New Correlation for the Viscosity of Normal Butane

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Outline

1. Motivation – Problems and Tasks
   - Convenience for engineers
   - Problems with consistency
2. Method, Theory, and Results
   - Structure-optimization method
   - Choice of primary data sets
   - Viscosity-surface correlation without critical enhancement
   - Treatment of critical enhancement
   - Viscosity-surface correlation with critical enhancement
3. Comparisons
   - Viscosity in the limit of zero density and at low densities
   - Viscosity in the fluid region
4. Conclusion and Outlook

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[1]
- Consistency of the formulations for water:
  - Equation of state (EOS): Wagner and Pruß (2002)[2]
  - Viscosity η: Huber *et al.* (2009)[3]
  - Thermal conductivity λ: Huber *et al.* (2012)[4]

1 Lemmon, E. W., Huber, M. L., and McLinden, M. O., Standard Reference Data Program, National Institute of Standards and Technology, Gaithersburg (2013).

2 Wagner, W. and Pruß, A., *J. Phys. Chem. Ref. Data* **31**, 387-535 (2002).

3 Huber, M. L., Perkins, R. A., Laesecke, A., Friend, D. G., Sengers, J. V., Assael, M. J., Metaxa, I. M., Vogel, E., Mares, R. and Miyagawa, K., *J. Phys. Chem. Ref. Data* **38**, 101-125 (2009).

4 Huber, M. L., Perkins, R. A., Friend, D. G., Sengers, J. V., Assael, M. J., Metaxa, I. M., Miyagawa, K., Hellmann, R. and Vogel, E., *J. Phys. Chem. Ref. Data* **41**, 1-23 (2012).

Ethane: EOS, λ – inconsistent

- Correlations recommended in REFPROP

  EOS Bücker and Wagner (2006)[5]

  η, λ Friend *et al.* (1991)[6]

→ Consistent for η: new viscosity-surface correlation published in *J. Phys. Chem. Ref. Data*[7]

Propane: EOS, λ – inconsistent

- Correlations recommended in REFPROP

  EOS Lemmon *et al.* (2009)[8]

  η Vogel *et al.* (1998)[9]

  λ Marsh *et al.* (2002)[10]

→ Consistent for η: manuscript submitted to *J. Phys. Chem. Ref. Data*

5 Bücker, D. und Wagner, W., *J. Phys. Chem. Ref. Data* **35**, 205-266 (2006).

6 Friend, D. G., Ingham, H., und Ely, J. F., *J. Phys. Chem. Ref. Data* **20**, 275-347 (1991).

7 Vogel, E., Span, R., and Herrmann, S., *J. Phys. Chem. Ref. Data* **44**, 043101 (2015).

8 Lemmon, E. W., McLinden, M. O., and Wagner, W., *J. Chem. Eng. Data*, **54**, 3141-3180 (2009).

9 Vogel, E., Küchenmeister, C., Bich, E., and Laesecke, A., *J. Phys. Chem. Ref. Data*, **27**, 947-970 (1998).

10 Marsh, K., Perkins, R., and Ramires, M. L. V., *J. Chem. Eng. Data*, **47**, 932-940 (2002).

Problems with consistency

Normal Butane: EOS, η, λ – inconsistent

- Correlations recommended in REFPROP
  - **EOS** Bücker and Wagner (2006)[11]
  - **η** Vogel *et al.* (1999)[12]
  - **λ** Perkins *et al.* (2002)[13]
- Characterization
  - **EOS** classical including the critical region, an additional parametric crossover EOS not needed
  - **η** not including a critical enhancement, but using an old-fashioned classical MBWR
  - **λ** including a critical enhancement according to a simplified crossover model by Olchowy and Sengers (1988)[14], but again based on an old-fashioned classical MBWR

11 Bücker, D. and Wagner, W., *J. Phys. Chem. Ref. Data* **35**, 929-1019 (2006).
12 Vogel, E., Küchenmeister, C., Bich, E., *High Temp. - High Pressures*, **31**, 173-186 (1999).
13 Perkins, R., Ramires, M. L. V., Nieto de Castro, C. A., and Cusco, L. *J. Chem. Eng. Data*, **47**, 1263-1271 (2002).
14 Olchowy, G. A. and Sengers, J. V., *Phys. Rev. Lett.*, **61**, 15-18 (1988).

Correlation method using structure optimization

Selection criteria

- Combination of different terms
- Requirement of reliable experimental data
- Use of simple functional dependencies, e.g., $\eta = \eta(T, \rho)$
- Viscosity-surface correlations for normal butane:
  - Vogel *et al.* (1999) $\rightarrow$ recommended within REFPROP
  - Quiñones-Cisneros and Deiters (2006)[15] $\rightarrow$ not recommended

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

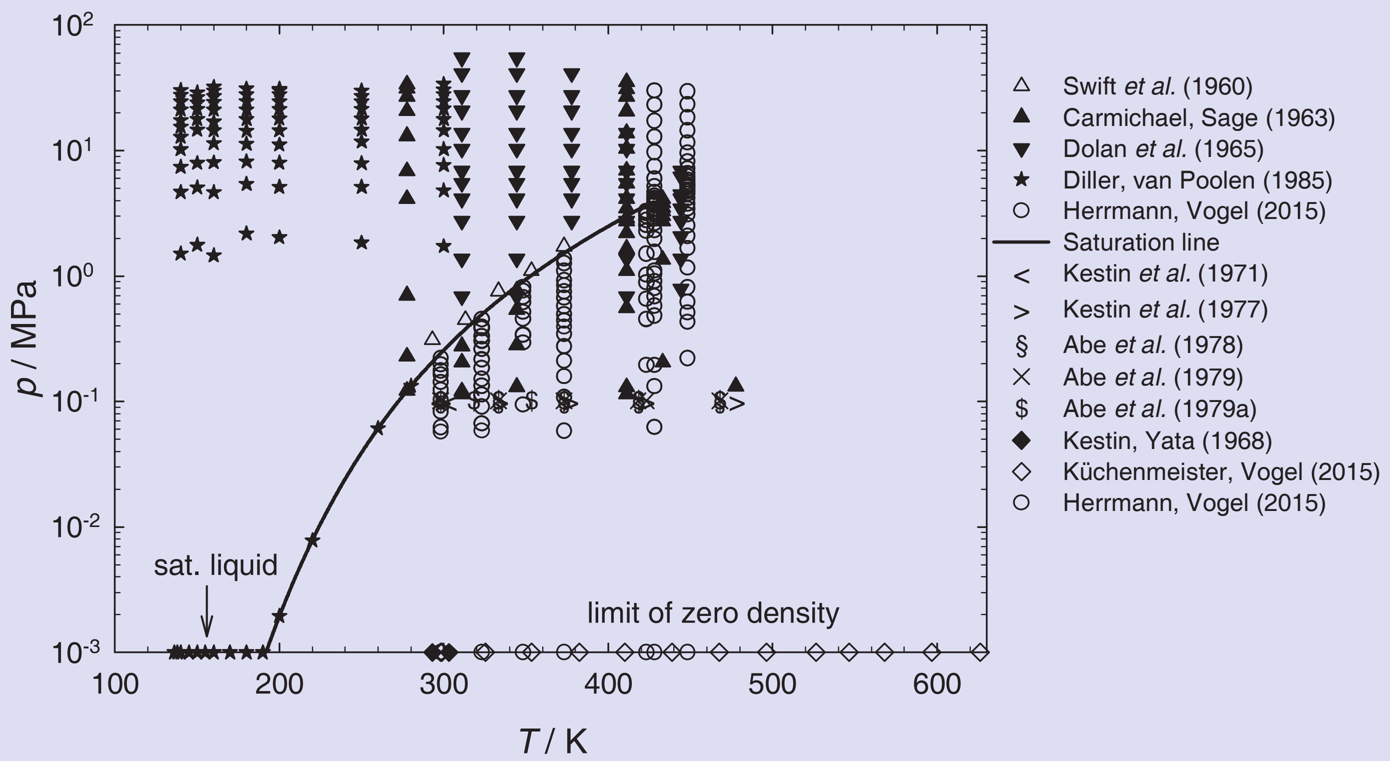
15 Quiñones-Cisneros, S. E. and Deiters, U. K., *J. Phys. Chem. B* **110**, 12820-12834 (2006).

Normal Butane – Primary Experimental Viscosity Data

Authors	Year	Method[16]	Number of points	T K	ρ kg m^{-3}	$\Delta\eta/\eta$ %
Kestin, Yata	1968	OD	2	293–303	0	0.4
Küchenmeister, Vogel	2015[17]	OD	14	298–626	0	0.3
Herrmann, Vogel	2015	VW	7	298–448	0	0.3
Kestin *et al.*	1971	OD	2	297–303	2–3	0.4
Kestin *et al.*	1977	OD	5	299–478	1–2	0.4–1.0
Abe *et al.*	1978	OD	5	298–468	2	0.4–1.0
Abe *et al.*	1979	OD	6	298–468	2	0.4–1.0
Abe *et al.*	1979	OD	7	298–468	2	0.4–1.0
Swift *et al.*	1960	FC	5	293–373	468–579	2.5
Dolan *et al.*	1963	C	50	311–444	13–623	2.5
Carmichael, Sage	1963	RC	45	278–478	2–631	2.5
Diller, van Poolen	1985	OQC	89	136–300	573–742	2.5
Herrmann, Vogel	2015	VW	289	298–448	1–498	0.5

[16] C, capillary; FC, falling cylinder; OD, oscillating disk; OQC, oscillating quartz crystal; RC, rotating cylinder; VW, vibrating wire
[17] re-evaluated data

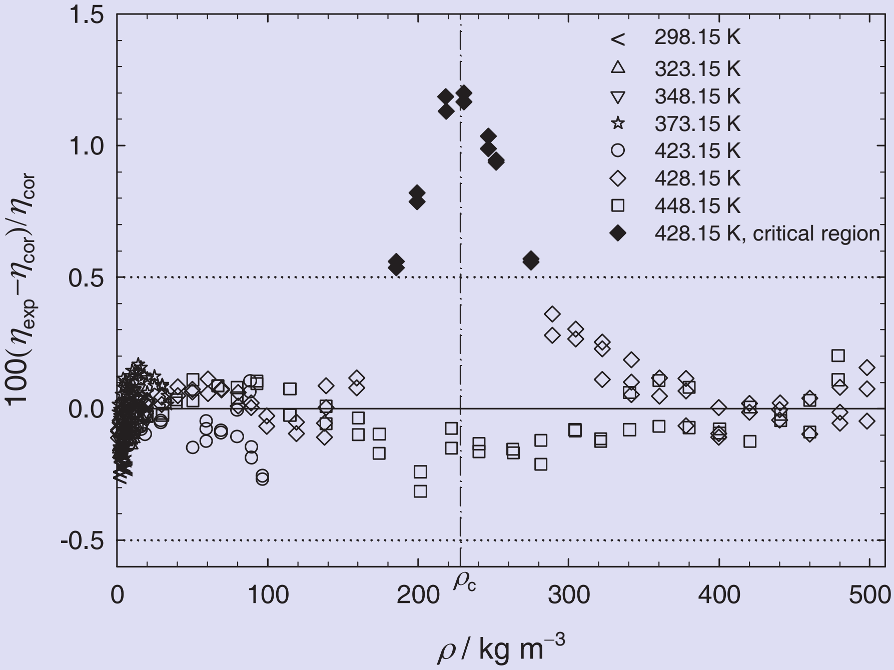
Normal Butane – p,T diagram with primary experimental data



Normal Butane – Correlation without critical enhancement

New data for normal butane of Herrmann and Vogel (2015)[18]

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



[18] Herrmann, S. and Vogel, E., *J. Chem. Eng. Data*, **60**, 3703-3720 (2015).

Critical enhancement according to Bhattacharjee *et al.* (1981)[19]

- Viscosity η 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 $\longrightarrow$ complete global solution by Olchowy and Sengers (1988) for the mode-coupling theory:

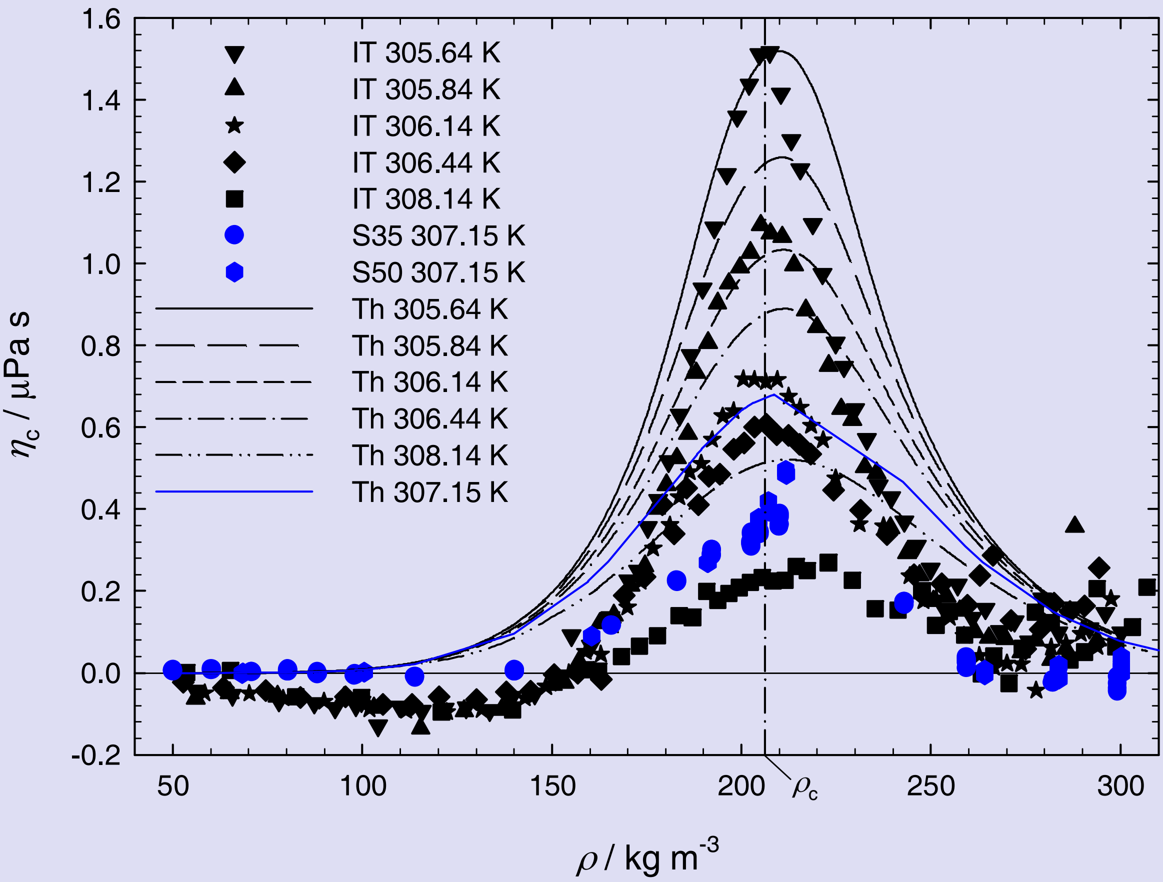
$$\eta_c = \eta_b [\exp(z_\eta H) - 1] \ .$$

- Simplified closed-form solution earlier developed (Bhattacharjee *et al.*) $\longrightarrow$ recently used for IAPWS water (Huber *et al.*, 2009):

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

[19] Bhattacharjee, J. K., Ferrell, R. A., Basu, R. S., and Sengers, J. V., *Phys. Rev. A* **24**, 1469-1475 (1981).

Critical enhancement — ethane: theory vs. experiment



Viscosity-surface correlation for normal butane

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

$$\frac{\eta_{0,\mathrm{bank}}(T)}{\mu\mathrm{Pa\ s}} = \sum_{i=0}^{-8} A_{0,i}\tau^i \qquad \text{Result}: A_{0,0}, A_{0,-1}, A_{0,-6}, A_{0,-7}.$$

- Bank of terms for the total correlation:

$$\frac{\eta_{\mathrm{bank}}(T,\rho)}{\mu\mathrm{Pa\ s}} = \frac{\eta_0(T)}{\mu\mathrm{Pa\ s}} A_0 + \sum_{i=0}^{8}\sum_{j=1}^{20} A_{ij}\tau^i\delta^j + \sum_{k=0}^{5}\sum_{l=1}^{5} A_{kl}\tau^k\delta^l \mathrm{e}^{-\delta}$$

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

- Final result for normal butane:

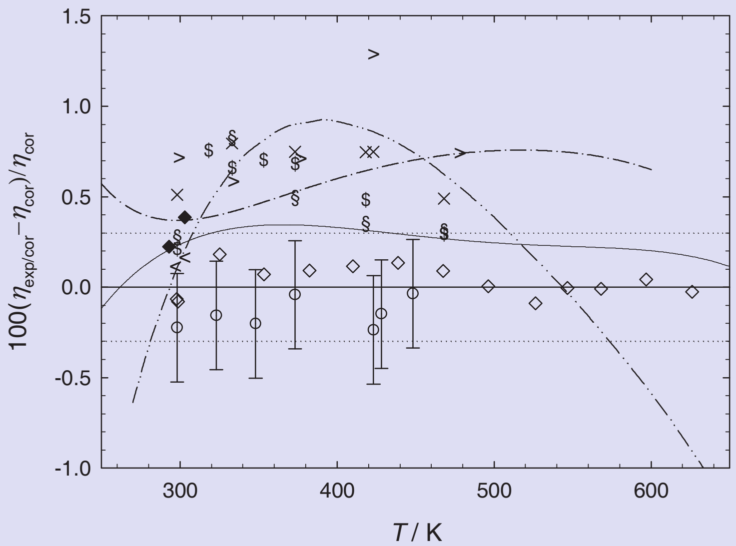
$$\frac{\eta_{\mathrm{cor,\,n-C_4H_{10}}}(T,\rho)}{\mu\mathrm{Pa\ s}} = \sum_{i=1}^{10} A_i\tau^{t_i}\delta^{d_i} + \sum_{i=11}^{13} A_i\tau^{t_i}\delta^{d_i}\mathrm{e}^{-\delta}$$

$$+ \sum_{i=14}^{15} A_i\tau\delta\,\mathrm{e}^{-\beta_i(\delta-1)^2-\varepsilon_i|\tau-1|}.$$

Comparison equation vs. experiment

Viscosity in the limit of zero density and at low densities

- Agreement within the experimental uncertainty
- Error bars: ±0.3 %



◆, ◇, ○ experimental data in the limit of zero density

<, >, §, x, $ experimental data at atmospheric pressure

— · — Younglove, Ely (1987)[20]

—— Vogel *et al.* (1999)

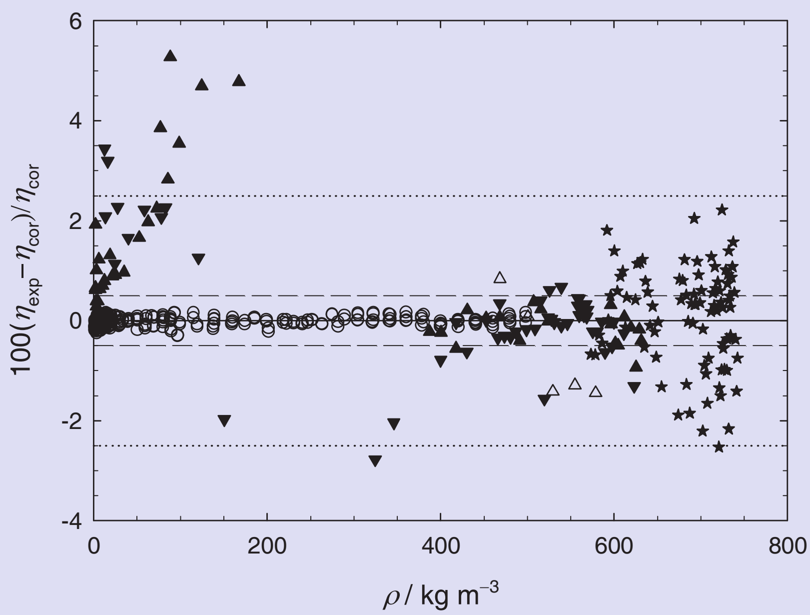
— · · — Quiñones-Cisneros, Deiters (2006)

[20] Younglove, B. A. and Ely, J. F., *J. Phys. Chem. Ref. Data* **16**, 577-798 (1987).

Comparison equation vs. experiment

Viscosity in the fluid region

- New data dominant
- Large deviations particularly at small densities for earlier primary data
- Deviations of data in the near critical region $< \pm 0.15\%$



△, ▼, ▲, ★ earlier experimental data

○ new experimental data

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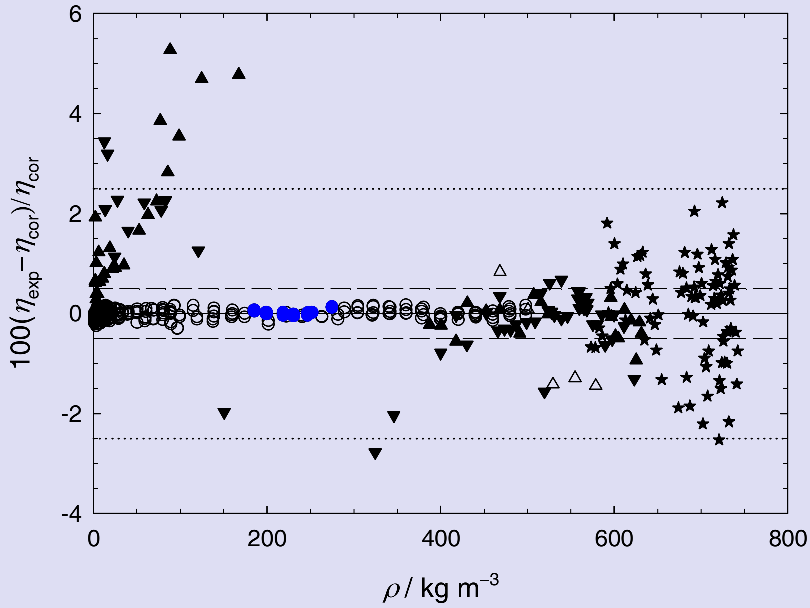
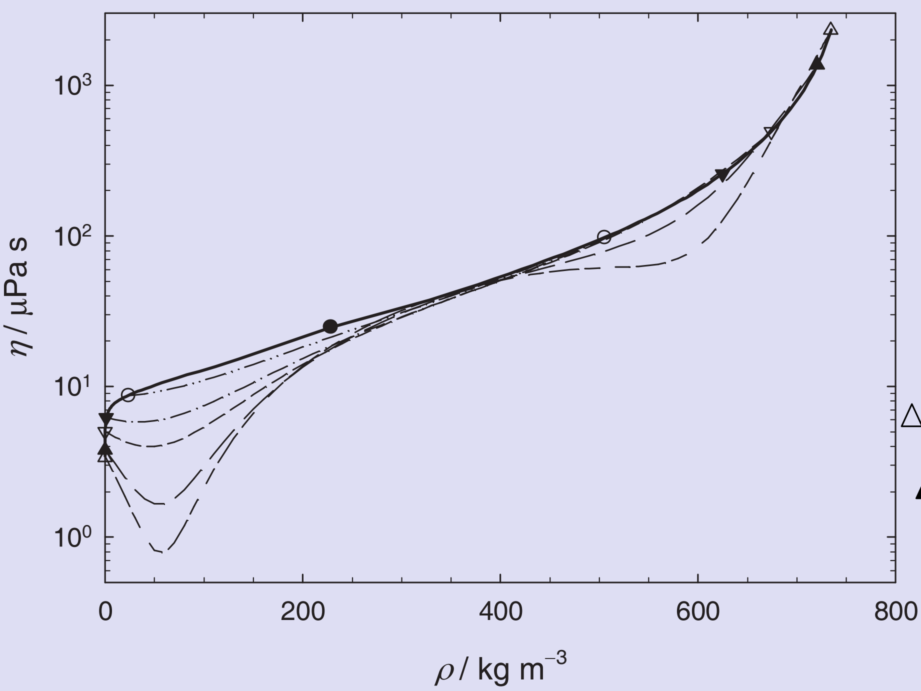


△, ▼, ▲, ★ earlier experimental data

○ new experimental data

Correlation in the two-phase region



△ triple point

● critical point

saturated-vapor and saturated-liquid curves

△– — –△ 134.895 K

▲— —▲ 150 K

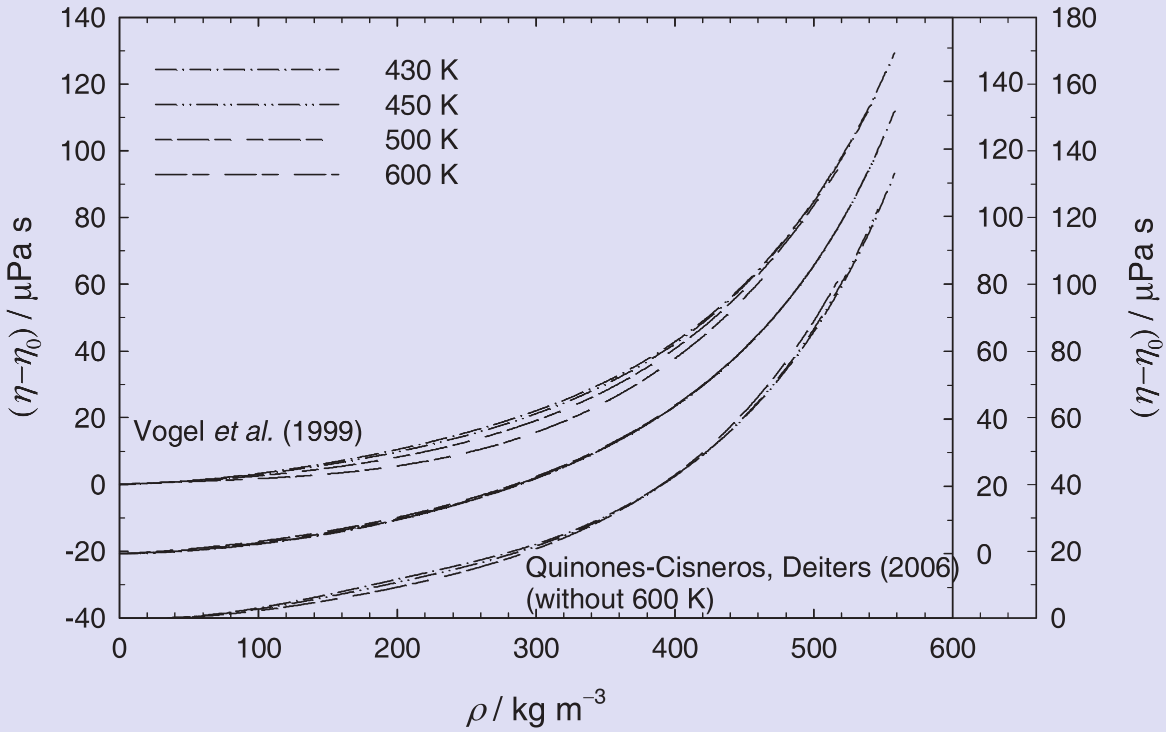
▽– – –▽ 200 K

▼–·–▼ 250 K

○–··–○ 350 K

Consistency test using behavior of η_{Res}

Comparison to viscosity-surface correlations from literature:
Vogel *et al.* (1999) and Quiñones-Cisneros and Deiters (2006)



Conclusion and Outlook

- New viscosity-surface correlation 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 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

Conclusion and Outlook

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