\tau)^{0.25k} + A_{1,7}\tau^{2.5} + A_{1,8}\tau^{5.5} \right].
\]

Experimental data for \(B_{1}^{*}\) and \(\eta_{1}\) of Küchenmeister and Vogel and of Herrmann \textit{et al.} used to determine \(\varepsilon/k_{B}\) and \(\sigma\) needed for calculating coefficients \(A_{1,k}\).
Isobutane — Thermodynamic scaling

- Viscosity represented by a single variable $\rho^{\gamma}/T$ instead of separate variables $\rho$ and $T$
- Scaling exponent $\gamma$ separately be determined
- $\delta, \tau$ used for higher density terms as unknown function $G(\delta^\gamma \tau)$, applied to exp. data\(^{11}\)

$$\eta_h(\tau, \delta) = a_{01} \tau^0 \delta^3 + a_{210} \tau^2 \delta^{10} + \tau^{1/2} \delta^{-2/3} \left[a_5(\delta^\gamma \tau)^5\right]$$

with $\gamma = 5.6$

\[< 120 \text{ K}\]
\[+ 125 \text{ K}\]
\[> 130 \text{ K}\]
\[\triangle 135 \text{ K}\]
\[\triangle 140 \text{ K}\]
\[\blacktriangle 150 \text{ K}\]
\[\blacktriangledown 160 \text{ K}\]
\[\blacktriangledown 180 \text{ K}\]
\[\bigcirc 200 \text{ K}\]
\[\bullet 250 \text{ K}\]
\[\square 300 \text{ K}\]

- saturated liquid calculated values


S. Herrmann (Hochschule Zittau/Görlitz) Viscosity Formulation for Isobutane July 26th, 2018, S. 9

Isobutane — Critical enhancement of viscosity

New data for isobutane of Herrmann *et al.* (2015)\(^{12}\) compared to preliminary correlation

- Deviations up to +1.67 % near critical density ($\rho_c = 225.5 \text{ kg m}^{-3}$)

\[< 298.15 \text{ K}\]
\[+ 348.15 \text{ K}\]
\[\triangle 373.15 \text{ K}\]
\[\square 405.15 \text{ K}\]
\[\bigcirc 410.15 \text{ K}\]
\[\blackdiamond 423.15 \text{ K}\]
\[\blacktriangledown 448.15 \text{ K}\]
\[\times 473.15 \text{ K}\]
\[> 498.15 \text{ K}\]

- 410.15 K, data influenced by critical enhancement

Critical enhancement according to Bhattacharjee et al. (1981)\textsuperscript{13}

- Viscosity $\eta$ corresponds to an asymptotic power-law divergence:
  \[ \eta \approx \eta_b (Q_0 \xi)^z \eta. \]
- Critical enhancement represents a multiplicative anomaly:
  \[ \eta_c = \eta_b [(Q_0 \xi)^z \eta - 1]. \]
- Crossover is needed $\rightarrow$ complete global solution by Olchowy and Sengers (1988) for the mode-coupling theory:
  \[ \eta_c = \eta_b [\exp(z \eta H) - 1]. \]
- Simplified closed-form solution earlier developed (Bhattacharjee et al.) $\rightarrow$ recently used for IAPWS water (Huber et al., 2009):
  \[ \eta_c = \eta_b [\exp(z \eta Y) - 1]. \]


Viscosity-surface correlation for Isobutane

Bank of terms for higher-density and critical regions

- Reduced quantities: $\tau = \frac{T}{T_c}, \delta = \frac{\rho}{\rho_c}$
- Bank of terms for the higher-density terms and the critical region:
  \[
  \eta - \eta_0(\tau) - \eta_1(\tau)\delta = \eta_{h+c,\text{bank}}(\tau, \delta) = \sum_{i=0}^{5} \sum_{j=2}^{10} A_{ij} \tau^i \delta^j + \tau^{1/2} \delta^{-2/3} \left[ \sum_{k=1}^{5} A_k (\delta \gamma \tau)^k \right]
  + \sum_{m=0}^{1} A_m \tau \delta \mu_m e^{-\beta_m (\delta - \gamma_m)^2 - \epsilon_m |\tau - \zeta_m|}.
  \]
Final result for viscosity of isobutane

- Reduced quantities: \( \tau = \frac{T_c}{T} \), \( \delta = \frac{\rho}{\rho_c} \)
- Separate zero-density viscosity and initial-density dependence correlation
- Result from structure-optimization method for higher-density and critical regions

\[
\eta_{\text{cor}, \text{C}_4\text{H}_{10}}(\tau, \delta) = \frac{A_{0,\text{PF}}}{\tau^{1/2} \left[ A_{0,0} \tau^{1/2} (T_c)^{-1/2} + A_{1,0} e^{-\left(\frac{T_c}{\tau}\right)^{1/3}} \right]} \times \left\{ 1 + A_{1,\text{PF}} \left[ \sum_{k=0}^{6} A_{1,k}(\tau)^{0.25k} + A_{1,7} \tau^{2.5} + A_{1,8} \tau^{5.5} \right] \delta \right\} + \sum_{i=1}^{10} A_i \tau^i \delta^{d_i} + \tau^{1/2} \delta^{-2/3} A_{11} (\delta^{5.6} \tau)^4 + \sum_{i=12}^{13} A_i \tau \delta e^{-\beta_i (\delta - 1)^2 - \epsilon_i (\tau - 1)}.
\]

Comparison equation vs. experiment and correlations

- Viscosity in the limit of zero density and at low densities
- Agreement within the experimental uncertainty
- Error bars: ±0.3 %

![Graph showing comparison between experimental data and correlation equations](image-url)
Viscosity in the fluid region

- New data dominant
- Large deviations particularly at small and high densities for earlier primary data

\[ \frac{\nu_{\text{exp}} - \nu_{\text{cor}}}{\nu_{\text{cor}}} \]

\( \rho / \text{kg m}^{-3} \)

\[ \nabla, \diamondsuit, \square \] earlier experimental data

\[ \bullet \] new experimental data
Behavior in the two-phase region

![Graph showing viscosity behavior in the two-phase region]

Comparison to viscosity formulation from literature

**Viscosity formulation of Vogel et al. (2000)**

- Error bars: uncertainty of former correlation of Vogel et al.

![Graph comparing viscosity formulation with error bars]

- 200 K
- 300 K
- 350 K
- 400 K
- 410 K
- 450 K
- 500 K
- 600 K

\[ \eta / \mu \text{Pa s} \]

\[ \rho / \text{kg m}^{-3} \]
Conclusion and Outlook

- New viscosity formulation was generated for isobutane based on new precise experimental viscosity data
- The structure-optimization method of Setzmann and Wagner (Ruhr-Universität Bochum) was used
- The viscosity was correlated as $\eta(\tau, \delta)$
- The zero-density and initial-density viscosity parts were treated separately
- Thermodynamic scaling for higher-density terms, scaling exponent $\gamma$ inferred
- Critical enhancement was included using new data of Herrmann et al.
  - Theory: divergence at the critical point
  - Correlation: finite values when approaching the critical point due to used experimental data from the near-critical region

- Investigation on further fluids for which new experimental data are available in literature