Measurements of the Viscosity of Hydrogen and a (Hydrogen+Methane) mixture with a Two-Capillary Viscometer

Benjamin Betken[1,2*], Anders Austegard[1], Francesco Finotti[1], Chiara Caccamo[1], Hans Georg Jacob Stang[1], Bahareh Khosravi[3], and Roland Span[2]

[1]SINTEF Energy Research, Postboks 4761 Torgarden, NO-7465 Trondheim, Norway

[2]Ruhr University Bochum, Thermodynamics, Universitätsstraße 150, Bochum 44801, Germany

[3]Department of Chemical Engineering, Norwegian University of Science Technology (NTNU), NO-7491, Trondheim, Norway

S1 Derivation of the virial correction

Generalization of the Hagen-Poiseuille equation to a non-ideal gas and integration from the inlet to the outlet of the capillary yields

$$-\frac{8\dot{n}}{\pi R^4}\int_0^L \mathrm{d}z = \int_{P_{\mathrm{in}}}^{P_{\mathrm{out}}} \frac{\rho}{\eta}\mathrm{d}P, \tag{S1}$$

where $\dot{n}$, R, L, ρ, η, and P are the molar flow rate, inner radius of the capillary, length of the capillary, molar density, dynamic viscosity, and pressure, respectively. Substitution of ρ and η by pressure-dependent second-order viral expansions

$$\rho = \frac{1}{R_{\mathrm{gas}}T}\frac{P}{1 + B_P P + C_P P^2}, \tag{S2}$$

$$\eta = \eta_0\left(1 + b_\eta P + c_\eta P^2\right), \tag{S3}$$

* Corresponding author. benjamin.betken@thermo.ruhr-uni-bochum.de

and neglecting higher-order terms, yields a simplified, analytically integrable expression for the pressure integral in Eq. (S1), as derived by Berg [1]

$$\int_{P_{\mathrm{in}}}^{P_{\mathrm{out}}} \frac{\rho}{\eta}\mathrm{d}P = \frac{1}{R_{\mathrm{gas}}T\eta_0}\int_{P_{\mathrm{in}}}^{P_{\mathrm{out}}} P - \left(B_P + b_\eta\right)P^2 - \left[\left(C_P + c_\eta\right) - \left(B_P + b_\eta\right)^2\right]P^3\mathrm{d}P, \qquad \text{(S4)}$$

where R_{gas} is the universal gas constant, B_P and C_P are the second and third virial coefficients, and b_η and c_η are the second and third viscosity virial coefficients, respectively. Based on Eq. (S4), Berg [1,2] derived a correction function, to account for non-ideal gas behavior and pressure dependency of the viscosity. However, in contrast to Berg [2], the hydrodynamic model used in this work, is not based on the ideal gas equation of state, but multiparameter Helmholtz equations of state are used to solve the pressure integral in Eq. (S1). Thus, non-ideal gas behavior is already considered. Therefore, an adjusted virial correction is derived below, to correct for the neglected pressure dependency, underlying Eq. (5) in the article.

Add a term

$$2B_PC_PP^4 - 2B_PC_PP^4 + C_P^2P^5 - C_P^2P^5 = 0, \qquad \text{(S5)}$$

and rearrange Eq. (S4) to obtain

$$\begin{aligned}\int_{P_{\mathrm{in}}}^{P_{\mathrm{out}}} \frac{\rho}{\eta}\mathrm{d}P = \frac{1}{R_{\mathrm{gas}}T\eta_0}\int_{P_{\mathrm{in}}}^{P_{\mathrm{out}}} & P[1 - B_PP - C_PP^2 + (B_PP + C_PP^2)^2] - 2B_PC_PP^4 \\ & - C_P^2P^5 - b_\eta P^2 + \left(b_\eta^2 + 2b_\eta B_P - c_\eta\right)P^3\mathrm{d}P.\end{aligned} \qquad \text{(S6)}$$

Approximation of

$$1 - B_PP - C_PP^2 + (B_PP + C_PP^2)^2 \approx \frac{1}{1 + B_PP + C_PP^2}, \qquad \text{(S7)}$$

applying the binomial theorem, which is valid at low pressures, yields

$$\int_{P_{\mathrm{in}}}^{P_{\mathrm{out}}} \frac{\rho}{\eta}\,\mathrm{d}P = \frac{1}{R_{\mathrm{gas}}T\eta_0}\int_{P_{\mathrm{in}}}^{P_{\mathrm{out}}} \frac{P}{1 + B_P P + C_P P^2} - 2B_P C_P P^4 - C_P^2 P^5 - b_\eta P^2 + \left(b_\eta^2 + 2b_\eta B_P - c_\eta\right)P^3\mathrm{d}P. \tag{S8}$$

Combination of Eqs. (S2) and (S8), and integration from the inlet to outlet pressure, gives

$$\int_{P_{\mathrm{in}}}^{P_{\mathrm{out}}} \frac{\rho}{\eta}\,\mathrm{d}P = \frac{(P_{\mathrm{out}} - P_{\mathrm{in}})(\rho_{\mathrm{in}} + \rho_{\mathrm{out}})}{2\eta_0} + \frac{1}{R_{\mathrm{gas}}T\eta_0}\left[-\frac{1}{3}b_\eta(P_{\mathrm{out}}^3 - P_{\mathrm{in}}^3) + \left(b_\eta^2 + 2b_\eta B_P - c_\eta\right)\frac{(P_{\mathrm{out}}^4 - P_{\mathrm{in}}^4)}{4} - \frac{4}{5}B_P C_P\left(P_{\mathrm{out}}^5 - P_{\mathrm{in}}^5\right) - \frac{1}{6}C_P^2(P_{\mathrm{out}}^6 - P_{\mathrm{in}}^6)\right], \tag{S9}$$

where the first term on the right-hand was obtained by application of Eq. (S2) according to

$$\frac{1}{R_{\mathrm{gas}}T\eta_0}\int_{P_{\mathrm{in}}}^{P_{\mathrm{out}}} \frac{P}{1 + B_P P + C_P P^2}\,\mathrm{d}P = \frac{(P_{\mathrm{out}} - P_{\mathrm{in}})(\rho_{\mathrm{in}} + \rho_{\mathrm{out}})}{2\eta_0}. \tag{S10}$$

Substitution of the integrand in Eq. (S10) by $R_{\mathrm{gas}}T\rho$ in accordance with Eq. (S2), is applicable, if the pressure difference between the inlet and outlet of the capillary is small. Combining Eqs. (S1) and (S9), and rearranging Eq. (S1), the molar flow rate reads

$$\dot{n} = \frac{\pi R^4(P_{\mathrm{in}} - P_{\mathrm{out}})(\rho_{\mathrm{in}} + \rho_{\mathrm{out}})}{16L\eta_0} + \frac{\pi R^4(P_{\mathrm{in}}^2 - P_{\mathrm{out}}^2)}{16LR_{\mathrm{gas}}T\eta_0}\left[-\frac{2}{3}b_\eta\frac{(P_{\mathrm{out}}^3 - P_{\mathrm{in}}^3)}{(P_{\mathrm{out}}^2 - P_{\mathrm{in}}^2)} + \left(b_\eta^2 + 2b_\eta B_P - c_\eta\right)\frac{(P_{\mathrm{in}}^2 + P_{\mathrm{out}}^2)}{2} - \frac{8}{5}B_P C_P\frac{\left(P_{\mathrm{out}}^5 - P_{\mathrm{in}}^5\right)}{(P_{\mathrm{out}}^2 - P_{\mathrm{in}}^2)} - \frac{1}{3}C_P^2\frac{(P_{\mathrm{out}}^6 - P_{\mathrm{in}}^6)}{(P_{\mathrm{out}}^2 - P_{\mathrm{in}}^2)}\right], \tag{S11}$$

Neglecting terms proportional to $B_P C_P$ and C_P^2 and substitution of

$$\dot{n}_0 = \frac{\pi R^4 (P_{\text{in}} - P_{\text{out}})(\rho_{\text{in}} + \rho_{\text{out}})}{16 L \eta_0}, \tag{S12}$$

yields

$$\dot{n} = \dot{n}_0 [1 + g_{\text{virial}}], \tag{S13}$$

where

$$g_{\text{virial}} = \frac{b_\eta}{R_{\text{gas}} T} \frac{(P_{\text{in}} + P_{\text{out}})}{(\rho_{\text{in}} + \rho_{\text{out}})} \left[-\bar{P} + \left(b_\eta + 2B_P - \frac{c_\eta}{b_\eta} \right) \frac{(P_{\text{in}}^2 + P_{\text{out}}^2)}{2} \right]. \tag{S14}$$

Here, $\bar{P}$ is obtained analogous to Berg [2]

$$\bar{P} = \frac{2}{3} \frac{(P_{\text{in}}^3 - P_{\text{out}}^3)}{(P_{\text{in}}^2 - P_{\text{out}}^2)}. \tag{S15}$$

As mentioned in the article, the viscosity virial coefficients b_η and c_η were obtained from second-order polynomial fits to experimental viscosities as functions of pressure to data from Gracki et al. [3] for hydrogen and helium, and to experimental data of this work for the (hydrogen + methane) mixture. The values of b_η and c_η are summarized in Table S1.

Table S1: Values fort the second and third viscosity virial coeffiecients b_η and c_η, respectively, for helium, hydrogen, and the (hydrogen + methane) mixture at T = 298.15 K.

Chemical	b_η / MPa^{-1}	c_η / MPa^{-2}	Reference
Helium	$-3.0 \cdot 10^{-4}$	$2.4 \cdot 10^{-5}$	Gracki et al. [3]
Hydrogen	$1.4 \cdot 10^{-3}$	$3.5 \cdot 10^{-5}$	Gracki et al. [3]
(Hydrogen + Methane)	$1.1 \cdot 10^{-3}$	$1.4 \cdot 10^{-4}$	This work

S2 Pressure and temperature dependent helium viscosity ratio $\eta^{\mathrm{He}}_{P,T}/\eta^{\mathrm{He}}_{0,T}$

The measurement of the pressure and temperature dependent helium viscosity ratio $\eta^{\mathrm{He}}_{P,T}/\eta^{\mathrm{He}}_{0,T}$ with the two-capillary viscometer is briefly described here. A detailed description is given in Secs. 2.3 and 2.4 in the article. $\eta^{\mathrm{He}}_{P,T}/\eta^{\mathrm{He}}_{0,T}$ was obtained from measurements, operating both capillaries at the target temperature T and the upstream capillary at the target pressure P. Additionally, a second set of measurements is required, operating the upstream capillary at the lowest feasible pressure, to determine the ratio of the impedances of the upstream and downstream capillary $Z_{\mathrm{down},\,T}(0)/Z_{\mathrm{up},\,T}(0)$ at low pressure, according to Eq. (21) in the article. Variation of the impedance of the upstream capillary with pressure is accounted for, by determining the pressure induced dilation of the inner radius of the upstream capillary from the capillary's dimensions and material properties. The pressure and temperature dependent helium viscosity ratio was then obtained, combining Eqs. (19) to (21) in the article. The values of $\eta^{\mathrm{He}}_{P,T}/\eta^{\mathrm{He}}_{0,T}$ for the (298.15, 323.15, and 348.15) K isotherms are given in Table S2. Data reported for the 348.15 K isotherm, were obtained from measurements, carried out within the work of Khosravi et al. [4].

Table S2: Experimental ($\eta^{\mathrm{He}}_{P,T}/\eta^{\mathrm{He}}_{0,T}$, T, P) data, where $\eta^{\mathrm{He}}_{P,T}/\eta^{\mathrm{He}}_{0,T}$ is the ratio of the viscosity of helium at temperature T and pressure P, and the zero-density viscosity of helium at temperature T. $U(\eta^{\mathrm{He}}_{P,T}/\eta^{\mathrm{He}}_{0,T})$ is the expanded uncertainty (k = 2) of $\eta^{\mathrm{He}}_{P,T}/\eta^{\mathrm{He}}_{0,T}$ (including uncertainties in temperature[a] and pressure[b]). Data for the 348.15 K isotherm were obtained from measurements carried out within the work of Khosravi et al. [4].

T / K	P / MPa	$\eta^{\mathrm{He}}_{P,T}/\eta^{\mathrm{He}}_{0,T}$ / -	$U(\eta^{\mathrm{He}}_{P,T}/\eta^{\mathrm{He}}_{0,T})$ / -
298.15	2.98252	0.9979	0.0016
298.15	4.98887	0.9981	0.0019
298.15	7.54135	0.9999	0.0025
298.15	9.99661	1.0011	0.0044
298.15	12.01158	1.004	0.027
298.15	14.9943	1.0041	0.0076
323.15	2.96016	0.9984	0.0017
323.15	5.22308	0.9996	0.0019
323.15	7.99300	1.0008	0.0029

T / K	P / MPa	$\eta^{He}_{P,T}/\eta^{He}_{0,T}$ / -	$U(\eta^{He}_{P,T}/\eta^{He}_{0,T})$ / -
323.15	10.0922	1.0008	0.0052
323.15	12.3945	1.003	0.011
323.15	15.0012	1.006	0.022
323.14	18.4185	1.0149	0.0054
348.14	3.81169	1.0000	0.0038
348.16	4.93204	0.9989	0.0022
348.14	6.23245	1.0007	0.0045
348.14	9.69174	0.9994	0.0075
348.14	12.5090	1.0065	0.0071
348.14	14.7584	1.0067	0.0078

[a] The expanded uncertainty (k = 2) in temperature is $U(T)$ = 84 mK.

[b] The expanded uncertainties (k = 1.73) in pressure are $U(P)$ = 0.69 kPa for 1 MPa < $P \leq$ 3 MPa, $U(P)$ = 1.38 kPa for 3 MPa < $P \leq$ 10 MPa, and $U(P)$ = 10 kPa for P > 10 MPa, respectively.

References

[1] R.F. Berg, Derivation of the original virial correction function used in: Berg, Rev. Sci. Instrum., 75, (2004). personal communication, Trondheim, 2022.

[2] R.F. Berg, Quartz capillary flow meter for gases, Rev. Sci. Instrum. 75 (2004) 772–779. https://doi.org/10.1063/1.1642751.

[3] J.A. Gracki, G.P. Flynn, J. Ross, Viscosity of Nitrogen, Helium, Hydrogen, and Argon from − 100 to 25°C up to 150–250 atm, J. Chem. Phys. 51 (1969) 3856–3863. https://doi.org/10.1063/1.1672602.

[4] B. Khosravi, A. Austegard, S.W. Løvseth, H.G.J. Stang, J.P. Jakobsen, Experimental investigation of viscosity using a new two-capillary viscometer with a modified hydrodynamic model for CO2, submitted to Metrologia (2023).