Viscosity and Density Measurements on Compressed Liquid n-Tetradecane a)

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AIMS:

• **Long-term**: To develop a reference correlation for the viscosity of normal tetradecane (n-C\textsubscript{14}) at high pressures and in a wide range of temperatures.

• **Short-term** (present work):
  1. To measure the **viscosity** of n-C\textsubscript{14} in wide temperature and pressure ranges — special attention to \((T,p)\) ranges where viscosity data are scarce (or non-existent, v.g.: \(T<293\) K).
  2. To **correlate the present viscosity** data with density.
MOTIVATION

1. General economic importance of alkanes;

2. Increasing importance of paraffins (and their mixtures) for energy storage systems as PHASE CHANGE MATERIALS;

3. Lack of rigorous viscosity data for n-tetradecane, at low temperatures and moderately high pressures ($p<10$ MPa). Ranges that are relevant for the development of some sustainable processes.
SUMMARY OF THE PRESENT WORK

• New measurements of the **viscosity** of n-tetradecane (n-$C_{14}$) at moderately high pressures, using the **vibrating wire** technique.

• New measurements of the **density** of n-tetradecane using a model HP Anton Paar U-tube densimeter.

• Development of a **correlation** of viscosity with density, using a modified hard-spheres model.
Density

Experimental results obtained using an Anton Paar DMA HP model vibrating U-Tube instrument with model DMA 5000 as reading unit.

Measurements were performed along nine isotherms in the range \(283 \leq T \leq 373\) K and pressures from (0.1 to 70) MPa

The experimental data were correlated by a modified Tait equation, proposed by J.H. Dymond, R. Malhotra, The Tait equation: 100 years on, Int. J. Thermophys. 9 (1988) 941–951.

\[
\rho = \rho_0 \left\{1 - C \ln \left( \frac{D + p}{D + p_0} \right) \right\}^{-1}
\]

with \( \rho_0 = \sum_{i=0}^{2} b_i T^i \)
Deviations of the density of n-tetradecane (this work) from the correlation

\[ \frac{\rho_{\text{exp}} - \rho_{\text{cal}}}{\rho_{\text{cal}}} \]

$p / \text{MPa}$

$283 \text{ K}; \bigstar 288 \text{ K}; \bigcirc 293 \text{ K}; \square 298 \text{ K}; \bullet 308 \text{ K}; \triangle 318 \text{ K}; \text{---} 338 \text{ K}; \diamondsuit 358 \text{ K}; \blacklozenge 373 \text{ K}$
Deviations of literature density data (after 1978) from the correlation of our results

Snyder and Winnick’s, 1970 data are not shown (0.8%<dev<1%)

Gouel; △ Valência et al.; ○ Kariznovi et al.; ◇ Gawronska et al.; □ Khasanshin et al.
# Literature viscosity data for liquid n-C\textsubscript{14}

<table>
<thead>
<tr>
<th>Year</th>
<th>First author</th>
<th>Temperature range/K</th>
<th>Pressure range/MPa</th>
<th>NP</th>
<th>Method</th>
<th>Purity /%</th>
<th>Nominal uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>1986</td>
<td>Ducoulombier</td>
<td>293-373</td>
<td>0.1 - 100</td>
<td>24</td>
<td>falling body</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>1989</td>
<td>Knapstad</td>
<td>293-423</td>
<td>0.1</td>
<td>10</td>
<td>Oscillating viscometer</td>
<td>99</td>
<td>(0.33-0.56) %</td>
</tr>
<tr>
<td>2001</td>
<td>Franjo</td>
<td>298.15</td>
<td>0.1</td>
<td>1</td>
<td>capillary</td>
<td>99</td>
<td>± 5 \times 10^{-4} mm\cdot s^{-1}</td>
</tr>
<tr>
<td>2003</td>
<td>Nayak</td>
<td>298-308</td>
<td>0.1</td>
<td>3</td>
<td>capillary</td>
<td>99</td>
<td>±0.001 mPa s</td>
</tr>
<tr>
<td>2007</td>
<td>Hernández-Galván</td>
<td>313-393</td>
<td>0.69 - 60</td>
<td>40</td>
<td>rolling-ball\textsuperscript{a)}</td>
<td>99</td>
<td>±2.0 %</td>
</tr>
<tr>
<td>2012</td>
<td>Mahajan</td>
<td>298.15</td>
<td>0.1</td>
<td>1</td>
<td>capillary</td>
<td>99</td>
<td>±0.003 mPa s\textsuperscript{c)}</td>
</tr>
<tr>
<td>2013</td>
<td>Kariznovi</td>
<td>300-343</td>
<td>0.1-10</td>
<td>15</td>
<td>Cambridge Viscometer\textsuperscript{b)}</td>
<td>99</td>
<td>5%</td>
</tr>
</tbody>
</table>

\textsuperscript{a)} Kinematic Viscosity; \textsuperscript{b)} Cambridge Viscometer Model SPC; \textsuperscript{c)} repeatability; NA – not available
Literature viscosity data ($\eta$ vs. $p$) for compressed liquid $n$-$C_{14}$ (up to 100 MPa)

- Ducoulombier 1986
- Hernández-Galván 2007
- Kariznovi 2013

Uncertainty:
- Ducoulombier 1986: Uncertainty NA
- Hernández-Galván 2007: Uncertainty = 5%
- Kariznovi 2013: Uncertainty = 5%

Data range:
- $\eta$ vs. $p$ for compressed liquid $n$-$C_{14}$ up to 100 MPa

Graph showing the relationship between viscosity ($\eta$) and pressure ($p$) for the specified conditions.
Literature viscosity ($\eta$ vs. $T$) data for compressed liquid $n$-$C_{14}$
Literature viscosity data with specified uncertainty less than 5%

\((p>0.1\text{ MPa})\)
Viscosity:

New measurements of the viscosity of n-tetradecane along eight isotherms in the range $(283 \leq T \leq 358)$ K and pressures up to 70 MPa, have been performed using the vibrating wire technique in the forced mode of operation.
Vibrating wire sensor

1 - top washers;
2 - upper claw chucks;
3 - vibrating wire;
4 - rod spacers;
5 - bottom claw chucks;
6 - upper rod clamping;
7 - magnetic circuit;
8 - magnets;
9 - lower rod clamping,
10 - bottom washers

Raw data

Hydrodynamic Model

Viscosity
Updated view: Viscosity ($\eta$ vs. $T$) for n-$C_{14}$ ($p \geq 0.1$ MPa) with uncertainty less than 5%
Updated view: Viscosity ($\eta$ vs. $p$) for $n$-$C_{14}$ ($p \geq 0.1$ MPa) with uncertainty less than 5%
Correlation scheme: A modified hard-spheres model of transport properties of fluids for VISCOSITY

Heuristic development\(^1\) of the kinetic theory for dense hard-sphere fluids, applied to the van der Waals model of a liquid, proposed by Dymond.\(^2\)

\[
\eta^* = 6.035 \times 10^8 \left( \frac{1}{MRT} \right)^{1/2} \left( V_m \right)^{2/3} \eta
\]

\[
\eta^* = f \left( \frac{V_m}{V_0} \right) \quad V_0 = f(T)
\]

Viscosity Correlation
Smooth Hard-Spheres

\[ V_0(T) \times 10^6 \left( \text{m}^3 \text{mol}^{-1} \right) = V_{0,\text{ref}} + t \left( T - T_{\text{ref}} \right) + m \left( T - T_{\text{ref}} \right)^2 \]

**Viscosity Correlation**
Smooth Hard-Spheres

\[ \frac{1}{\eta^*} = \sum_{i=0}^{4} a_i \left( \frac{V_m}{V_0} \right)^i \]

\[ \eta^* = \frac{1}{\sum_{i=0}^{4} a_i \left( \frac{V_m}{V_0} \right)^i} \]

Viscosity at \( T_{\text{ref}} \)

**Viscosity Correlation**
Smooth Hard-Spheres

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**Viscosity Correlation**
Smooth Hard-Spheres

\[ \frac{1}{\eta^*} = \sum_{i=0}^{4} a_i \left( \frac{V_m}{V_0} \right)^i \]

Viscosity at \( T_{\text{ref}} \)
Deviations (\(\eta\ vs. \rho\)) for \(n-C_{14}\) (\(p \geq 0.1\) MPa) obtained in the present work with the vibrating-wire technique, from the present correlation scheme.

Correlations
\(\eta(T, \rho) \& \rho(T, \rho)\)

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3-8 Sept 2017
21st ECTP, Graz, Austria
Deviations of \( n-C_{14} \) viscosity \textbf{literature data} at 0.1 MPa, from our correlation.
Deviation of the viscosity literature data for \( n-C_{14} \) from our correlation as a function of pressure.

\[
100\left(\frac{\eta_{\text{exp}} - \eta_{\text{cal}}}{\eta_{\text{cal}}}\right) / \eta_{\text{cal}}
\]

\( p \) / MPa

- Ducoulombier 1986
- Hernández-Gálvan 2007
- Kariznovi 2013
Conclusions:

- This work provides new viscosity measurements in ranges where literature data were scarce or totally absent (No literature data below 293 K even at 0.1 MPa!).

- New density measurements were also performed and used to develop a provisional viscosity correlation, which may be used to obtain $\eta = \eta(T,p)$ with low uncertainty in wide ranges of $T$ and $p$.

- However, large inconsistency between literature results is observed, exceeding the nominal uncertainty of most of the available measurements, which hinders the possibility to develop reference correlations for the viscosity of n-tetradecane.

- A reference correlation for the viscosity of $n$-$C_{14}$, needs new independent measurements, using several experimental methods, covering the low temperature and intermediate pressure ranges (up to 10 MPa).
Acknowledgments:

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