New Formulation for the Viscosity of Normal Butane

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Outline

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).

Problems with consistency

Normal Butane: EOS, η, λ – inconsistent

- Correlations recommended in REFPROP
  - EOS: Bücker and Wagner (2006)[5]
  - η: Vogel *et al.* (1999)[6]
  - λ: Perkins *et al.* (2002)[7]
- 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)[8], but again based on an old-fashioned classical MBWR

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

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

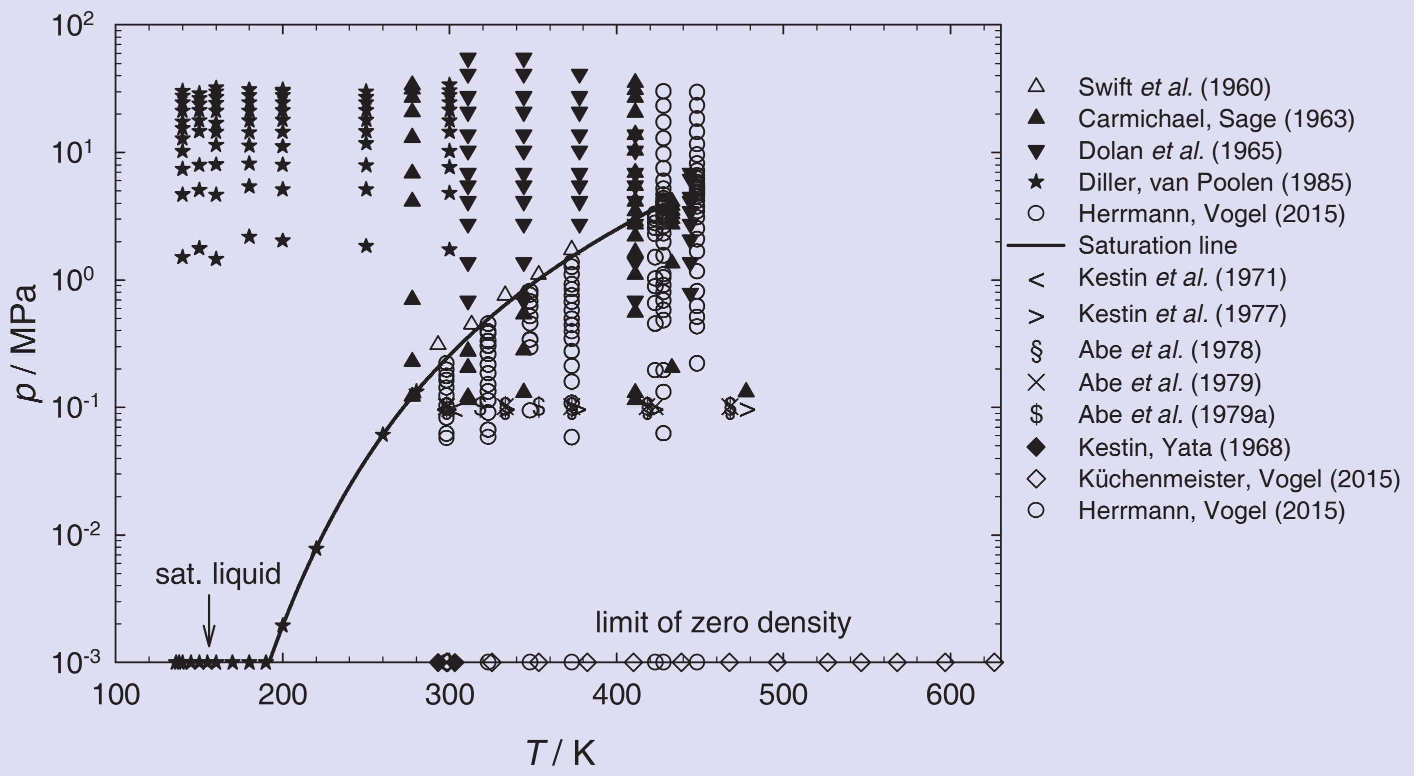
Normal Butane – Primary Experimental Viscosity Data

Authors	Year	Method[9]	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[10]	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

[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



Normal Butane — Correlation without critical enhancement

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

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

- Rainwater-Friend theory[11,12] used for separate initial-density dependence of viscosity:

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

- Bank of terms for the higher-density terms:

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

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

$$\eta_{\mathrm{cor,n-C_4H_{10}}}(\tau, \delta) = \eta_0(\tau) + \eta_1(\tau)\delta + \sum_{i=1}^{9} A_i \tau^{t_i}\delta^{d_i} + \tau^{1/2}\delta^{-2/3} A_{10} (\delta^\gamma \tau)^3 \,.$$

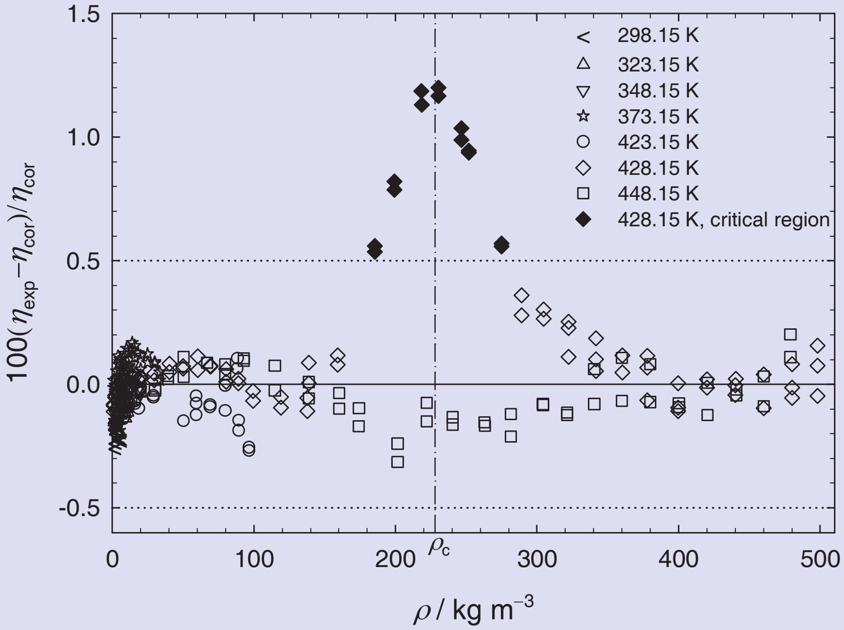
11 Friend, D. G. and Rainwater, J. C., *Chem. Phys. Lett.* **107**, 590-594 (1984).

12 Rainwater, J. C. and Friend, D. G., *Phys. Rev. A* **36**, 4062-4066 (1987).

Normal Butane – Correlation without critical enhancement

New data for normal butane of Herrmann and Vogel (2015)[13]

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



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

Critical enhancement according to Bhattacharjee *et al.* (1981)[14]

- 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):

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

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

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:

$$\eta_{\mathrm{h+c,bank}}(\tau,\delta) = \sum_{i=0}^{5}\sum_{j=2}^{10} A_{ij}\tau^i\delta^j + \tau^{1/2}\delta^{-2/3}\left[\sum_{k=1}^{3} A_k(\delta^{\gamma}\tau)^k\right] + \sum_{m=0}^{1} A_m\tau\delta\mu_m \,\mathrm{e}^{-\beta_m(\delta-\gamma_m)^2-\varepsilon_m|\tau-\zeta_m|}.$$

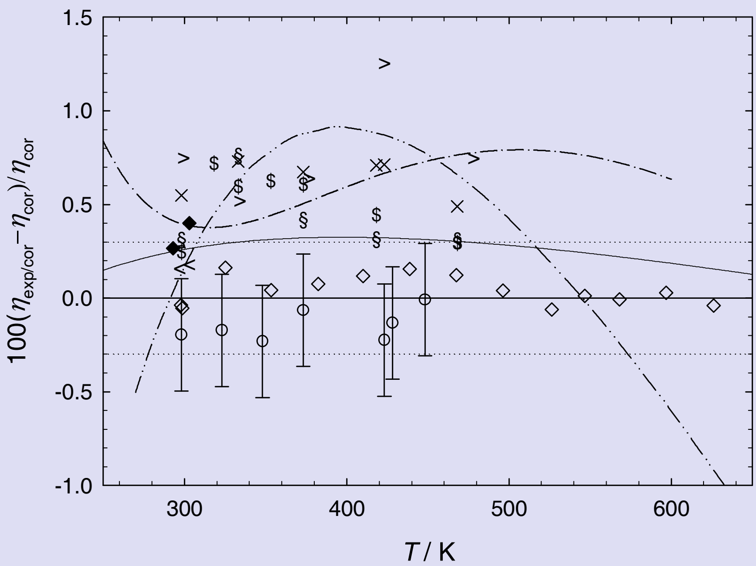
- Final result for normal butane:

$$\eta_{\mathrm{cor,\,n-C_4H_{10}}}(\tau,\delta) = \eta_0(\tau)+\eta_1(\tau)\delta+\sum_{i=1}^{9} A_i\tau^{t_i}\delta^{d_i} + \tau^{1/2}\delta^{-2/3}A_{10}(\delta^{5.7}\tau)^3 + \sum_{i=11}^{12} A_i\tau\delta\,\mathrm{e}^{-\beta_i(\delta-1)^2-\varepsilon_i|\tau-1|}.$$

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)[15]

—— Vogel *et al.* (1999)

— · · — Quiñones-Cisneros, Deiters (2006)[16]

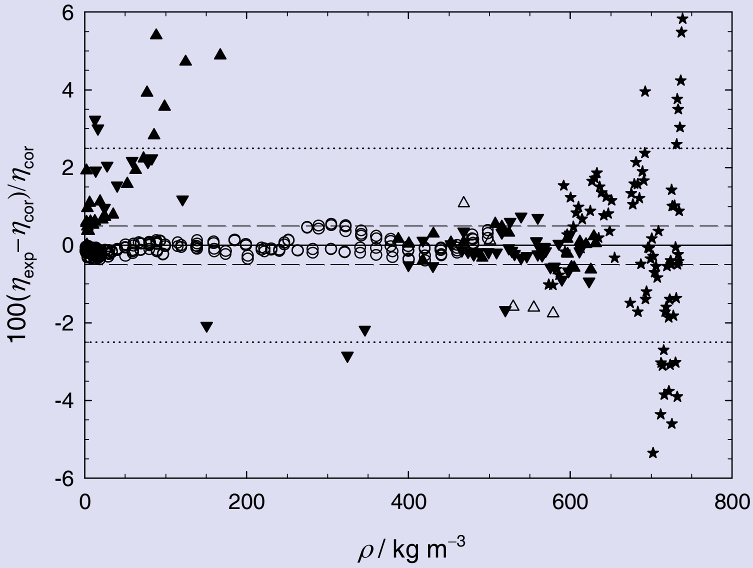
[15] Younglove, B. A. and Ely, J. F., *J. Phys. Chem. Ref. Data* **16**, 577-798 (1987).

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

Comparison equation vs. experiment

Viscosity in the fluid region

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



△, ▼, ▲, ★ earlier experimental data

○ new experimental data

Comparisons | Viscosity in the fluid region

Comparison equation vs. experiment

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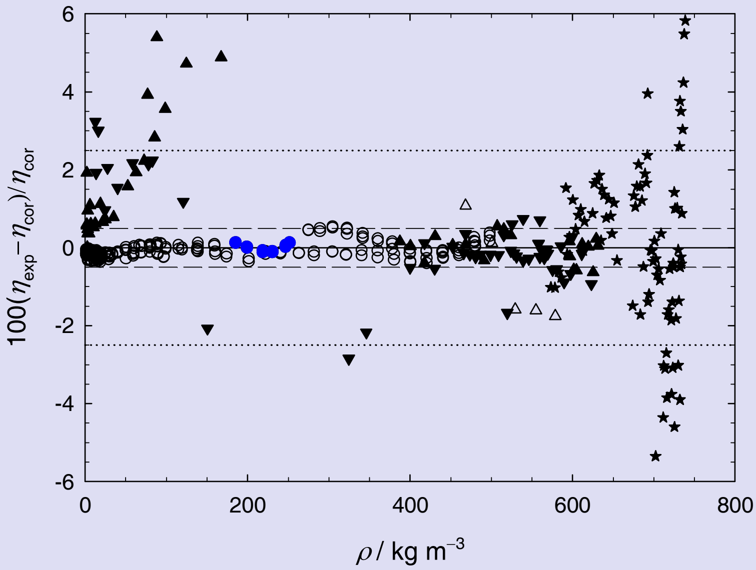
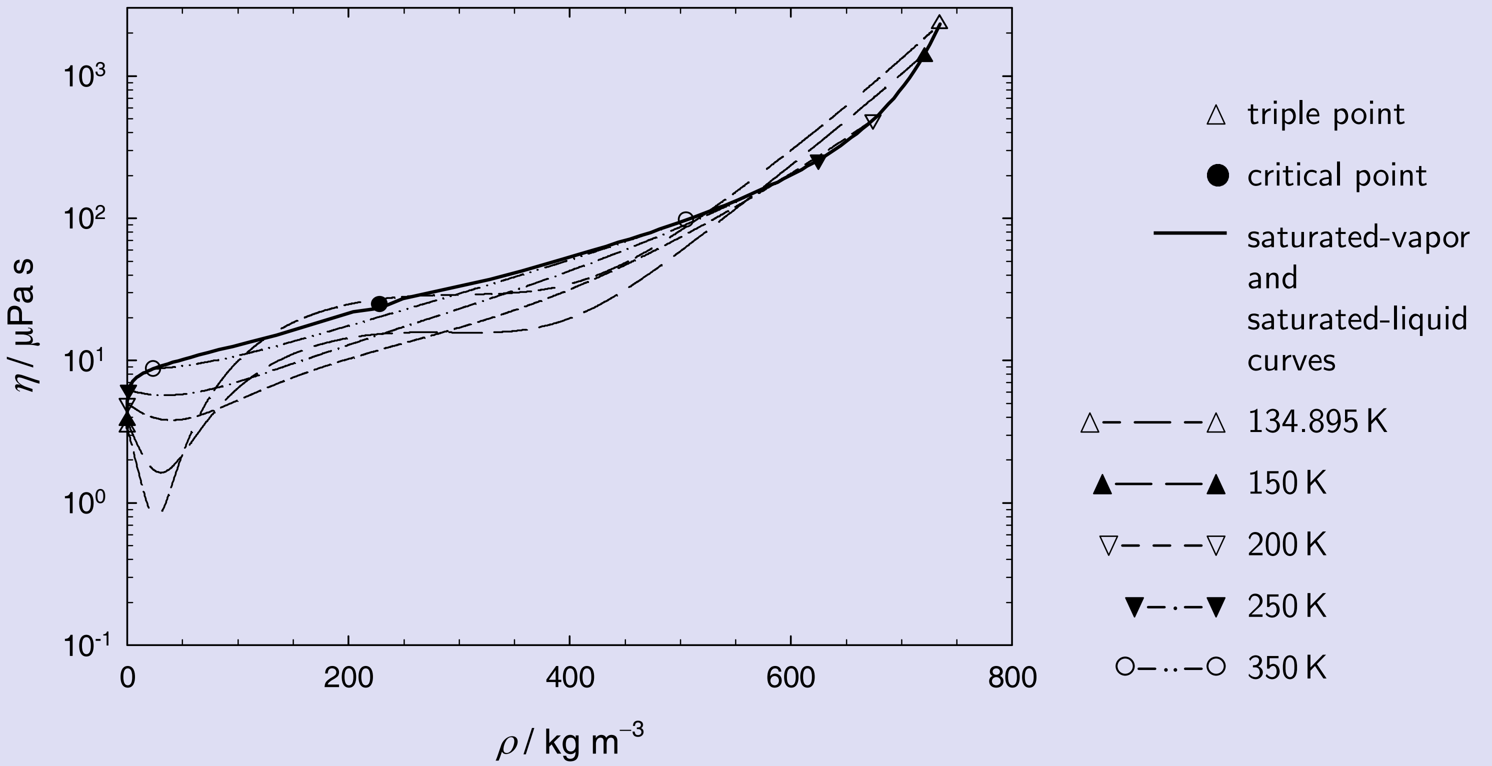


△, ▼, ▲, ★ earlier experimental data

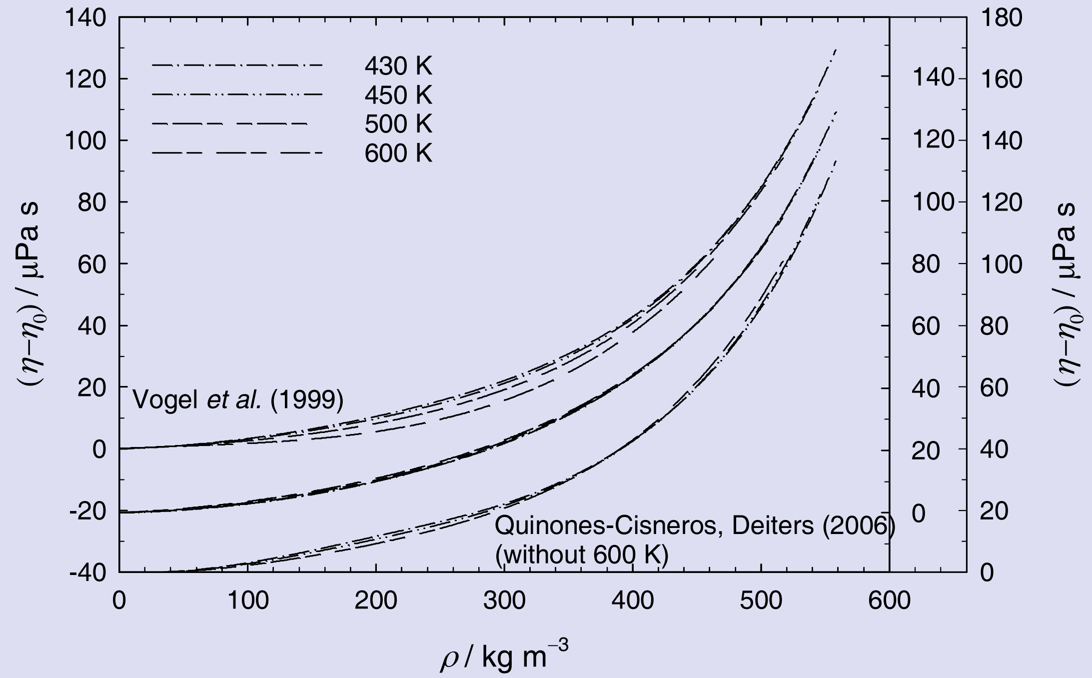
○ new experimental data

Behavior in the two-phase region



Consistency test using behavior of η_{Res}

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



Conclusion and Outlook

- 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

$\rightarrow$ precise data using a vibrating-wire viscometer are available

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S. Herrmann (Hochschule Zittau/Görlitz) Viscosity Formulation for Normal Butane September 4th, 2017, S. 17