Third Industrial Fluid Properties Simulation Challenge
Molecule Transferability Problem

Recommended Dynamic Viscosities for Selected Diols and Triols

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Primary Source of Recommendation:

All ten viscosity values were measured directly with falling-body type viscometers for the simulation challenge at ExxonMobil Research and Engineering. Several values were also measured independently by Scott Bair at the Georgia Institute of Technology in a similar apparatus. Experimental details are given below. The benchmark values, with their uncertainties, are provided in Table 2, below.

Experimental Details:

Materials

1,3-butanediol (#107-88-0, 99%), and 1,4-butanediol (110-63-4, 99+%) were purchased from Aldrich. 1,2-butanediol (584-03-2, 98+%) and 2-methyl-1,3,-propanediol (#2163-42-0, 98+%) were obtained from TCI-America. 1,2,4-butanetriol (3068-00-6, 96%) was obtained from Pfaltz & Bauer. All fluids were used as received, except for 1,2,4-butanediol, which was distilled into 3 separate fractions in order to remove light impurities detected from a GC/MS analysis. The middle fraction was collected for use in the viscosity measurements. A GC/MS analysis of the distilled fraction revealed that the distillation removed > 90% of the impurities from the original sample. We estimate the distilled 1,2,4-butanediol purity to be > 99%.

Apparatus and Procedure

Pressurized falling body viscometers were used for all measurements. A comprehensive description of the instrument and its operation can be found elsewhere [1]. Briefly, a cylindrical sinker with guiding lugs falls within a close fitting cylindrical tube containing the fluid whose viscosity is to be measured. The sinker is constructed from a magnetic material, while the tube and cylindrical bore surrounding the sinker is non-magnetic; this allows the sinker position to be continuously monitored (and falling velocity determined) with a linear variable differential transformer (LVDT). Care must be taken when the fluid to be measured has magnetic properties. The cartridge assembly holding the sinker fits within a cylindrical vessel that is filled with a pressurizing fluid. An isolating piston separates the cartridge assembly from the surrounding pressurizing fluid and allows the system to respond to externally applied pressure. The vessel is seated on a rotatable arm, which allows the assembly to be positioned such that the sinker falls straight down through the viscous fluid.

Temperature is regulated with heated air passed over a 600 W cartridge heater upstream of the temperature regulator. The air flows through channels within the cylindrical bore surrounding the viscometer cartridge. Temperature can be maintained within ± 0.1 °C during the viscosity measurement. Pressures of up to 1.2 GPa are attained by hand-pumping a pressure-fluidizing medium (2-ethylhexyl sebacate) through a pressure intensifier with a theoretical pressure ratio of 36:1. A pressure transducer is used to measure pressure and has been separately calibrated against a commercial Manganin cell. The transducer has an accuracy of ± 2 MPa at 800 MPa.

Approximately 1.5 mL of fluid is loaded into the viscometer cartridge and sealed, ensuring that no air is trapped inside. The cartridge is loaded into the cylindrical vessel, sealed and allowed to equilibrate at the target temperature for approximately 20 minutes prior to measurement. Once equilibrated, the sinker fall is initiated by inverting the viscometer assembly. The LVDT signal is passed through a signal conditioner and the sinker position is monitored on a digital oscilloscope, from which the fall velocity is measured. Each state point is measured three times, and variability among repeat measurements is typically less than 1%.

For idealized sinker geometries, the relationship between geometry, fluid density and viscosity, and the sinker falling velocity have been worked out; however, as is more usual, the actual relationship between falling velocity and fluid viscosity has been determined by calibration to fluids of known viscosity. Specifically, the viscosity η is computed as

$$\eta = Ct\,\frac{\rho_s - \rho(P,T)}{\rho_{ref}} \tag{1}$$

where t is the sinker fall time required to achieve a specified change in LVDT output (seconds per 100 mV), ρ_s is the density of the sinker, ρ is the fluid density at the temperature and pressure of the measurement, and ρ_{ref} is a reference density, usually taken to be an approximation to $\rho_s - \rho$. The fluid density at the measurement state point is estimated given an experimental reference datum, typically at room temperature and atmospheric pressure. A linear density correction is applied to estimate the density at the target temperature, and the pressure correction is found from the Tait equation.[2] While this density estimation method is only approximate, it suffices for the data analysis. In particular, the viscosity computed by Eq. (1) is fairly insensitive to errors in density; a 1% error in ρ leads to approximately a 0.1% error in viscosity.

For the measurements reported here, ASTM viscosity standard fluids S3, S20, S200 and HT150 (Cannon Instrument Company), and S6, S20, and S60 (Poulten, Selfe & Lee Ltd.) have been used to calibrate the sinker response. Fall times at a given temperature and pressure are measured three times, and the viscosity is computed from Eq. (1) from the average of the runs. Repeatability of measured fall times is typically between 0.5-1%. Table 1 shows a comparison of the viscosity obtained with our viscometer to literature data for several isotherms of n-octane. The recommended viscosity values at the state points of the challenge problem are given in Table 2.

Comparison with Literature and Determination of Uncertainty:

While the repeatability of viscosity measurements on our instrument is usually less than 1%, reported values in the literature from different types of viscometer offer a better gauge of the uncertainty in the recommended values. Table 3 compares the viscosity of 1,4-butanediol between 298.15 and 355 K at atmospheric pressure, which has been reported in the literature by several groups [4-6]. The collection of data is consistent to within approximately 3%. Additional data for the 1,n-butanediols at 373 K are also given in table 4 and show very good agreement with the data of Sun *et al*. To the best of our knowledge, no viscosity data for 2-methyl-1,3-butanediol and 1,2,4-butanetriol are available in the open literature. This is a representative, but not complete, compilation of the available data on the fluids. In addition, no data on any of the contest compounds could be found at elevated pressures.

In our estimates of the uncertainty of the reported benchmark values, we have considered and propagated the components of uncertainty associated with the purity of the samples used; the measurement uncertainties of temperature, pressure, and rate of fall; the theory and calibration of the instrument; the densities used to determine the viscosity; the repeatability of the measurements as indicated above; and comparisons of literature values for these fluids and other fluids measured in these instruments. From these considerations, we estimate that the combined expanded uncertainty (coverage factor of two, or confidence interval of about 95%) of the viscosity values in Table 2 is 3% for all of the reported values.

References:

[1] S. Bair "A Routine High-Pressure Viscometer for Accurate Measurements to 1 GPa", Trib. Trans. **47**, p.356-60 (2004).

[2] S. Bair "Pressure-Viscosity Behavior of Lubricants to 1.4 GPa and its Relation to EHD Traction" Trib. Trans. 43(1) p.91-99 (2000)

[3] K. Harris, R. Malhortra, and L.A. Woolf "Temperature and Density Dependence of the Viscosity of Octane and Toluene" J. Chem. Eng. Data **42**(6) p. 1254-1260 (1997).

[4] Lech, T. Czechowski, G. and Jadzyn, J. "Viscosity of the Series of 1,n-Alkanediols" J. Chem. Eng. Data 46(3) p.725-727 (2001).

[5] Sun, T. DiGuillo, R.M., and Teja, A.S. "Densities and Viscosities of Four Butanediols between 293 and 463K" J. Chem. Eng. Data 37(2) p.246-248 (1992).

[6] Yang, C., Ma P., Zhou, Q. "Excess Molar Volume, Viscosity, and Heat Capacity for the Mixtures of 1,4-butanediol + water at Different Temperatures" J. Chem. Eng. Data 49(3) p. 582-587 (2004).

Table 1. Comparison of n-Octane Viscosities to Literature Data

T = 298.15 K				T = 353.15 K			
P	η	η_{Harris}	% diff	P	η	η_{Harris}	% diff
MPa	mPa·s			MPa	mPa·s		
0.1	0.513	0.516	-0.6	0.1	0.297	0.292	1.7
49	0.795	0.814	-2.3	49	0.463	0.466	-0.6
99	1.16	1.18	-1.7	99	0.642	0.658	-2.4
149	1.62	1.64	-1.5	149	0.864	0.878	-1.6
199	2.20	2.23	-1.3	199	1.119	1.127	-0.7
249	2.04	2.96	-0.8	248	1.411	1.419	-0.6
299	3.86	3.89	-0.8	298	1.776	1.763	0.7
349	5.04	5.07	-0.7	370	2.378	2.363	0.6

Table 2. Viscosity of Contest Molecules at 373 K, 0.1 and 250 MPa

Species	T	P	η
	K	MPa	mPa·s
1,4-butanediol	373	0.1	4.74 ± 0.14
1,3-butanediol	373	0.1	3.77 ± 0.11
1,2-butanediol	373	0.1	2.43 ± 0.07
2-methyl-1,3-propanediol	373	0.1	5.00 ± 0.15
1,2,4-butanetriol	373	0.1	17.1 ± 0.5
1,4-butanediol	373	250	13.7 ± 0.4
1,3-butanediol	373	250	14.6 ± 0.4
1,2-butanediol	373	250	10.4 ± 0.3
2-methyl-1,3-propanediol	373	250	21.8 ± 0.7
1,2,4-butanetriol	373	250	52.8 ±1.6

Table 3. Comparison of 1,4-butanediol viscosities at 0.1 MPa

T K	This work	Lech *et al* [4]	Sun *et al* [5]	Yang *et al* [6]
	η mPa·s			
298.15	68.1	67.0	71.1	70.6
312.25	36.1	35.6	37.3	37.0
331.05	17.0	17.2	17.5	17.7
354.65	7.87	8.22	7.99	8.20
373.15	4.74		4.80	

Table 4. Comparison of 1,n-butanediol viscosities at 373 K

Species	This work η	Sun *et al* [4] η
	mPa·s	
1,2-butanediol	2.43	2.50
1,3-butanediol	3.77	3.80
1,4-butanediol	4.74	4.76