Update: Reference Correlation for the Viscosity of Ethane

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Motivation

Need for update of viscosity correlation for ethane

- Current viscosity correlation published in 2015 by Vogel *et al.*[1]
- η_0 part contains only two coefficients $\eta_0(\tau) = n_{0,-1}\tau^{-1} + n_{0,-3}\tau^{-3}$ with $\tau = T_c/T$

→ Extrapolation behavior down to low temperatures good, but limited to higher temperatures due to unphysical maximum at 1143 K

- Hellmann[2] recently published new zero-density viscosity correlation for ethane based on *ab initio* calculations characterized by a very low uncertainty
- Replacement of zero-density viscosity correlation possible, but would cause little inconsistencies to original work of Vogel *et al.*

Advantages of update

- η_0 consistent to other parts of reference correlation
- Improvement of uncertainty and extrapolation behavior of viscosity correlation

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

2 Hellmann, R., *J. Chem. Eng. Data* **63**, 470-481 (2018).

Ethane – New zero-density viscosity correlation of Hellmann

Characteristics and procedure of the new η_0 correlation

- Very low uncertainties ($k = 2$) of calculated values from (90 to 1200) K: 0.3% for $250 \leq T/\mathrm{K} \leq 700$ and 1.0% down to 90 K and up to 1200 K
- Approach used for modeling the zero-density viscosity characterized by pure fitting without strong theoretical basis
- Correlation extrapolates very well down to 0 K and up to at least 6000 K
- Zero-density viscosity correlation of Hellmann is given as function of temperature:

$$\eta_0(T) = \frac{T^{1/2}}{h_1 + \frac{h_2}{\exp(T^{1/3})} + \left[h_3 + \frac{h_4}{\exp(T^{1/3})}\right]\frac{1}{T^{1/2}} + \frac{h_5 T}{\exp(2T^{1/3})}}.$$

- Rewritten using reciprocal reduced temperature τ and critical temperature T_c :

$$\eta_0(\tau) = \frac{(T_c/\tau)^{1/2}}{h_1 + \frac{h_2}{\left\{\exp[(1/\tau)^{\frac{1}{3}}]\right\}^{(T_c)^{\frac{1}{3}}}} + \left[h_3 + \frac{h_4}{\left\{\exp[(1/\tau)^{\frac{1}{3}}]\right\}^{(T_c)^{\frac{1}{3}}}}\right]\left(\frac{\tau}{T_c}\right)^{\frac{1}{2}} + \frac{h_5}{\left\{\exp[(1/\tau)^{\frac{1}{3}}]\right\}^{2(T_c)^{\frac{1}{3}}}}\frac{T_c}{\tau}}.$$

Ethane – 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
- Using the correlation of Hellmann as pretreated terms
- Assessment of the resulting correlation using statistical parameters and adequate description of experimental data

Viscosity-surface correlation for Ethane

- Reduced quantities: $\tau = \frac{T_c}{T}$, $\delta = \frac{\rho}{\rho_c}$
- Separate zero-density viscosity of Hellmann included $[\eta_{0,\mathrm{Hellmann}}(\tau)]$
- Bank of terms:

$$\eta_{\mathrm{bank}}(\tau,\delta) = \eta_{0,\mathrm{Hellmann}}(\tau) + \sum_{i=0}^{8}\sum_{j=1}^{20} A_{ij}\tau^{i}\delta^{j} + \sum_{k=0}^{5}\sum_{l=1}^{5} A_{kl}\tau^{k}\delta^{l}\,\mathrm{e}^{-\delta} + \sum_{m=0}^{1} A_m\tau\delta\,\mathrm{e}^{-\beta_m(\delta-\gamma_m)^2-\varepsilon_m|\tau-\zeta_m|}.$$

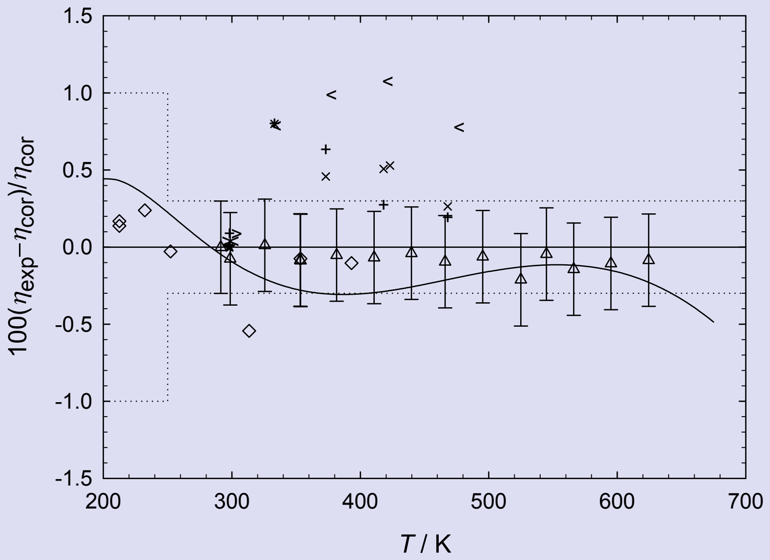
- Final result for ethane:

$$\eta_{\mathrm{cor},\,C_2H_6}(\tau,\delta) = \eta_0(\tau) + \sum_{i=1}^{7} A_i\tau^{t_i}\delta^{d_i} + \sum_{i=8}^{11} A_i\tau^{t_i}\delta^{d_i}\,\mathrm{e}^{-\delta} + + \sum_{i=12}^{13} A_i\tau\delta\,\mathrm{e}^{-\beta_i(\delta-1)^2-\varepsilon_i|\tau-1|}.$$

Comparison of new equation to experiment and equation of Vogel *et al.*

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

★ reference value at 298.15 K

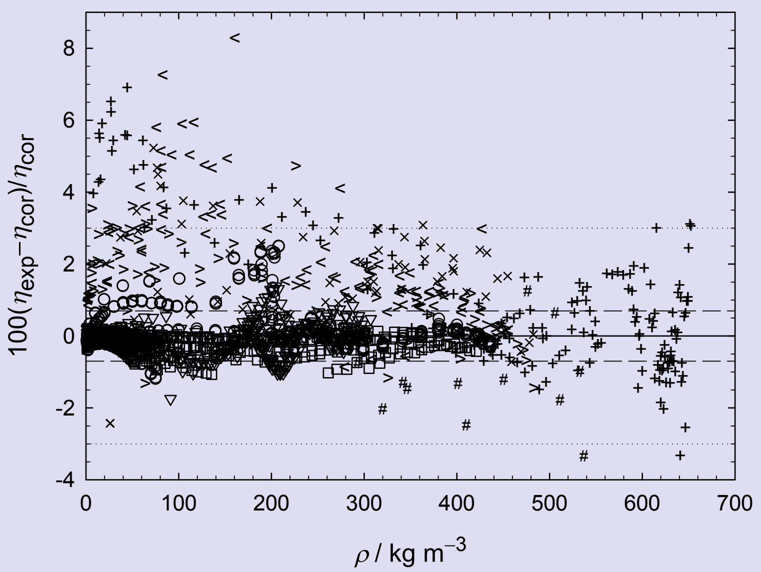
<, >, x, + experimental data at atmospheric pressure

—— zero-density contribution of the correlation of Vogel *et al.* (2015)

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

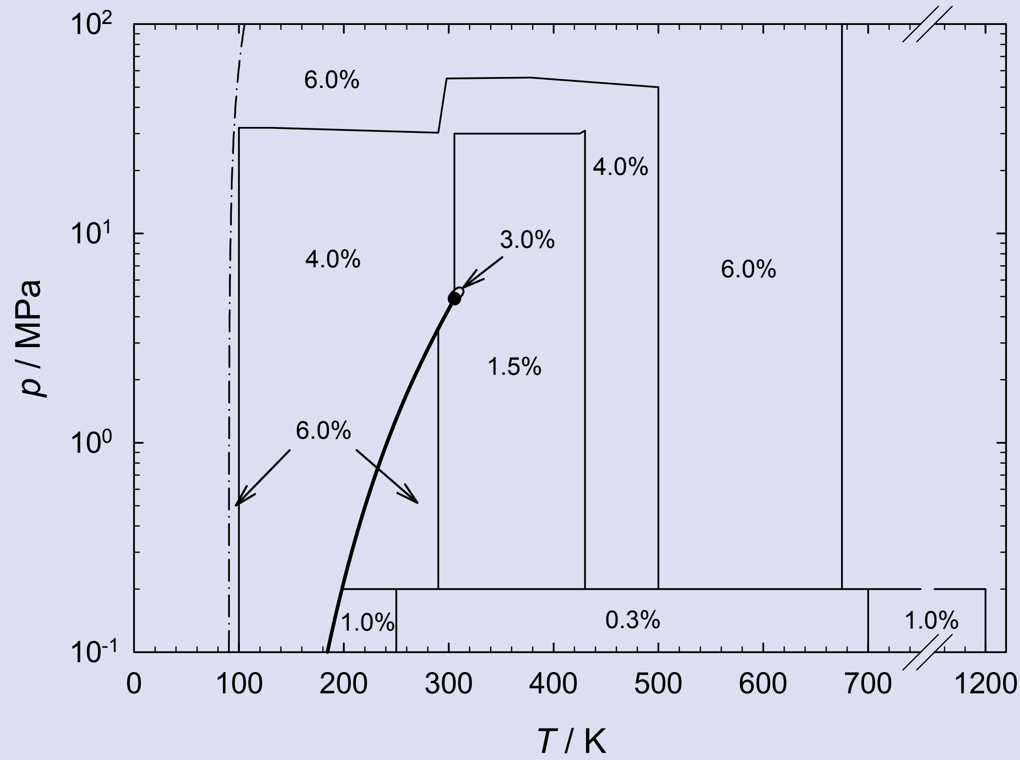


#, >, <, +, X earlier experimental data

□, ▽ newly evaluated experimental data

○ new experimental data

Range of validity extended at low pressures



Conclusion and Outlook

- Update of viscosity formulation for ethane was generated including new zero-density correlation from Hellmann
- The structure-optimization method of Setzmann and Wagner (Ruhr-Universität Bochum) was used
- The zero-density was treated separately as pretreatment
- The viscosity was correlated as $\eta(T, \rho)$
- Critical enhancement was included using newly evaluated and new data of Iwasaki and Takahashi and Seibt *et al.*

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- Maybe new equation of state will come up in a few years

→ Second update using a new eos for ethane could be needed

Update published in *J. Phys. Chem. Ref. Data*

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Update: Reference Correlation for the Viscosity of Ethane [J. Phys. Chem. Ref. Data 44, 043101 (2015)]

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An update of the reference correlation for the viscosity of ethane [E. Vogel *et al.*, J. Phys. Chem. Ref. Data **44**, 043101 (2015)] was developed because recently a new zero-density viscosity correlation based on theoretically calculated values of the dilute-gas viscosity became available. The original zero-density contribution was replaced, and the generation of the complete viscosity correlation was repeated using the residual viscosity concept and a state-of-the-art linear optimization algorithm. A term representing the critical enhancement was again included, so that a total of 18 coefficients resulted for the final formulation. The viscosity in the limit of zero density is now described with an expanded uncertainty of 0.3% (coverage factor $k = 2$) in the temperature range $250 \leq T/\mathrm{K} \leq 700$ and of 1.0% at temperatures $90 \leq T/\mathrm{K} < 250$ and $700 < T/\mathrm{K}$