New Formulation for the Viscosity of Normal Butane

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Outline

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   • Problems with consistency

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Motivation – Problems and Tasks

Convenience for engineers

- Use of a Standard Database Program for Thermophysical Properties — consistent with respect to thermodynamic and transport properties: REFPROP

- Consistency of the formulations for water:
  - Viscosity $\eta$: Huber et al. (2009)
  - Thermal conductivity $\lambda$: Huber et al. (2012)

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Problems with consistency

Normal Butane: EOS, $\eta$, $\lambda$ — inconsistent

- Correlations recommended in REFPROP
  - $\eta$: Vogel et al. (1999)
  - $\lambda$: Perkins et al. (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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1 Lemmon, E. W., Huber, M. L., and McLinden, M. O., Standard Reference Data Program, National Institute of Standards and Technology, Gaithersburg (2013).

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Normal Butane – Correlation method using structure optimization

Selection criteria
- Combination of different terms
- Requirement of reliable experimental data
- Use of simple functional dependencies, e.g., $\eta = \eta(T, \rho)$

Procedure
- Evaluation and classification of all available viscosity data
- Selection of terms for the complete fluid range of thermodynamic states including the near-critical region
- Assessment of the resulting correlation using statistical parameters and adequate description of experimental data

Normal Butane – 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>Kestin, Yata</td>
<td>1968</td>
<td>OD</td>
<td>2</td>
<td>293–303</td>
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<td>0.4</td>
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<td>Küchenmeister,</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vogel</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Herrmann, Vogel</td>
<td>2015</td>
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<td>14</td>
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<td>297–303</td>
<td>2–3</td>
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<td>1977</td>
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<td>5</td>
<td>299–478</td>
<td>1–2</td>
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<td>Abe et al.</td>
<td>1978</td>
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<td>Abe et al.</td>
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<td>6</td>
<td>298–468</td>
<td>2</td>
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<td>Abe et al.</td>
<td>1979</td>
<td>OD</td>
<td>7</td>
<td>298–468</td>
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<td>0.4–1.0</td>
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<tr>
<td>Swift et al.</td>
<td>1960</td>
<td>FC</td>
<td>5</td>
<td>293–373</td>
<td>468–579</td>
<td>2.5</td>
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<tr>
<td>Dolan et al.</td>
<td>1963</td>
<td>C</td>
<td>50</td>
<td>311–444</td>
<td>13–623</td>
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<tr>
<td>Carmichael, Sage</td>
<td>1963</td>
<td>RC</td>
<td>45</td>
<td>278–478</td>
<td>2–631</td>
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<td>Diller, van Poolen</td>
<td>1985</td>
<td>OQC</td>
<td>89</td>
<td>136–300</td>
<td>573–742</td>
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<td>Herrmann, Vogel</td>
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<td>VW</td>
<td>289</td>
<td>298–448</td>
<td>1–498</td>
<td>0.5</td>
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</tbody>
</table>

9 C, capillary; FC, falling cylinder; OD, oscillating disk; OQC, oscillating quartz crystal; RC, rotating cylinder; VW, vibrating wire
10 re-evaluated data
Normal Butane – $p, T$ diagram with primary experimental data

- Swift et al. (1960)
- Carmichael, Sage (1963)
- Dolan et al. (1965)
- Diller, van Poolen (1985)
- Herrmann, Vogel (2015)

Saturation line

- Kestin et al. (1971)
- Kestin et al. (1977)
- Abe et al. (1978)
- Abe et al. (1979)
- Abe et al. (1979a)
- Kestin, Yata (1968)
- Küchenmeister, Vogel (2015)
- Herrmann, Vogel (2015)

Saturation line

- Swift et al. (1960)
- Carmichael, Sage (1963)
- Dolan et al. (1965)
- Diller, van Poolen (1985)
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- Kestin et al. (1977)
- Abe et al. (1978)
- Abe et al. (1979)
- Abe et al. (1979a)
- Kestin, Yata (1968)
- Küchenmeister, Vogel (2015)
- Herrmann, Vogel (2015)

Viscosity Formulation for Normal Butane

- Reduced quantities: $\tau = \frac{T}{T_c}$, $\delta = \frac{p}{p_c}$
- Bank of terms for separate zero-density viscosity correlation:

$$
\eta_{0,\text{bank}}(\tau) = \frac{A_{0,PF}}{\tau^{1/2} \exp \left[ \sum_{i=0}^{8} A_{0,i}(\ln \tau)^i \right]}
$$

**Result:** $A_{0,0}, A_{0,1}, A_{0,2}$.

- Rainwater-Friend theory\textsuperscript{11,12} used for separate initial-density dependence of viscosity:

$$
\eta_1(\tau) = \eta_0(\tau) A_{1,PF} \tau^{1/2} \left[ \sum_{i=0}^{6} A_{1,i}(\tau)^{0.25i} + A_{1,7} \tau^{2.5} + A_{1,8} \tau^{5.5} \right].
$$

- Bank of terms for the higher-density terms:

$$
\eta_2 - \eta_0(\tau) - \eta_1(\tau) \delta = \eta_{h,\text{bank}}(\tau, \delta) = \sum_{i=0}^{5} \sum_{j=2}^{10} A_{ij} \tau^i \delta^j + \tau^{1/2} \delta^{-2/3} \left[ \sum_{k=1}^{3} A_k (\delta^\gamma \tau)^k \right].
$$

- First result for normal butane without terms for critical enhancement:

$$
\eta_{\text{cor, \text{n-C}_{4}H_{10}}}(\tau, \delta) = \eta_0(\tau) + \eta_1(\tau) \delta + \sum_{i=1}^{9} A_i \tau^i \delta^d_i + \tau^{1/2} \delta^{-2/3} A_{10} (\delta^\gamma \tau)^3.
$$

Viscosity formulation without critical enhancement

New data for normal butane of Herrmann and Vogel (2015)\(^{13}\)

- Deviations up to +1.20 % near critical density \((\rho_c = 228.0 \text{ kg m}^{-3})\)

![Graph showing deviations up to +1.20 % near critical density](image)


Critical enhancement according to Bhattacharjee et al. (1981)\(^{14}\)

- Viscosity \(\eta\) corresponds to an asymptotic power-law divergence:

  \[
  \eta \approx \eta_b (Q_0 \xi)^{\eta}.
  \]

- Critical enhancement represents a multiplicative anomaly:

  \[
  \eta_c = \eta_b [(Q_0 \xi)^{\eta} - 1].
  \]

- 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):

  \[
  \eta_c = \eta_b [\exp(z_\eta Y) - 1].
  \]

Method, Theory, and Results  
Viscosity formulation with critical enhancement

**Viscosity-surface correlation for normal butane**

- Reduced quantities: $\tau = \frac{T_c}{T}$, $\delta = \frac{\rho}{\rho_c}$
- Separate zero-density viscosity and initial-density dependence correlation as before
- Bank of terms for the higher-density terms and the critical region:

  $$\eta_{h+c, \text{bank}}(\tau, \delta) = \sum_{i=0}^{5} \sum_{j=2}^{10} A_{ij} \tau^i \delta^j + \tau^{1/2} \delta^{-2/3} \left[ \sum_{k=1}^{3} A_k (\delta^\gamma \tau)^k \right]$$

  $$+ \sum_{m=0}^{1} A_m \tau \delta \mu_m e^{-\beta_m (\delta - \gamma_m)^2 - \epsilon_m |\tau - \zeta_m|}.$$ 

- Final result for normal butane:

  $$\eta_{\text{cor}, \text{n-C}_4\text{H}_{10}}(\tau, \delta) = \eta_0(\tau) + \eta_1(\tau) \delta + \sum_{i=1}^{9} A_i \tau^i \delta^{d_i} + \tau^{1/2} \delta^{-2/3} A_{10} (\delta^5 \tau)$$

  $$+ \sum_{i=11}^{12} A_i \tau \delta \epsilon_i (\delta - 1)^2 - \epsilon_i |\tau - 1|.$$ 

**Comparisons**  
Viscosity in the limit of zero density and at low densities

- Agreement within the experimental uncertainty
- Error bars: $\pm 0.3 \%$

![Graph showing comparison](image)

- $\blacklozenge$, $\blacklozenge$, $\blacklozenge$ experimental data in the limit of zero density
- $\blacktriangledown$, $\blacktriangledown$, $\blacktriangledown$, $\blacktriangledown$, $\blacktriangledown$ experimental data at atmospheric pressure
- $\blacktriangledown$ Younglove, Ely (1987)$^{15}$
- $\blacktriangledown$ Vogel et al. (1999)
- $\blacktriangledown$ Quiñones-Cisneros, Deiters (2006)$^{16}$

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Comparisons

Viscosity in the fluid region

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

\[
\frac{\eta_{\text{exp}} - \eta_{\text{cor}}}{\eta_{\text{cor}}} \times 100
\]

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

- \( \triangle, \nabla, \star \) earlier experimental data
- \( \bigcirc \) new experimental data

S. Herrmann (Hochschule Zittau/Görlitz)  Viscosity Formulation for Normal Butane  September 4th, 2017, S. 13
Comparisons

Viscosity in the fluid region

Behavior in the two-phase region

![Graph of viscosity vs density in the two-phase region]

Consistency test using behavior of $\eta_{\text{Res}}$

Comparison to viscosity formulations from literature:
Vogel et al. (1999) and Quiñones-Cisneros and Deiters (2006)
New viscosity formulation was generated for normal butane based on new precise experimental viscosity data

The structure-optimization method of Setzmann and Wagner (Ruhr-Universität Bochum) was used

The zero-density and initial-density viscosity parts were treated separately

The viscosity was correlated as $\eta(T, \rho)$

Critical enhancement was included using new data of Herrmann and Vogel

Theory: divergence at the critical point
Correlation: finite values when approaching the critical point due to used experimental data from the near-critical region

Further work on isobutane
precise data using a vibrating-wire viscometer are available