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Benchmarks for the Third Industrial Fluid Properties Simulation Challenge ☆

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Abstract

We outline the procedures used to establish benchmark physical property data for the Third Industrial Fluid Properties Simulation Challenge. For both challenge problems, this involved measurement of new data, including bubble-point pressures of ethanol/HFC-227ea mixtures at 343.13 K, and the viscosity of 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 2-methyl-1,3-propanediol, and 1,2,4-butanetriol at 373 K and 0.1 and 250 MPa. When possible, measurements were compared with published literature data. Recommended values are provided with corresponding uncertainty estimates.
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1. Introduction

As with previous contests [1,2], a benchmarking committee was formed to establish benchmark data for use in evaluating entries in the Third Industrial Fluid Properties Simulation Challenge [3]. Members of the benchmark committee reviewed the open literature to determine the availability of data to be computed, as the problems were designed so that answers were not available to contest participants before the contest conclusion. The committee also provided a comprehensive review of the experimental procedures employed in generating benchmark data, with particular emphasis on establishing uncertainty estimates for the reported results.

In this paper, we outline the procedures by which benchmark property values were determined for both the so-called state conditions transferability and molecule transferability problems. Motivation and details of these challenge problems can be found in the paper providing an overview of the challenge [3]. Additional contributors to the benchmark project are listed in acknowledgments section.

2. State conditions transferability problem

The state conditions transferability problem challenged entrants to predict the bubble point of ethanol 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea) mixtures at 343.13 K. All bubble-point pressures were determined in a static vapor–liquid equilibrium apparatus. The same apparatus and protocols were used to determine the experimental values at 283.17 K provided as input to the problem, and the benchmark val-

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Table 1
Experimental data for the system ethanol and HFC-227ea: isotherm I at 283.17 K

Mole fraction ethanol	Bubble-point pressure (Pa)
0.0	2.801×10^5
0.0545	2.698×10^5
0.1123	2.639×10^5
0.2152	2.561×10^5
0.3173	2.487×10^5
0.4137	2.404×10^5
0.5097	2.297×10^5
0.6066	2.099×10^5
0.7328	1.756×10^5
0.7893	1.485×10^5
0.8553	1.078×10^5
0.9001	7.633×10^4
0.9392	4.784×10^4
0.9670	2.757×10^4
1.0	3.075×10^3

ues at 343.13 K. Both sets of values are provided in Tables 1 and 2.

2.1. Experimental details

2.1.1. Materials

Anhydrous ethanol (CAS #64-17-5; purity =99.5%, 200 proof) was purchased from Quantum Chemicals. 1,1,1,2,3,3,3-heptafluoropropane or HFC-227ea (431-89-0; purity >99.999%) was obtained from DuPont. HFC-227ea was degassed by repeated freeze-pump-thaw cycles using liquid nitrogen to freeze. Ethanol was degassed with the help of an ultrasonic bath at room temperature. Otherwise the samples were used as received.

2.1.2. Apparatus and procedure

A static vapor–liquid equilibrium (VLE) apparatus was used to measure both isotherms. Complete details about the apparatus used and data evaluation can be found in the paper by Kao et al. [4]. Briefly, the idea of the static technique is to maintain the mixture under conditions of temperature and pressure at which liquid and vapor phases coexist, to mix them thoroughly until equilibrium is established, and then to sample and analyze the two phases without disturbing the equilibrium appreciably.

The pressure was measured with an accuracy of ±0.01% over the range of pressure measured. The temperature was controlled and measured with an accuracy of ±0.01 K over the range of temperatures considered. Mixtures are prepared by transferring

Table 2
Benchmark bubble-point pressures for ethanol and HFC-227ea at 343.13 K

Mole fraction rthanol	P (Pa)
0.0604	$1.422 \times 10^6 \pm 3000$
0.1228	$1.366 \times 10^6 \pm 3000$
0.3314	$1.222 \times 10^6 \pm 2000$
0.5219	$1.097 \times 10^6 \pm 2000$
0.7260	$8.859 \times 10^5 \pm 1800$
0.8547	$6.165 \times 10^5 \pm 1200$
0.9440	$3.215 \times 10^5 \pm 600$

known amounts of the pure components into the evacuated equilibrium cell, which has a total volume of 75 cm^3. The added quantities were determined to ±0.001 g by weighing, which translates into an error of less than 0.01% in mole fraction. Upon equilibration, changes in the liquid phase concentrations occur, but these changes are quite small because the vapor phase volume in the cell is small in comparison to the liquid phase volume, and the density of the vapor phase is much smaller than that of the liquid.

For full determination of the vapor–liquid equilibrium conditions, direct sampling of the liquid and vapor phases is possible, but it is generally easier to employ an indirect technique to determine the compositions. This involves application of material balances to the binary system from the known overall composition and system cell volume, and estimation of the thermodynamic properties with a suitable equation of state. This information can be used in a standard iterative binary VLE calculation to solve for the unknown compositions [5]. This method has been shown to yield accurate results without the necessity of sampling and analyzing the equilibrated system phases [4].In the present case, however, we report only liquid phase compositions, and this more detailed analysis is not necessary.

In Table 1, we provide the experimental results at 283.17 K (10.02°C) that had been previously available on the contest web site. In Table 2 we provide the benchmark bubble-point pressures and their uncertainties. In Table 3, we provide a more complete set of measurements at 343.13 K (69.98°C).

2.2. Comparison with literature and determination of uncertainty

As part of the uncertainty analysis of these measurements, we have compared the pure fluid values with two of the standard sources of vapor pressures for these fluids. DIPPR®801 [6] lists an uncertainty of their vapor pressure correlation for ethanol and HFC-227ea of < 1 and <5%, respectively. REFPROP 7.1 [7] lists an uncertainty of their Helmholtz equation of state model for ethanol and HFC-227ea of 0.5 and 0.2%, respectively, and REF-

Table 3
Experimental data for the system ethanol and HFC-227ea: isotherm II at 343.13 K

Mole fraction ethanol	Bubble-point pressure (Pa)
0.0	1.487×10^6
0.0604	1.422×10^6
0.1228	1.366×10^6
0.2311	1.285×10^6
0.3314	1.222×10^6
0.4265	1.163×10^6
0.5219	1.097×10^6
0.6138	1.018×10^6
0.7260	8.859×10^5
0.8029	7.456×10^5
0.8547	6.165×10^5
0.9055	4.628×10^5
0.9440	3.215×10^5
0.9725	2.025×10^5
1.0	7.274×10^4

Table 4
Comparisons for pure component vapor pressures

	$T = 283.17$ K	$T = 343.13$ K
Ethanol		
This work	0.466 psia	10.55 psia
REFPROP 7.1	0.456 psia	10.45 psia
REFPROP 8.0	0.461 psia	10.52 psia
DIPPR 801	0.458 psia	10.49 psia
HFC-227ea		
This work	40.63 psia	215.72 psia
REFPROP 7.1	40.65 psia	215.70 psia
REFPROP 8.0	40.54 psia	215.63 psia
DIPPR 801	40.78 psia	215.78 psia

PROP version 8.0 [8] cites these as 0.5 and 0.1%, respectively. Table 4 shows these comparisons.

For the bubble-point pressure benchmark data, the experimental uncertainties of 0.2% are consistent with those reported for other carefully designed apparatus used to measure bubble-point pressures in the 0.2–1.2 MPa pressure range [9,10]. These uncertainties consider and propagate the components of uncertainty associated with the purity of the samples used; the uncertainty of the compositions; the measurement uncertainties of temperature and pressure; the theory, calibration, precision, and repeatability of the VLE apparatus; and the comparisons for the pure fluids and for other binary mixtures. From these considerations, we estimate that the combined expanded uncertainty (coverage factor of two, or confidence interval of about 95%) of the bubble-point pressure values in Table 2 is 0.2% for all of the reported values.

3. Molecule transferability problem

The molecule transferability problem required participants to compute the viscosities of 1,3-butanediol, 1,4-butanediol, 1,2 butanediol, 2-methyl-1,3-propanediol, and 1,2,4-butanetiol at 373 K and two pressures (0.1 and 250 MPa). All 10 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 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 6.

3.1. Experimental details

3.1.1. Materials

1,3-Butanediol (CAS #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 three 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-butanetriol purity to be >99%.

3.1.2. 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 [11]. 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 are non-magnetic; this allows the sinker position to be continuously monitored (and falling velocity determined) with a linear variable differential transformer (LVDT). 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 was 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 were attained by hand-pumping a pressurizing medium (2-ethylhexyl sebacate) through a pressure intensifier with a theoretical pressure ratio of 36:1. A pressure transducer was used to measure pressure and was separately calibrated against a commercial Manganin cell. The transducer has an accuracy of 2 MPa at 800 MPa.

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

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

where t is the sinker fall time required to achieve a specified change in LVDT output (seconds per 100 mV), ρ_s the density of the sinker, ρ 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

Table 5
Comparison of n-octane viscosities to the literature data of Harris et al. [13]

$T = 298.15\ K$				$T = 353.15\ K$			
P (MPa)	η (mPa s)	η_{Harris}	%Diff	P (MPa)	η (mPa s)	η_{Harris}	%Diff
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

measurement state point was estimated given an experimental reference datum, typically at room temperature and atmospheric pressure. A linear density correction was applied to estimate the density at the target temperature, and the pressure correction was found from the Tait equation [12]. While this density estimation method is only approximate, it sufficed for the data analysis. In particular, the viscosity computed by Eq. (1) is fairly insensitive to errors in density; an error of 1% in ρ leads to approximately an error of 0.1% 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.) were used to calibrate the sinker response. Fall times at a given temperature and pressure were measured three times, and the viscosity was computed from Eq. (1) from the average of the runs. Repeatability of measured fall times was typically between 0.5 and 1%. Table 5 compares the viscosity obtained with our viscometer to literature data [13] for several isotherms of n-octane. The recommended viscosity values at the state points of the challenge problem are given in Table 6. In addition, viscosity isotherms at 373 K across an extended pressure range for the contest molecules are plotted in Fig. 1.

3.2. Comparison with literature and determination of uncertainty

While the repeatability of viscosity measurements on our instrument was usually less than 1%, reported values in the literature from different types of viscometers offer a better gauge of the uncertainty in the recommended values. Table 7 com-
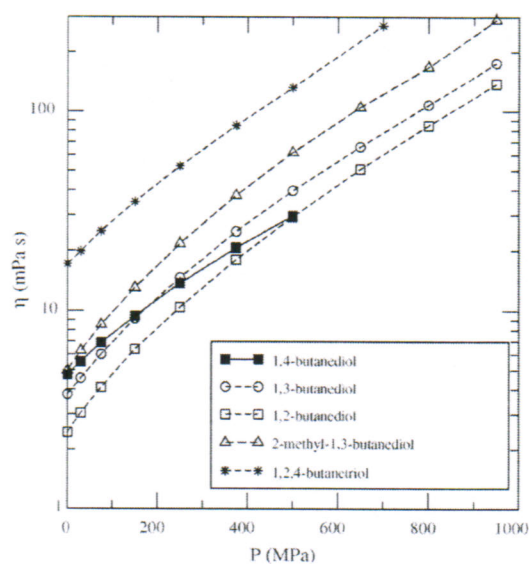

Fig. 1. Viscosity vs. pressure for contest molecules at 373 K.

pares the viscosity of 1,4-butanediol between 298.15 and 373 K at atmospheric pressure, which has been reported in the literature by several groups [14–16]. The collection of data is consistent to within approximately 3%. The present data for the 1,n-butanediols at 373 K are also compared to the data of Sun et al. [15] in Table 8, and show very good agreement. To the best of our knowledge, no viscosity data for 2-methyl-1,3-propanediol 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 esti-

Table 6
Viscosity of contest molecules at 373 K, 0.1 and 250 MPa

Species	P (MPa)	η (mPa s)
1,4-Butanediol	0.1	4.74 ± 0.14
1,3-Butanediol	0.1	3.77 ± 0.11
1,2-Butanediol	0.1	2.43 ± 0.07
2-Methyl-1,3-propanediol	0.1	5.00 ± 0.15
1,2,4-Butanetriol	0.1	17.1 ± 0.5
1,4-Butanediol	250	13.7 ± 0.4
1,3-Butanediol	250	14.6 ± 0.4
1,2-Butanediol	250	10.4 ± 0.3
2-Methyl-1,3-propanediol	250	21.8 ± 0.7
1,2,4-Butanetriol	250	52.8 ± 1.6

Table 7
Comparison of 1,4-butanediol viscosities at 0.1 MPa

T (K)	η (mPa s)			
	This work	Lech et al.[14]	Sun et al.[15]	Yang et al.[16]
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 8
Comparison of 1,n-butanediol viscosities at 373 K

Species	η (mPa s)	
	This work	Sun et al.[15]
1,2-Butanediol	2.43	2.50
1,3-Butanediol	3.77	3.80
1,4-Butanediol	4.74	4.76

mates 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 6 is 3% for all of the reported values.

4. Summary

In accordance with the organizing principles of the Simulation Challenge, we have attempted to provide validated experimental data of high quality, to stimulate members of the simulation community to test their models and methods in a predictive way. Molecular simulation techniques are seen as holding great promise as a predictive tool in the chemical and petrochemical industries. It is hoped that, to the extent that molecular simulation methods succeed in solving the contest problems, the Simulation Challenge will serve as a well-publicized barometer to industry of the utility of these emerging approaches.

Acknowledgements

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