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Wide-Ranging Viscosity Measurements of Rocket Propellant RP-2

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Expanding on earlier viscosity measurements of rocket propellants from 293 to 373 K at atmospheric pressure, the viscosity of rocket propellant RP-2 was measured from 270 to 425 K with pressures to 137 MPa. The instrument was an oscillating-piston viscometer, modified and recalibrated at the National Institute of Standards and Technology with dodecane as a reference fluid over the full temperature and pressure range. Based on the recalibrations, the repeatability of the measurements was found to be approximately 3%, whereas the uncertainty of the instrument is estimated at 5%. The measured viscosities of RP-2 were compared with values calculated with a five-component surrogate mixture model developed at the National Institute of Standards and Technology. The experimental data have a stronger pressure dependence than the mixture model and are up to 29% higher at high compressions.

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I. Introduction

NEXT to density, viscosity is the most important thermophysical property to characterize the technical performance of fluids. This is particularly true for liquid fuels that are subject to widely ranging conditions of temperature and pressure. An important difference between density and viscosity is their range of variation with temperature and pressure. In our previous studies of compressed liquid rocket propellants, fuels, and fuel constituents [1–8], the densities varied only by a factor of 1.7 from 497 $\mathrm{kg \cdot m^{-3}}$ to 856 $\mathrm{kg \cdot m^{-3}}$ for temperatures from 270 to 470 K, with pressures from 0.083 up to 50 MPa. In addition, densities at elevated pressures can be reliably predicted from data at moderate pressures with Tait-type equations of state. For viscosity, the situation is remarkably different. Our previous measurements showed that, in the narrow temperature range from 293 to 373 K, the viscosity of rocket propellant RP-2 at atmospheric pressure varies by a factor of 3 [3]. Considerably higher variations of the viscosity can be expected for the mentioned temperature and pressure range of our density measurements and from fluid to fluid. The strong temperature dependence of viscosity is a particular characteristic of this property for liquids, but its pressure dependence can be also significantly stronger than that of other properties. On the modeling side, there are no equivalents to density equations of state for reliable predictions of viscosities at high pressures from data at moderate pressures. Therefore, the need for measured viscosities is greater than for other properties.

In this work, the viscosity of rocket propellant RP-2 was measured with an oscillating-piston viscometer from 270 to 425 K and with pressures up to 137 MPa. Because this is our first publication of results measured with this technique, details of the measuring principle of the instrument, its calibration, and its operation are discussed. The experimental results are compared with viscosity values that were predicted with a surrogate mixture model.

II. Experimental

A. Materials

Dodecane was used to test the calibration of the viscometer. Anhydrous dodecane was obtained from a commercial source with a stated purity of higher than 99% by mole and a water content of less than 0.003% by mole. This material was used without further purification except for degassing by four cycles of freezing with liquid nitrogen, pumping vacuum on the solid, and reheating back to room temperature. The RP-2 sample was provided by Edwards Air Force Base, California, and was characterized at the National Institute of Standards and Technology (NIST) in previous reports [9–11]. The RP-2 was also degassed in four freeze–pump–thaw cycles.

B. Viscometer

A commercial oscillating-piston viscometer was used for the viscosity measurements. This technique is a variant of the falling-body and rolling-sphere viscometers [12,13], where the viscosity of a liquid is deduced from the time that elapses when a sensing element falls or rolls gravitationally a certain distance in the liquid in one direction.

In the oscillating-piston viscometer, a cylindrical sensing element in a tube filled with sample liquid is actuated into reciprocating motion by two magnetic coils outside of the tube. A schematic is shown in Fig. 1. The tube is inclined by 45 deg against the direction of gravity. One coil pulls the sensing cylinder toward it while inducing an electromotive force in the second coil. The change in mutual inductance between the coils makes it possible to determine the position of the sensing cylinder and to reverse the actuation of the coils to complete a full cycle of the sensor. The displacement amplitude is $\Delta x = 5.1$ mm. The cycle time period is the measurand that is mapped to viscosity by calibration with viscosity reference standards.

The viscosity-sensing elements are stainless steel cylinders of 24 mm length in a stainless steel tube with a bore of 7.963 mm. The measurable viscosity range depends on the diameter of each sensing cylinder. The diameters vary between 7.925 mm for a viscosity range from 0.02 to 2 $\mathrm{mPa \cdot s}$ to a diameter of 7.620 mm for a viscosity range from 5 to 100 $\mathrm{mPa \cdot s}$. The results reported here were obtained with a sensing cylinder of 7.8105 mm diameter for the range 0.5 to 10 $\mathrm{mPa \cdot s}$.

The instrument is calibrated by the manufacturer in three steps. First, the strength of the electromagnetic coupling is adjusted for each piston. Second, cycling periods are mapped to the viscosities of certified viscosity reference standard liquids at room temperature and ambient pressure. Finally, cycling periods were mapped to the viscosities of *n*-decane and dodecane from 298.15 to 423.15 K with pressures to 68 MPa. Because of a lack of certified viscosity reference standards for extended ranges of temperature and especially pressure, the sensing piston (1–20) $\mathrm{mPa \cdot s}$ could be calibrated with dodecane only up to 2.2 $\mathrm{mPa \cdot s}$ at a pressure of 41.4 MPa and 298.15 K. Sensing pistons for higher viscosity ranges can be calibrated only with certified viscosity reference standards at atmospheric pressure.

The pressure in the viscometer is generated with a high-pressure syringe pump rated to 137 MPa with a maximum sample volume of 65 mL. Pressure was measured with a commercial transducer rated to 207 MPa with a full-scale uncertainty of 0.05%. The transducer

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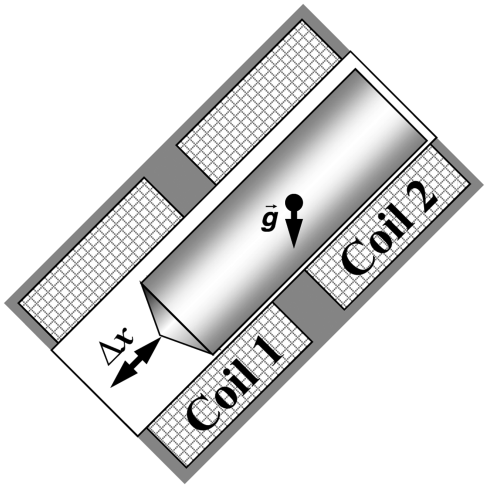

Fig. 1 Schematic of oscillating-piston viscometer technique. The inner diameter of viscometer cell is 7.963 mm. The outer diameter of the sensing piston (0.5–10 mPa · s) is 7.8105 mm. The displacement amplitude is $\Delta x = 5.1$ mm. The inclination angle of the viscometer cell against the direction of gravity is 45 deg.

calibration was checked with a primary pressure balance at 55.2, 41.4, 27.6, and 13.8 MPa, and the highest deviation was −0.17% at the lowest calibration pressure as opposed to 0.8% based on the full-scale uncertainty.

The temperature of the sample liquid in the viscometer is measured with a commercial 100 Ω platinum resistance temperature detector (RTD) that was calibrated and mounted on the outside of the pressure vessel by the manufacturer. The RTD is in a sealed space and cannot be removed from the pressure vessel to check its calibration. The manufacturer-quoted uncertainty of the temperature measurement is 0.1 K.

To reciprocate the sensing cylinder between the two coils, alternating magnetic fields are generated by currents through the coils. These currents cause resistive heating of the coils and of the high-pressure tube with the sensing cylinder and the sample. Thus, when the viscometer operates, the temperature of the sample increases by about 1 K. To maintain the viscometer temperature constant, the magnetic actuation of the sensing cylinder is operated continuously, even during pressure changes.

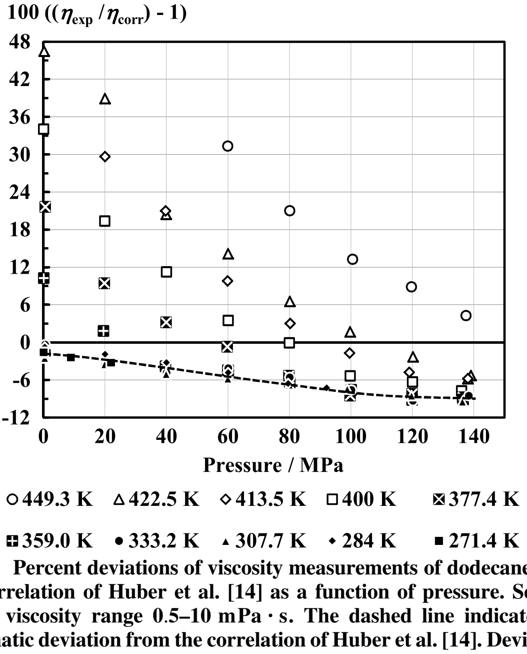

Fig. 2 Percent deviations of viscosity measurements of dodecane from the correlation of Huber et al. [14] as a function of pressure. Sensing piston viscosity range 0.5–10 mPa · s. The dashed line indicates the systematic deviation from the correlation of Huber et al. [14]. Deviations above the line are for viscosities below 0.85 mPa · s.

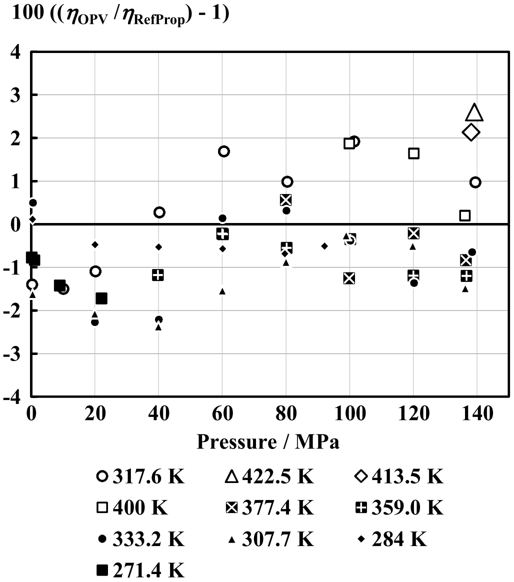

Fig. 3 Percent deviations of viscosity measurements of dodecane from the correlation of Huber et al. [14] after shift of calibration. Sensing piston viscosity range 0.5–10 mPa · s.

The calibration of the viscometer with three sensing pistons was tested with measurements of dodecane in the temperature range 271.4 to 449.3 K with pressures to 137 MPa. The most consistent results were obtained with the piston for the viscosity range 0.5–10 mPa · s. Percent deviations between viscosities measured with this piston, and reference data calculated with the correlation of Huber et al. [14] as implemented in NIST's computer program REFPROP version 9.0 [15], are shown in Fig. 2 as a function of pressure. Two trends can be distinguished in the deviations. Most obvious is a systematic increase with decreasing pressure at 359 K and higher temperatures to a maximum deviation of 47% at 422.5 K and 0.2 MPa pressure. The common characteristic of these systematically increasing deviations is that they begin when the viscosity of the sample decreases below an approximate value of 0.85 mPa · s. Thus, this sensing piston cannot be used in the manufacturer-specified viscosity range of 0.5–10 mPa · s but only to a lower viscosity limit of 0.85 mPa · s. The pressures at which the deviations begin to increase systematically can be inferred in Fig. 2 for each isotherm from the dashed line that indicates the second trend of the deviations where they aggregate in a band of approximately ±2% from an average of −8% at 137 MPa to −1.5% at 0.1 MPa. The correlation of Huber et al. [14] represents the most recent literature viscosity data for dodecane at these temperatures and pressures, with an average absolute deviation of 1.1% and with a maximum deviation of 3.4%. To account for the systematic deviation, a pressure-dependent shift was applied to those measured viscosity data of dodecane above 0.85 mPa · s so that the deviations ranged within ±2% in the entire pressure range. The deviations between measured viscosities with the calibration adjustment applied and reference values for dodecane are shown in Fig. 3.

III. Results

Viscosity measurements of RP-2 were carried out on nine isotherms with increments of 10 K from 270 to 300 K to resolve the steep viscosity increase in this region, and with increments of 25 K from 325 to 425 K. The pressure was changed in increments of 10 MPa between 10 and 130 MPa. In addition, measurements were carried out at the highest pressure of 137 MPa and at the lowest pressure of approximately 0.3 MPa on each isotherm. The measurements resulted in viscosity values for RP-2 that vary from 0.63 to 13.5 mPa · s in the investigated temperature and pressure range. The data are listed in Table 1 and displayed in Fig. 4 as a function of pressure. Viscosity data below 0.85 mPa · s were disregarded because the sensing piston 0.5–10 mPa · s was found to

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Table 1 Measured viscosity data of RP-2 and deviations from values predicted with the preliminary surrogate model

Temperature, K	Pressure, MPa	Dynamic viscosity, mPa · s	Percent deviation, %
270.42	0.24	3.10	3.5
270.41	9.846	3.52	3.5
280.26	0.26	2.42	2.2
280.25	9.873	2.76	2.8
280.23	19.88	3.13	3.3
280.22	29.89	3.56	4.7
280.22	39.91	4.05	6.5
280.22	49.92	4.65	9.4
280.22	59.96	5.27	11.6
280.22	70.00	5.99	14.1
280.22	80.06	6.80	16.5
280.30	90.10	7.67	18.7
280.27	100.17	8.66	20.6
280.25	110.21	9.76	22.3
280.24	120.23	11.0	23.9
280.22	130.28	12.4	25.0
280.22	137.31	13.5	25.5
289.99	0.26	1.93	−0.2
289.98	9.89	2.19	0.3
289.98	19.88	2.49	1.8
289.98	29.90	2.82	3.2
289.98	39.91	3.19	4.7
289.99	49.97	3.57	5.8
289.99	59.99	4.03	8.1
290.01	70.04	4.49	9.3
290.05	80.03	5.08	12.5
290.05	90.08	5.74	15.6
290.04	100.12	6.43	17.9
290.03	110.17	7.27	21.5
290.04	120.22	8.21	25.2
290.05	130.27	9.17	27.5
290.05	137.32	9.89	28.8
299.95	0.36	1.57	−2.3
299.96	9.88	1.77	−1.8
299.96	19.90	2.01	−0.3
299.96	29.91	2.27	0.8
299.96	39.92	2.55	2.1
299.96	49.93	2.85	3.5
299.96	59.96	3.20	5.8
299.97	69.99	3.56	7.2
299.96	80.06	3.94	8.5
299.97	90.09	4.37	10.3
299.96	100.14	4.87	12.8
299.96	110.19	5.43	15.7
299.96	120.23	6.04	18.4
299.97	130.30	6.72	21.2
299.97	137.31	7.23	23.2
324.98	0.37	1.04	−3.5
325.15	9.87	1.16	−3.4
325.01	19.86	1.30	−3.2
325.01	29.90	1.47	−1.8
324.99	39.91	1.63	−1.2
324.98	49.95	1.80	−0.7
324.99	59.97	1.98	0.3
324.98	70.02	2.17	1.1
324.98	80.04	2.39	2.4
325.01	90.09	2.63	4.3
325.01	100.11	2.88	6.3
325.02	110.16	3.14	7.4
325.02	120.18	3.43	9.5
325.02	130.25	3.74	11.4
325.04	137.26	3.99	13.1
350.03	19.89	0.917	−5.6
350.04	29.90	1.02	−5.8
350.05	39.93	1.12	−5.7
350.07	49.95	1.23	−5.0
350.04	60.00	1.34	−5.0
350.04	70.03	1.47	−4.4
350.04	80.09	1.60	−3.5
350.04	90.11	1.75	−1.6
350.04	100.17	1.90	−0.6
350.03	110.19	2.06	0.6
350.04	120.24	2.23	2.1
350.04	130.30	2.41	3.8
350.04	137.34	2.54	4.5
374.99	39.94	0.870	−3.7
375.07	49.96	0.936	−5.3
375.00	59.98	1.02	−5.5
374.99	70.02	1.09	−6.5
375.03	80.07	1.18	−6.1
375.05	90.11	1.27	−5.7
375.05	100.15	1.38	−4.4
375.05	110.18	1.48	−3.7
375.05	120.24	1.59	−2.6
375.05	130.29	1.71	−1.6
375.05	137.30	1.79	−0.8
400.05	80.04	0.933	−5.9
400.05	90.07	0.994	−6.5
400.04	100.08	1.06	−6.4
400.04	110.14	1.14	−5.9
400.03	120.20	1.21	−5.7
400.02	130.24	1.30	−4.7
400.03	137.26	1.36	−4.3
425.04	110.16	0.938	−5.0

yield systematically deviating values in that range. At the three highest pressures at 280 K, the viscosity of RP-2 exceeded the upper limit of 10 mPa · s of the sensing piston range. These viscosity data are communicated here although the performance of the sensing piston when used above its range could not be benchmarked due to a lack of extended range viscosity standards at high pressures, and because these viscosity data appear consistent with those below 10 mPa · s in the viscosity–pressure diagram shown in Fig. 4. A more detailed assessment of these data will be discussed in the next section.

IV. Comparison with Surrogate Mixture Model Predictions

Huber et al. [16] developed a preliminary property model for RP-2 that was based on a surrogate mixture with five components and mole fractions, as listed in Table 2. Of the five components, only the viscosities of *n*-dodecane and heptylcyclohexane had been measured over extended ranges of temperature and pressure. The first viscosity data of RP-2 had been determined by Outcalt et al. [3] at a pressure of 0.083 MPa from 293.15 to 373.15 K in an open gravitational capillary

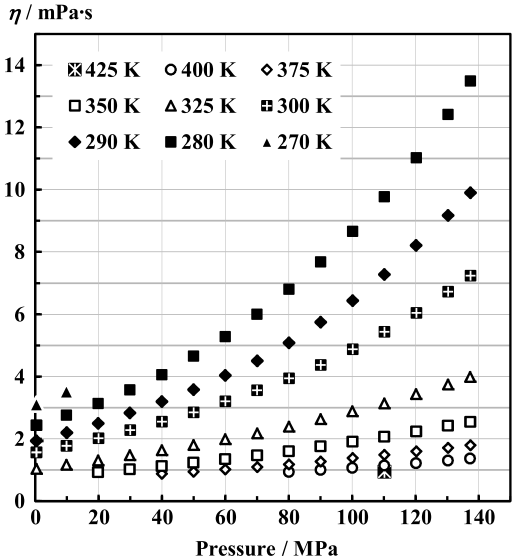

Fig. 4 Viscosities of RP-2 measured with sensing piston 0.5–10 mPa · s and with calibration shift applied as a function of pressure.

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Table 2 Compounds and their mole fractions of the surrogate mixture in the preliminary property model for RP-2 by Huber et al. [16]

	Compound	Formula	Mole fraction
1	α-methyldecalin	$C_{11}H_{20}$	0.354
2	5-methylnonane	$C_{10}H_{22}$	0.084
3	2,4-dimethylnonane	$C_{11}H_{24}$	0.071
4	n-dodecane	$C_{12}H_{26}$	0.158
5	heptylcyclohexane	$C_{13}H_{26}$	0.333

viscometer. The uncertainty of these viscosity data was conservatively estimated at 1.5% (coverage factor $k = 2$). More comprehensive comparisons and assessments of that instrument in the viscosity range of RP-2 lead to estimated uncertainties between 0.2 and 0.4% at the same level of confidence [17].

The viscosity data measured in the present work provide the first benchmark to test the accuracy of predicting the viscosity–pressure dependence of RP-2 with the preliminary property model. Percent deviations between the experimental data and predicted values are shown in Fig. 5 as a function of pressure. The data of Outcalt et al. [3] are reproduced with deviations between −0.78 and 0.48%. The deviations of the present data range from −6.5% at 375 K and 70 MPa to 28.8% at 290 K and 137 MPa. This exceeds the estimated uncertainty of 5% of the present data significantly. Two trends can be observed in Fig. 5: the deviations increase systematically with 1) decreasing temperature, and 2) even more so with increasing pressure. At the lowest pressures of approximately 0.3 MPa, the data deviate from −3.5% at 325 K to 3.5% at 270 K. The temperature trend of the deviations may be due to an uncertainty of the temperature measurement of the viscometer that is greater than the manufacturer-quoted margin of 0.1 K. However, the calibration tests of the instrument with dodecane resulted in deviations from −2.4 to 2.6% in the same temperature and pressure range in which the RP-2 measurements were conducted; compare Fig. 3. Therefore, the temperature systematic of the deviations cannot exclusively result from the viscometer but originates in part from the viscosity–temperature dependence implemented in the property model.

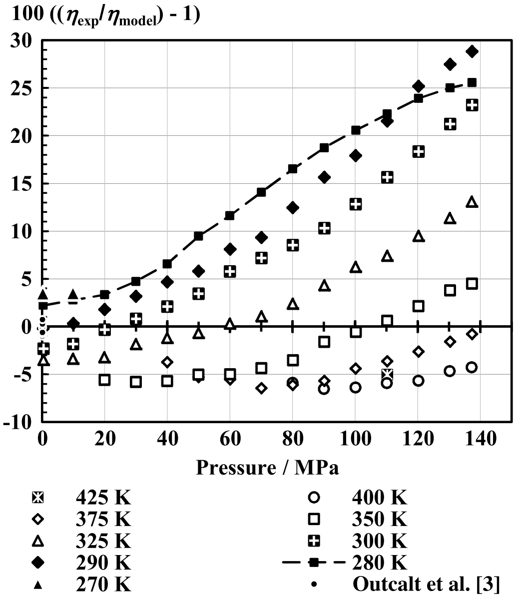

Fig. 5 Percent deviations of viscosity measurements of RP-2 from values predicted with the preliminary surrogate mixture model of Huber et al. [16] as a function of pressure. The deviations of the viscosity data of Outcalt et al. [3] at 0.083 MPa are also included.

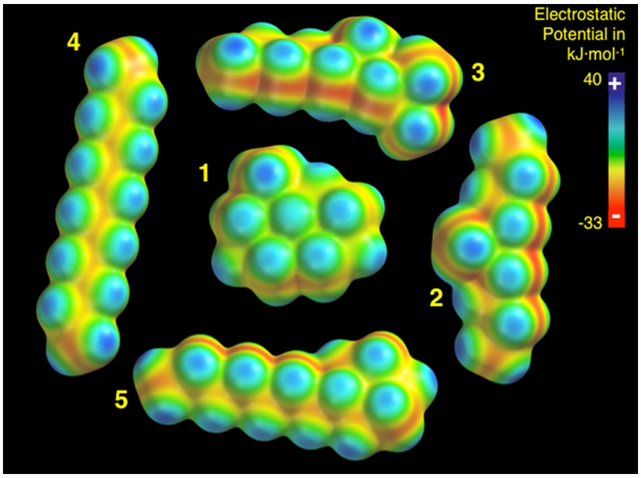

Fig. 6 Molecular sizes, shapes, and charge distributions of the RP-2 surrogate mixture constituents. The numbers correspond to the list order in Table 2.

Stronger increases of the deviations up to 28.8% are observed at temperatures below 350 K and with increasing pressure. In fact, the isotherms of the deviations appear to be parallel to the viscosity isotherms in Fig. 4 except for the deviations at 280 K above a pressure of 90 MPa. At these conditions, the measured viscosities were close to or higher than the upper limit of the sensing piston range of 10 mPa · s. In addition, the temperature of 280 K is below the lowest calibration temperature of 298.15 K. It is, therefore, likely that the uncertainty of the viscosities at 280 K above a pressure of 90 MPa increases with pressure from 5% to an estimated 12%.

The bulk of the deviations originates from two factors, one of them arising from the molecular interactions in RP-2, and the other related to the state of the art to represent viscosity as a function of temperature and pressure. The molecular aspect is illustrated in Fig. 6, which shows the sizes, shapes, and charge distributions of the components in the surrogate mixture according to Table 2. These images were computed with the same methodology as applied in previous papers [1,18]. They show that the main constituents of the surrogate mixture, α-methyldecalin and heptylcyclohexane, are most dissimilar in size and shape. While the α-methyldecalin molecule has the shape of a disc, heptylcyclohexane is a rather elongated molecule with a C_6 ring at one end. It is known that the viscosity is more susceptible to pressure when the molecular complexity of a pure component, or among components of a mixture, increases [13]. The present viscosity results indicate that the surrogate model mixture for RP-2 can be improved to reflect the complexity of molecular interactions in the actual liquid with its greater number and variety of constituents [9,10].

The second factor for the increasing deviations between experimental and predicted viscosities is related to the principal difficulty of predicting the exponential (and eventually hyperexponential) rise of viscosity with decreasing temperature and increasing pressure based on lower-viscosity data at higher temperatures and lower pressures [19,20]. However, recent thermodynamic scaling approaches that relate viscosity to the strength of the intermolecular repulsion rather than to the free volume appear to improve such predictive capability significantly [18,21].

V. Conclusions

This work contributes in three areas. Most importantly, it provides the first viscosity data for the complex mixture RP-2 at pressures up to 137 MPa and over an extended temperature range. Filling this gap of property information will lead to improved design and performance of rocket motors. Second, it provides operational and metrological information for a possibly unfamiliar viscometry technique and corroborates the measurement results with robust uncertainty estimates for this technique. Improvements of the instrument have already been implemented as a result of this work and will continue. Finally, the comparison with the measurement results provides a benchmark for the surrogate mixture property model for the viscosity of RP-2, and improvements based on this comparison are likely to lead also to more accurate predictions for other thermophysical properties of RP-2.

Acknowledgments

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