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Measurement of the Viscosity and Density of Two Reference Fluids, with Nominal Viscosities at T = 298 K and p = 0.1 MPa of (16 and 29) mPa·s, at Temperatures between (298 and 393) K and Pressures below 55 MPa

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We have measured the viscosity and density of certified reference materials N10 and S20 with nominal viscosities at T = 298 K and p = 0.1 MPa of (16 and 29) mPa·s, respectively, at temperatures in the range of (298 to 393) K and pressures between (0.1 and 55) MPa. These measurements extend the pressure range by 55 MPa and the temperature range by 20 K over which the viscosity and density of these fluids are known. Both a vibrating wire, with a wire diameter of 0.1 mm, and oscillating sinker viscometers were used for the measurements with standard uncertainties (k = 1) of ±1 % and ±2 %, respectively, whereas density was obtained from a vibrating tube densimeter with an uncertainty of ±0.1 %. The viscosity obtained from both instruments agreed within a reasonable multiple of the combined expanded uncertainty over the whole range of viscosities from (1.8 to 76) mPa·s, where the latter value represents the upper useful operating viscosity of the vibrating wire. The measured viscosity and density have been combined with the appropriate certified values for N10 and S20 at p = 101.325 kPa to obtain interpolation expressions with leading terms based on the cited values. Our equation represents the measured viscosities to within ±2 % and the densities to within ±0.2 % that are consistent with the expanded uncertainty (k = 2) of our measurements.

Introduction

The evaluation of the economics of a hydrocarbon-bearing formation requires measurements of many physical properties including both the density and viscosity of the reservoir hydrocarbon. These fluid properties are usually determined on an aliquot extracted after the borehole has been drilled but before the production system, consisting of metal tubes surrounded by cement, is installed. Typically, recoverable reservoir liquids have densities in the range of (700 to 1000) kg·m^{-3} and viscosities between (1 and 100) mPa·s; for organic liquids, the viscosity ranges from (10^{-3} to 10^{3}) Pa·s. Thus, fluids with known densities and viscosities that include these ranges are required for laboratory evaluation of proposed measurement techniques and calibration of other densimeters and viscometers as a function of both temperature and pressure. Here we are concerned solely with liquids that are Newtonian so that their viscosity is independent of the rate of shear. A detailed discussion of Newtonian and non-Newtonian behavior of fluids is given in ref 1.

The internationally accepted absolute standard for viscosity is that of water with a value of $\eta(\mathrm{H_2O}$, 293.15 K, 101.325 kPa) = (1.002 ± 0.0025) mPa·s. This value is primarily based on the measurements of Swindells et al.[2] with a capillary method and forms the basis for the ISO recommendation:[3] the uncertainty associated with this value can be ignored when values from different laboratories are compared, but when a true value of viscosity is required, an uncertainty of ±0.25 % should be assigned to this value. The variation of the viscosity of water at p = 101.325 kPa with temperature relative to the reference value has been discussed[4−9] and may be determined as a function of both temperature and pressure over a wide range from the correlation adopted by the International Association of Water and Steam (IAPWS),[10] which is a revision of ref 11.

Pure fluids are not generally recommended as reference materials because the viscosity usually depends significantly and indeterminately on the purity of the material.[4]

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Bauer and Meerlender[12] have discussed in detail the use of pure fluids with viscosities of less than 1 mPa·s as reference materials. The viscosity of pure fluids has been studied extensively, and these might also be used as standards with appropriate control of the fluid purity. Methylbenzene[13] and heptane[14,15] are potential pure fluid reference materials because their viscosities are known with sufficient certainty based on the agreement between the values obtained by independent laboratories using experimental techniques that utilize different principles. A knowledge of the density is also required for viscometers that provide kinematic viscosity, and for both fluids, these properties have been evaluated in refs 13, 16, and 17. However, the viscosity of these fluids is limited to viscosities of less than 1 mPa·s, which is at the lower end of the desired range. This is important because, typically, viscometers that are designed for minimal uncertainty when operated with fluids having viscosities close to that of water may return values with significantly higher uncertainty when used to determine the viscosities of higher-viscosity liquids.

The Bureau International des Poids et Mesures has recognized the need for suitable reference material for higher-viscosity standards and has prompted the measurement of the viscosities of candidate fluids. The International Association of Transport Properties has actively taken up this objective (http://transp.eng.auth.gr/), and under their auspices, Caetano et al.[18] have reported preliminary measurements of the viscosity of diisodecylphthalate at ambient pressure, with viscosities up to 121 mPa·s at $T = 293.3$ K, and have proposed this compound as a candidate for a moderate-viscosity standard; the criteria used to select compounds as potential viscosity standards have been described in refs 4 and 18. Until measurements of the viscosity of either diisodecylphthalate or another fluid as a function of temperature and pressure are complete and the viscosity is adopted by international agreement, the continued use of other fluids, known as certified reference materials for viscosity, is required to calibrate and compare viscometers intended for measurements with liquids.

A wide range of certified reference materials for viscosity are commercially available, and sources of them are listed in refs 4 and 5. These reference materials cover a wide range of viscosity and are supplied with certified viscosities and densities cited at discrete temperatures between (293 and 373) K and a pressure of 0.1 MPa; ref 4 provides tables of nominal values for key reference fluids. In some cases, either look-up tables or interpolation formulas are provided for both viscosity and density as a function of temperature. These reference materials are considered proprietary, and the chemical composition is unspecified; however, it has been reported that these fluids contain petroleum-based hydrocarbons, polyisobutenes, and silicone oils; other reference materials for higher viscosities include those formed from asphalts and molten glasses.[4] These organic fluids are Newtonian, noncorrosive, and usually have a high solubility in at least two organic solvents to enable appropriate cleaning. Unfortunately, these reference fluids must be consumed within a specified time period. In the case of petroleum-based oils, this is because the viscosity increases, presumably through evaporation of lower-molar-mass components, at a rate that varies from (0.01 to 0.03) % per month.

The certified values of these reference materials are always determined by comparison with the viscosity of water at $T = 293.15$ K and $p = 101.325$ kPa, either directly or indirectly, through a chain of intermediate reference liquids and a series of Master class instruments with overlapping ranges. In practice, it is necessary to have a range of capillary viscometers that vary from each other by the diameter of the capillary to cover a wide range of fluid viscosities, and these are usually of the suspended-level type but modified Ostwald viscometers have also been used. The Master viscometers differ from the usual capillary viscometer in the length of the capillary, which is usually at least 400 mm (about a factor of 2 greater than typically used), so as to reduce the correction terms owing to kinetic energy and surface tension. These Master viscometers are used to establish the kinematic viscosity by the so-called “step-up” procedure to ensure the smallest possible uncertainty in calibration;[19] the kinematic viscosity is often measured by the supplier according to ASTM D 2164 with an uncertainty cited as ±0.25 % relative to water. Nevertheless, in each sequential step of the comparison the errors accumulate and the uncertainty in the value of the viscosity increases as the difference from the value of the viscosity of water increases. This additional uncertainty in viscosity has been estimated, assuming all conditions of the viscosity measurement are otherwise optimum, to be 0.1 % at a viscosity of about 100 mPa·s.[4,20]

Fortunately, there are continuing programs of direct international comparisons made by exchanges of both master viscometers and reference materials between various suppliers to determine the consistency of the various national viscosity reference materials. These comparisons suggests that the viscosity of the reference materials can, at best, be certified to ±0.2 % with reference to water, even though in many cases agreement between laboratories is better than ±0.1 %.[21]

There are three factors that influence the accuracy of the measured viscosity: two of these have been discussed above, namely, the dependence of the viscosity scale on the value of the viscosity of water and the increase of uncertainty in the viscosity as the difference from the value of the viscosity of water increases. The third factor is the control of temperature because the viscosity of a liquid is very sensitive to temperature. This is particularly important for the calibration of a viscometer where it is generally necessary to control and know the temperature to within ±0.01 K of the temperature of certification in order to use the reference material within its specified uncertainty. In general, the temperature dependence of the viscosity of high-viscosity fluids is much greater than that for low-viscosity fluids so that the temperature control requirements cannot be relaxed with increasing viscosity. The uncertainty with which the pressure is measured is also a significant factor.

There are numerous methods by which the viscosity of liquids can be measured, and these have been reviewed by Johnson et al.,[22] Künzel et al.,[4] Nieuwoudt and Shankland,[23] Kawata et al.,[24,25] and Diller and van der Gulik.[26] Of those viscometers, vibrating wires have exact working equations, and it is our opinion that they are of simple construction and can be operated over a wide range of temperature and pressure; we have adopted a vibrating wire for this work. A majority of the measurements reported with a vibrating wire, and summarized in ref 27, have been applied to fluids with viscosities in the range of (0.008 to 6) mPa·s. However, there are a few measurements at higher viscosities including those reported by Charles et al.[28] for the viscosity of glycol at about 53 mPa·s, Gourgouillon et al.[29] who measured the viscosity of supercritical fluid-saturated polymer (PEG 400) with values of about 20 mPa·s, and Caudwell[30] who measured the viscosity of hydrocarbon mixtures with values up to 16 mPa·s. More recently, Caetano et al.[31] developed a vibrating wire viscometer with a nominal radius of 0.2 mm for which the radius of the wire was determined by calibration with water at $T = 293.15$ K and $p = 101.325$ kPa. They used the instrument to determine the viscosity of several fluids including certified reference materials with viscosities in the range of (0.5 to 135) mPa·s and showed that the overall uncertainty was less than 0.6 % over this range. Kandil et al.[27] have constructed a vibrating wire viscometer with a nominal wire diameter of 0.15 mm, for which the wire radius was determined from measurements with methylbenzene, and validated the operation of the instrument with certified reference materials at viscosities in the range of (2 to 100) mPa·s, with an uncertainty less than 0.6 %, and at temperature in the range of (298 to 373) K. The upper operating viscosity of this instrument was determined with measurement on certified reference material N100 at a temperature of $T = 301$ K where $\eta \approx 200$ mPa·s with an uncertainty of about 3 % that differs from an interpolation of the cited values by about 2 %.

In this work, we have used a vibrating wire viscometer, with a wire diameter of 0.1 mm, and a oscillating sinker viscometer (similar to a falling body viscometer described in ref 25) to measure the viscosity of certified reference materials N10 and S20 with nominal viscosities of (16 and 29) mPa·s at $T = 298$ K and $p = 0.1$ MPa, respectively, at temperature between (298 and 393) K and at pressure below 55 MPa for which neither the supplier nor the literature provides values. Our measured viscosities covered the range of (1.8 to 76) mPa·s, where the latter represents the upper useful operating viscosity of our vibrating wire. In the overlapping temperature range at $p = 0.1$ MPa, for both N10 and S20, the viscosities obtained from the vibrating wire differ from the certified reference values by less than 1 % when the resonance quality factor is greater than 2 and the values determined with the oscillating sinker viscometer differ from the cited values by less than 2 %. These results have been combined with the values of density and viscosity provided by the supplier at $p = 0.1$ MPa to obtain interpolation expressions for both properties with leading terms based on the cited values. In principle, this approach affords the use of these functions for samples taken from different lots from the same supplier or sources other than the one we used. On the basis of the international consistency of the values of the viscosity of these fluids,[21] small but still significant differences between the values for a certified reference material from those used by us might be accommodated by modification of the leading terms that represent values provided by the supplier.

The density of the certified reference materials is required to obtain viscosity from the Master viscometer kinematic viscosity (or if another viscometer is used because density is included in the working equations). Values of the density for the certified reference materials for viscosity are usually cited by the supplier and measured in accordance with ASTM D 1480 with an uncertainty cited as ±0.02 %. Wagner et al.[32] have reviewed the methods of determining liquid densities. In this work, we have used a vibrating U-tube densimeter to determine the density of the certified reference materials at temperatures between (298 and 393) K at pressures below 55 MPa.

Working Equations

In this work, we have used a vibrating wire viscometer and a commercially available oscillating sinker viscometer, which is similar to a falling body viscometer described in ref 25 and is often used in petroleum (p, V, T) laboratories to measure viscosity. Of these two viscometers, the oscillating sinker requires calibration over the viscosity range of interest and will be discussed further in the section concerning the apparatus and experimental procedures. For Newtonian fluids, the vibrating wire has exact working equations that have been fully described in refs 26 and 33 to 39. The working equations were obtained assuming the following:[36,37] (1) the radius of the wire is small in comparison with the length of the wire; (2) the compressibility of the fluid is negligible; (3) the radius of the body containing the fluid is large in comparison with the wire radius so that the boundary effects are negligible; and (4) the amplitude of oscillation is small. Only one important modification of the equations summarized by Kandil et al.[27] is discussed here. It was determined from the measurements that we elucidate further in the section concerning the apparatus and experimental procedures.

Our viscometer comprises a thin metallic wire clamped under tension between two fixed supports and immersed in the fluid. The wire is placed in a magnetic field and driven in steady-state transverse oscillations by passing an alternating current through it. The resulting complex voltage $\boldsymbol{V}$ developed across the wire is composed of two components:

$$\boldsymbol{V} = \boldsymbol{V}_1 + \boldsymbol{V}_2 \tag{1}$$

The first term, $\boldsymbol{V}_1$, arises simply from the electrical impedance of the stationary wire, whereas the second, $\boldsymbol{V}_2$, arises from the motion of the wire in the presence of the magnetic field. We represent $\boldsymbol{V}_1$ by

$$\boldsymbol{V}_1 = a + bf + i(c + df) \tag{2}$$

where f is the frequency at which the wire is driven and a, b, c, and d are adjustable parameters that are determined by regression with experimental results. Parameters a, b, c, and d account for the electrical impedance of the wire and also absorb the offset used in the lock-in amplifier to ensure that the voltage signal is detected in the most sensitive range possible. Equation 2 includes a term df that has not to our knowledge been used in measurements reported previously.[18,26–31,40–42]

The viscosity of a fluid of known density can be determined from $\boldsymbol{V}_2$ with the working equation (eq 3 of ref 27) for a wire clamped (or pinned) at both ends by adjusting the viscosity so that the in-phase and quadrature voltages obtained from the working equations are consistent with experimentally determined values over a range of frequency; if a mass is suspended from the lower end of the wire, then the wire tension varies according to Archimedes' principle, and density can also be obtained by modification of the working equation (eq 3 of ref 27).[15]

The vibrating wire viscometer is an absolute device that, in theory, requires no calibration constants to be determined. The hydrodynamic model includes the resonance frequency in the absence of fluid and damping, the internal damping of the wire in vacuum, the wire radius, and the wire density. When these parameters are known along with the density of the fluid sample, the viscosity of the fluid can be obtained from the width of the resonance curve. However, in practice the wire damping factor and radius cannot be determined to sufficient accuracy by independent methods, and those values are usually determined by calibration. To do this, measurements are made in both vacuum and a fluid for which the viscosity and density are known. The former yields the damping factor Δ_0. The wire radius, R, can be determined from a single measurement when immersed in, typically, methylbenzene[18,27,31,40] but ideally water as demonstrated by Caetano et al.[31] In this work, we have not determined the vacuum frequency; rather its value has been allowed to float in the analysis.

For a vibrating tube densimeter, Retsina et al.[36] reported a working equation for a straight tube clamped at both ends, filled with fluid, and surrounded by either another fluid or vacuum; this analysis assumes that the fluid within the tube does not flow and thus the viscosity of the fluid is neglected. If negligible internal damping is assumed, then the expression derived by Retsina et al.[36] for a tube within vacuum reduces to

$$\rho = \frac{K(T,p)}{f^2} + L(T,p) \tag{3}$$

which is the working equation routinely used for vibrating U-tubes;[43−46] it applies even when the cross section is nonuniform and the tube is curved into a U.[45] In eq 3, K and L are both temperature- and pressure-dependent and are determined through calibrations with two reference liquids of known density, such as water and nitrogen, or with one liquid of known density, such as water, and with vacuum. Thus, the calibration is performed with fluids that have $\eta \leq 1$ mPa·s. Berhardt and Pauly[47] and Ashcroft et al.[48] have determined the error arising from neglecting viscosity in the working equations by comparing the results obtained with the vibrating tube with values determined with a pycnometer: Berhardt and Pauly[47] considered fluids with viscosities in the range of (1 to 10^3) mPa·s (with an Anton Paar DMA 02C densimeter), whereas Ashcroft et al.[48] studied fluids with viscosities between (1 and 40) mPa·s with a glass U-tube (Anton Paar model DMA 602). Both refs 47 and 48 determined that the vibrating tube gave values greater than the pycnometer and provided empirical expressions as a function of viscosity to estimate the correction. Anton Paar[49] recommend for a model 512P densimeter (similar to that used by us and described in the section below) the correction to density for fluid viscosity that is given by

$$\Delta\rho = \rho[-0.5 + 0.45(\eta/\text{mPa·s})^{1/2}] \times 10^{-4} \tag{4}$$

and subtracted from eq 3. For a vibrating tube filled with a fluid of $\eta \approx 76$ mPa·s, the worst case in our experiment, eq 4 returns $10^2\Delta\rho/\rho = 0.034$ %, whereas extrapolation of the expression reported in ref 47 by about 26 mPa·s gives $10^2\Delta\rho/\rho = 0.044$ % and that of ref 48 provides $10^2\Delta\rho/\rho = 0.048$ %. However, it still remains a task for theoretical mechanics to explain this observation.

Apparatus and Experimental Procedure

The apparatus consists of a vibrating wire viscometer, oscillating sinker viscometer, and vibrating tube densimeter, and each of these instruments is described below.

Vibrating Wire Viscometer. The vibrating wire was formed from an ≈0.1 mm diameter, 52 mm long tungsten wire that was drawn taut, in the holder shown in Figure 1, between two clamps, also shown in Figure 1. Tungsten was the preferred material because both Young's modulus E (≈411 GPa) and density ρ_s (≈19 300 kg·m^{-3}) are high relative to the values for other materials. The former provides a stable resonance, and the latter provides sensitivity to the fluid around it, through the ratio ρ/ρ_s (in eqs 4 and 5 of ref 27). The wire used in this experiment was obtained from Goodfellow, Cambridge, U.K., with mass fraction purity greater than 99.95 %. The wire was cold drawn and, when viewed with a scanning electron microscope operated at a magnification of about 1000×, showed numerous axial grooves. However, when the wire was immersed in liquids, the effect of surface roughness was negligible provided the amplitude of vibration was small and the Reynolds number (eq 9 of ref 27 is related to the Reynolds number) that characterizes fluid flow around the cylindrical wire was less than 100. Further discussion of the effect of both different wire materials and surface roughness on the measurement of viscosity can be found in ref 41. It was also noted that the wire cross section was of elliptical rather than circular symmetry, which resulted in the resonance appearing as a doublet.

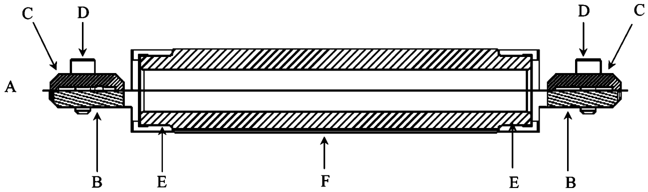

Figure 1. Cross section through the vibrating wire holder. Wire A is clamped at each end between two K-Monel plates B and C that are held together with screws D. The neck of plate B attachs to a spacer F fabricated from Shapal-M at an interlocking step E.

The wire was held at each end with clamps, shown in Figure 1. Each clamp was fabricated from Monel K-500 as two pieces, one a flat plate and one a circular boss that slid onto a separating tube described below and the other a flat plate. The two parts were held together with two M2, austenitic stainless steel 304, screws; at each end, one screw also served as a clamp for a wire that formed electrical contact between the wire holder and the electrical feedthrough within the pressure vessel. A pin, fabricated from Monel 400, was used both to maintain the axial symmetry of the wire and to align the two plates. These clamps were both mechanically supported and electrically isolated from each other with a ceramic tube, shown in Figure 1, which was fabricated from Shapal-M (which is aluminum nitride) obtained from Goodfellow, Cambridge, U.K. This material was chosen to reduce the effect of differential thermal expansion on the wire tension as the temperature departs from ambient because the linear thermal expansion coefficient of Shapal-M is $5.2 \cdot 10^{-6}$ K^{-1}, which is about 1.2 times that of tungsten at $T = 293$ K. The electrical resistivity of Shapal-M is $2 \cdot 10^{15}$ Ω·m. The tube had an outer diameter of 10.2 mm and an inner diameter of 5.16 mm to maintain adherence to assumption 3.[42,50] At each end of the tube was a step, shown in Figure 1, that was used to locate and retain the wire clamps.

To provide the tension, one end of the wire was clamped between the two plates B and C while the other end of the wire passed through the second open clamp and was attached to a mass for about 24 h, after which time the lower clamp was carefully tightened and the mass was removed. The tension mass was selected both to determine the fundamental resonance frequency and to maintain the tension between 20 % and 50 % of the tensile yield for tungsten (about 720 MPa). The wire holder was mounted within a pressure vessel and a magnetic field, described below, placed outside the pressure vessel.

The magnetic field was provided by two rectangular magnets that were mounted opposite each other on a C-shaped clamp formed from carbon steel. The magnets, each of length $L_B = 50.8$ mm, were located π apart and symmetrically along the wire of length $L = 52$ mm so that the ratio $L/L_B \approx 1.02$ so as to suppress higher harmonics.[41]

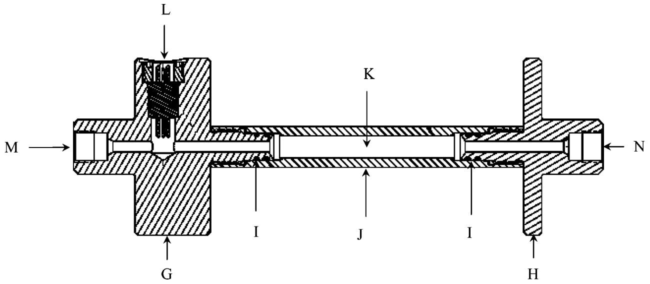

Figure 2. Cross-section through the vibrating wire pressure vessel fabricated, from 718 Inconel (per specification CMS.Z1CSU.0), as two end caps G and H that were threaded and sealed, with O-rings I, into tube J that contains vibrating wire K, which for the sake of clairity is not shown. Electrical connections passed through a feedthrough L, and fluid flowed from inlet M to outlet N.

The magnets were supplied by Dexter and were fabricated from (Nd, Pr, Dy)$_2$(Fe, Co)$_{14}$B (known commonly as NdFeB) for which the Curie temperature is about 583 K and the maximum operating temperature is about 473 K. In this arrangement, the magnets were not exposed to the fluid while, at a temperature of 298 K, providing a measured magnet flux density of about 0.38 T on the wire at T = 293 K. The largest force applied at a current of 5 mA was about 99 μN.

Prior to commencing measurements, we aligned the vibrating wire within the magnetic flux so as to preferentially excite the highest orthogonal mode of the fundamental oscillation that arises from the noncircular cross section of the wire. This was achieved by rotating the entire pressure vessel housing within the magnetic field in steps of about 0.05π and after each rotation determining the resonance response in vacuum. This tuning was defined as complete when the difference between the estimated and measured complex voltage as a function of frequency was a minimum. The wire was then thermally cycled at a temperature from (298 to 423) K and then back to 298 K five times over 12 h. The resonance frequency determined before the thermal cycles was about 1 % greater than that obtained after, which was about 1250 Hz. The thermal cycle was repeated twice, and after both of these cycles, the resonance frequencies differed by only 0.1 %. Presumably, the initial 1 % decrease in resonance frequency can be attributed to the relaxation of residual stresses in the wire arising from tensioning within the wire holder.

The pressure vessel, shown in Figure 2 without the vibrating wire holder installed, was fabricated from 718 Inconel (per specification CMS.Z1CSU.0), with a relative magnetic permeability of about 1.001. The outer diameter of the pressure vessel was 19 mm and the inner diameter was 10.4 mm with a maximum operating pressure of 70 MPa at the highest operating temperature. The fluid flowed into and out of the apparatus through two ports, shown in Figure 2, located at either end of the vessel. Electrical connections through the pressure vessel to the wire were made via an electrical feedthrough.

A sinusoidal voltage was generated by a lock-in amplifier (Stanford Research Systems model 850), with a maximum output of 5 V ac, and was passed through a resistance of about 1 kΩ connected in series to the tungsten wire so as to provide a constant current source. The voltage was varied between (5 and 5000) mV to maintain the amplitude of the wire motion, estimated from the applied force, magnetic flux, and viscosity, to be less than 10 % of its radius. Thus, in vacuum and air a driving current of 5 μA was used, whereas 5 mA was used when the wire was submerged in methylbenzene, N10, or S20. The W wire $\{c_p(\mathrm{W}, 298\ \mathrm{K}) \approx 133\ \mathrm{J{\cdot}kg^{-1}{\cdot}K^{-1}}$ and $\rho(\mathrm{W}, 298\ \mathrm{K}) \approx 19\ 300\ \mathrm{kg{\cdot}m^{-3}}\}$, of diameter 0.10 mm and mass $7.9{\cdot}10^{-6}$ kg, has a resistance of order 1 Ω, and in vacuum, a current of 5 μA resulted in a temperature increase of less than 3 μK over the 200 s data acquisition time. When the 0.10 mm diameter wire was immersed in S20 $\{c_p(298\ \mathrm{K}) \approx 2\ \mathrm{kJ{\cdot}kg^{-1}{\cdot}K^{-1}}$, $\rho(298\ \mathrm{K}) \approx 840\ \mathrm{kg{\cdot}m^{-3}}$, and $\kappa \approx 120\ \mathrm{mW{\cdot}m^{-1}{\cdot}K^{-1}}\}$, with the highest current of 5 mA, over the 200 s acquisition time, the fluid temperature was estimated to rise by 0.9 mK {assuming all electrical energy dissipated into the fluid volume enclosed by the wire holder (about 1.1×10^{-6} m^3)} and the resulting error in viscosity at T = 313 K, where η = 30 mPa·s and $\mathrm{d}\eta/\mathrm{d}T \approx -2.14$ mPa·s·K^{-1}, would be ≈0.006 %}. The temperature rise resulting from the wire motion within the fluid was always negligible.

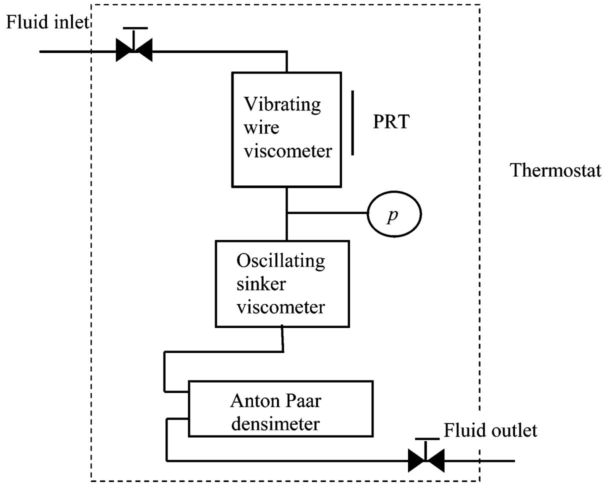

Figure 3. Schematic of the vibrating wire and oscillating sinker viscometers and vibrating tube densimeter within the air-bath thermostat including the pressure gauge and platinum resistance thermometer (PRT).

The frequency generated by the synthesizer was stepped over the resonance frequency of the wire, and the in-phase and quadrature voltages $\boldsymbol{V}$ that included the motional emf $\boldsymbol{V}_2$ were determined with the lock-in amplifier, typically, over the frequency range of ($f_\mathrm{r} \pm 5g$), where g is half the resonance line width at a frequency corresponding to an amplitude determined by 0.707 times that of the maximum amplitude and f_r is the fundamental transverse resonance frequency. Prior to acquiring $\boldsymbol{V}$, the majority of the contribution arising from drive voltage $\boldsymbol{V}_1$ was removed by setting the lock-in offset voltage at $f < (f_\mathrm{r} - 5\ g)$. The frequency sweep usually started at ($f_\mathrm{r} - 5g$) with positive frequency steps to ($f_\mathrm{r} + 5g$) and then with negative increments to ($f_\mathrm{r} - 5$ g) and took about 200 s for acquisition. However, the scan range depended on the quality factor Q $\{= f/(2g)\}$ of the wire resonance. The Q, shown in Figure 4, decreased from 16.5, for η(S20, 393 K, 0.1 MPa) ≈ 2.6 mPa·s, to 1.9, for η(S20, 298 K, 45.5 MPa) ≈ 76 mPa·s. For the latter, $g \approx 273$ Hz and $f_\mathrm{r} \approx 1195$ Hz, and the frequency range of the scan was about $\pm 4g$. At a constant drive current, as the viscosity increases there is also a corresponding decrease in the signal-to-noise ratio.

For each fluid temperature and pressure, the measured $\boldsymbol{V}$ was replicated by adjusting a, b, c, and d of eq 2, the resonance frequency in vacuum f_0 (eq 3 ref 27), and the viscosity η (eq 9 of ref 27) using R and Δ_0 from the calibration and the appropriate density. This numerical procedure separates the complex voltages $\boldsymbol{V}_1$ and $\boldsymbol{V}_2$ utilizing the different frequency dependences of eqs 2 and eq 3 of ref 27, respectively.

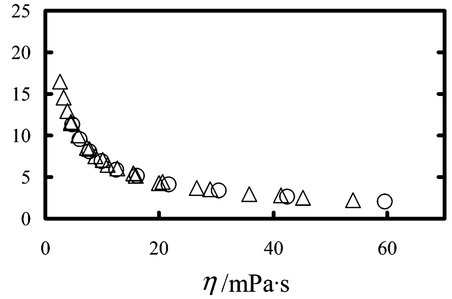

Figure 4. Variation of the resonance quality factor Q $\{= f/(2g)\}$ of the nominal 0.1 mm diameter wire as a function of viscosity η. ○, Certified reference fluid N10; △, standard reference specimen S20.

Table 1. Coefficients of Equation 5 Representing the Viscosity of Certified Reference Materials N10 and S20 at Temperature in the Range of (293.15 to 373.15) K at a Pressure of 0.1 MPa

fluid	e	f/K	g/K
N10	−2.5291	625.4536	−179.7562
S20	−2.7338	775.9450	−171.0497

Table 2. Coefficients of Equation 6 Representing the Density of Certified Reference Materials N10 and S20 at Temperature in the Range of (293.15 to 373.15) K at a Pressure of 0.1 MPa

fluid	h/kg·m^{-3}·K^{-1}	j/kg·m^{-3}
N10	−0.6626396	895.3405
S20	−0.6332246	875.2144

Measurements of $\boldsymbol{V}$ in vacuum were used to obtain $\Delta_0 = 50 \times 10^{-6}$ whereas measurements in methylbenzene at a temperature of 298.15 K and four pressures in the range of (13.8 to 55.2) MPa were combined with the viscosity and density of methylbenzene determined from the correlation reported by Assael et al.[13] to obtain $\langle R \rangle = (47.8_9 \pm 0.3_1) \times 10^{-6}$ μm (about 0.06 %), and no systematic variations of R from $\langle R \rangle$ were observed with pressure. According to ref 13, the viscosity of methylbenzene varies from (0.61 to 0.82) mPa·s, and the density covers the range of (872 to 898) kg·m^{-3}. The uncertainty in R is the major source of error in our measurements of viscosity, which have an estimated expanded uncertainty of ±2 %; for liquids, the working equations are insensitive to the value of Δ_0, and there is no requirement to determine this parameter with high precision. We did not include corrections to both the wire radius and density that account for variations in temperature and pressure. It has been reported that these amount to an additional uncertainty in viscosity of less than 0.1 %.[15]

As the viscosity increased, the Q and signal amplitude decreased, and the frequency range of the measurements increased. At viscosities greater than about 20 mPa·s, an additional parameter df was required in eq 2 to replicate the measured complex voltage $\boldsymbol{V}$ adequately as a function of frequency and account for the frequency-dependent background. Had we adopted the usual and accepted form of eq 2 without df (applied to high signal-to-noise ratio measurements at viscosities of <1 mPa·s) the estimated viscosities would have deviated significantly (more than 1 %) from those listed in Table 4, and in the worst case, for S20 with df the analysis gave η(298.15 K, 41. MPa) ≈ 76 mPa·s while the estimated viscosity without df was 103 mPa·s greater, they would have deviated by about 133 %.

The values of f_0, the frequency of the wire in the absence of fluid and internal damping, determined from the regression analysis (see eq 3 of ref 27) were repeatable at a certain temperature and $p = 0.1$ MPa to better than 0.5 % (about 7 Hz), and df_0/dT varied from (−0.3 to 0.1) Hz·K^{-1} over the temperature range of (298 to 398) K, which covers the range anticipated solely from the variation in wire tension that would arise from the difference in the linear thermal expansion coefficients between tungsten and Shapal-M; f_0 at a pressure greater than 0.1 MPa between temperatures was also reproducible to better than 0.5 %. However, we also found that f_0 decreased linearly with increasing pressure with df_0/dp in the range of −1.5 Hz·MPa^{-1} at $T = 298$ K to −0.8 Hz·MPa^{-1} at $T = 393$ K. We have not performed experiments to identify the source of this observed variation; plausible sources include variations in the wire tension, length, and rotation of one wire clamp relative to the other. According to the working equations,[27] f_0 is specific to the particular end condition chosen for the wire. In practice, it is impossible to know the end conditions for the tube exactly so that any applied condition will yield only a good approximation to the true f_0. Thus, to determine the viscosity accurately we allowed f_0 to float in the regression analysis. Had we fixed f_0 in the analysis to a value determined at $p = 0$ for each temperature the viscosities determined would have deviated from those obtained with the oscillating sinker by up to 50 %.

Table 3. Viscosity η Obtained Either from the Supplier or Equation 6 and the Density ρ Provided by the Manufacturer or Equation 5 for Certified Reference Materials N10 and S20 at Temperature T and $p = 0.1$ MPa

fluid	T/K	η/mPa·s	ρ/kg·m^{-3}
N10	298.15	15.68	878.8
	333.15	4.704[a]	855.6[a]
S20	298.15	29.11	859.4
	313.15	15.29	849.9
	333.15	7.792[a]	837.2[a]
	353.15	4.606[a]	824.6[a]
	393.15	2.138[b]	799.2[b]

[a] Interpolated from eqs 5 and 6. [b] Extrapolated from eqs 5 and 6.

For viscosity obtained from the vibrating wire viscometer, the uncertainty is, based on the work reported in refs 27 and 31, assumed to be 1 %.

Oscillating Sinker Viscometer. The viscosity was also determined with an oscillating sinker viscometer (model SPL 440) supplied by Cambridge Applied Systems, which had been used by Jakeways and Goodwin previously.[51] The method of determining viscosity from the time required for the sinker to traverse a known distance is similar to a falling cylinder viscometer, described by Kawata et al.[25] However, the operation of the instruments differs. For an oscillating cylinder, the sinker is permanently magnetized and forced to move by two electromagnets, located outside the tube, and the time required, under a constant applied force, to traverse the known distance between the electromagnets is determined. The tube containing the sinker is orientated $\pi/4$ relative to vertical. The internal volume of the viscometer is less than 2 cm^3. A piston designated for the viscosity range of (2.5 to 50) mPa·s was calibrated by the manufacturer with a cited uncertainty of ±1 % of full scale (or ±0.5 mPa·s).

Prior to determining the viscosity of N10 and S20, we calibrated the viscometer with certified reference material S60 (nominal viscosity of 104 mPa·s at $T = 298$ K and $p = 0.1$ MPa) at viscosities between 6.1 mPa·s at $T = 373$ K and 45 mPa·s at $T = 313$ K. The S60 was supplied by Cannon Instruments, with kinematic viscosities measured

Table 4. Viscosity η Obtained from the Oscillating Sinker (OS) and Vibrating Wire (VW) Viscometers along with the Weighted Mean of the Viscosity $\langle\eta\rangle$ and Density ρ Obtained from the Vibrating Tube (VT) for Certified Reference Materials N10 and S20 at Temperatures T and Pressures p with Expanded Uncertainties (Confidence Interval of 0.995)

fluid	T/K	p/MPa	η(OS)/mPa·s	η(VW)/mPa·s	$\langle\eta\rangle$/mPa·s	ρ(VT)/kg·m^{-3}
N10	298.15 ± 0.01	0.129 ± 0.056	15.40 ± 0.62	15.94 ± 0.31	15.83 ± 0.28	878.3 ± 1.8
		13.930 ± 0.084	21.51 ± 0.87	21.65 ± 0.44	21.62 ± 0.39	886.7 ± 1.8
		27.68 ± 0.11	30.2 ± 1.2	30.33 ± 0.63	30.30 ± 0.56	894.9 ± 1.8
		41.46 ± 0.14	42.3 ± 1.7	42.17 ± 0.89	42.19 ± 0.79	900.9 ± 1.8
		55.27 ± 0.17	57.9 ± 2.4	59.4 ± 1.2	59.0 ± 1.1	907.8 ± 1.8
	333.15 ± 0.01	0.167 ± 0.056	4.81 ± 0.19	4.718 ± 0.097	4.737 ± 0.086	856.0 ± 1.7
		13.864 ± 0.084	6.09 ± 0.24	6.05 ± 0.12	6.06 ± 0.11	864.5 ± 1.7
		27.68 ± 0.11	7.80 ± 0.31	7.73 ± 0.16	7.74 ± 0.14	872.7 ± 1.8
		41.49 ± 0.14	9.94 ± 0.40	9.78 ± 0.20	9.81 ± 0.18	880.3 ± 1.8
		55.28 ± 0.17	12.74 ± 0.51	12.37 ± 0.26	12.44 ± 0.24	887.2 ± 1.8
S20	298.15 ± 0.01	0.102 ± 0.056	30.0 ± 1.2	28.69 ± 0.58	28.93 ± 0.52	858.1 ± 1.7
		13.917 ± 0.084	41.0 ± 1.6	41.22 ± 0.84	41.17 ± 0.75	865.0 ± 1.7
		27.71 ± 0.11	54.9 ± 2.2	53.9 ± 1.1	54.08 ± 0.99	874.0 ± 1.8
		41.50 ± 0.14	73.4 ± 3.0	76.6 ± 1.6	75.85 ± 1.40	879.7 ± 1.8
	313.15 ± 0.01	0.132 ± 0.056	14.78 ± 0.59	15.13 ± 0.30	15.06 ± 0.27	848.8 ± 1.7
		13.853 ± 0.084	19.83 ± 0.80	20.30 ± 0.41	20.20 ± 0.37	857.2 ± 1.7
		27.69 ± 0.11	26.5 ± 1.1	26.44 ± 0.54	26.46 ± 0.48	864.7 ± 1.7
		41.47 ± 0.14	35.2 ± 1.4	35.62 ± 0.74	35.53 ± 0.66	871.5 ± 1.7
		55.26 ± 0.17	46.1 ± 1.9	45.14 ± 0.95	45.34 ± 0.84	877.8 ± 1.8
	333.15 ± 0.01	0.178 ± 0.056	7.84 ± 0.31	7.73 ± 0.16	7.75 ± 0.14	837.3 ± 1.7
		13.886 ± 0.084	10.03 ± 0.4	9.94 ± 0.2	9.96 ± 0.18	846.6 ± 1.7
		27.66 ± 0.11	13.01 ± 0.52	12.60 ± 0.26	12.68 ± 0.23	854.2 ± 1.7
		41.50 ± 0.14	16.15 ± 0.65	15.96 ± 0.33	16.00 ± 0.29	861.2 ± 1.7
		55.28 ± 0.17	20.64 ± 0.83	19.82 ± 0.41	19.98 ± 0.37	868.0 ± 1.7
	353.15 ± 0.01	0.210 ± 0.056	4.63 ± 0.19	4.59 ± 0.10	4.601 ± 0.089	825.0 ± 1.7
		13.891 ± 0.084	5.89 ± 0.24	5.75 ± 0.12	5.78 ± 0.11	834.5 ± 1.7
		27.71 ± 0.11	7.29 ± 0.29	7.18 ± 0.15	7.21 ± 0.14	843.1 ± 1.7
		41.50 ± 0.14	9.06 ± 0.36	8.81 ± 0.19	8.86 ± 0.17	851.5 ± 1.7
		55.27 ± 0.17	11.20 ± 0.45	10.81 ± 0.23	10.89 ± 0.20	859.3 ± 1.7
	393.15 ± 0.01	13.922 ± 0.084	2.73 ± 0.11	2.570 ± 0.068	2.613 ± 0.057	811.3 ± 1.6
		27.70 ± 0.11	3.32 ± 0.13	3.113 ± 0.076	3.164 ± 0.066	821.3 ± 1.6
		41.48 ± 0.14	4.01 ± 0.16	3.712 ± 0.087	3.778 ± 0.076	830.3 ± 1.7
		55.26 ± 0.17	4.82 ± 0.19	4.40 ± 0.099	4.485 ± 0.088	838.2 ± 1.7

with long-capillary Master viscometers according to ASTM D 2164 at temperatures between (293 and 373) K and densities, determined over the same temperature range, in accordance with ASTM D 1480. The uncertainty in the kinematic viscosity was cited as ±0.25 % relative to water, and the uncertainty in density was cited as ±0.02 % and, when used as calibration fluid, did not limit the uncertainty of the oscillating sinker viscometer. Our measurements of the viscosity of S60, with the oscillating sinker, differed by a few percent from those cited by the supplier, and the observed differences were used to correct all subsequent viscosity measurements.[51] After the viscosity of N10 and S20 had been determined, the viscosity measurements with S60 were repeated, and after applying the same temperature-dependent correction, the differences between our results and those reported by the supplier were less than ±2 % over the viscosity range from (6.1 to 45) mPa·s; at any temperature in our range, the repeatability was about ±1 %. Thus, for viscosities between (6 and 45) mPa·s, the viscometer had a precision of ±2 % that was twice the uncertainty assigned by the manufacture at $\eta = 46$ mPa·s and a factor of 4 lower than the cited uncertainty at $\eta = 6$ mPa·s.

For S20 with η(298 K, 41 MPa) = 76 mPa·s, the sinker was used outside the range of (2 to 50) mPa·s recommended by the manufacturer and our validation measurements with S60. Thus, we used reference fluid S6 and N35 to determine the performance of the sinker at viscosities less than 2 mPa·s and greater than 50 mPa·s, respectively; the manufacturer's cited values were interpolated to other temperatures with polynomials that introduced an additional uncertainty of less than 1 % into the viscosity of the fluids. For S6 with a viscosity of 1.83 mPa·s, the oscillating sinker gave $\eta = 1.97$ mPa·s, whereas for N35 at a viscosity of 58.12 mPa·s the sinker gave $\eta = 62.45$ mPa·s. Both results obtained from the oscillating sinker viscometer are about 7 % above an interpolation of the manufactures' cited values, about 3 times the estimated uncertainty, and are a measure of the upper bound uncertainty for the viscosity obtained with this instrument.

Vibrating Tube Densimeter. For a vibrating wire, clamped at both ends, measurements of the density are required to determine viscosity from the working equations. The density of N10 and S20 was determined with a vibrating U-tube densimeter (Anton Parr model 512) with an uncertainty cited by the manufacturers of ±0.1 %. The measured densities were corrected for the effect of viscosity according to eq 4, and for our measurements, this fractional correction to the density never exceeded 0.03 %. Prior to performing measurements, the densities of both heptane and water, which were degassed by boiling while maintaining $p \leq 10$ Pa, were determined at temperatures in the range of (298 to 393) K and pressures below 55 MPa. Our results were compared with values obtained by combining the measured temperature and pressure with correlations reported by Span and Wagner[52] for heptane and Wagner and Pruss[53] for water, and they were found to differ by less than ±0.1 %. On the basis of these measurements, we conclude that the U-tube densimeter has an uncertainty of ±0.1 %. An uncertainty of ±0.1 % in the density yields an uncertainty of ±0.05 % in the viscosity determined from the vibrating wire, and the uncertainty of the density measurements should not introduce any additional and significant error into the values of viscosity.[31]

Thermostat, Thermometer and, Pressure Gauge. The vibrating wire and oscillating sinker viscometers and the vibrating tube densimeter were interconnected, as shown in Figure 3, and thermostated in an air bath whose temperature was controlled with a precision of better than ±0.1 K.

The temperature of the vibrating wire viscometer and the vibrating tube densimeter were determined with a platinum resistance thermometer with a nominal resistance of 100 Ω, which when compared against a standard 25 Ω platinum resistance thermometer that had been calibrated on the ITS-90 scale was found to have an uncertainty of less than ±0.01 K. The resistance was determined with a multimeter and converted to temperature with an uncertainty, including the calibration, of about ±0.01 K. The temperature of the oscillating sinker viscometer was also determined with a platinum resistance thermometer imbedded into the viscometer with an uncertainty of ±0.01 K. These three thermometers showed, in the worst case, a vertical temperature gradient over 1 m of about 1 K. The worst-case temperature gradient over the height of the viscometer was less than 0.01 K.

Pressure was generated with a positive displacement pump and measured, in the range of (0 to 55) MPa, with a transducer (Honeywell Sensotec, model THE/0743-11TJA, serial number 833326 with a maximum operating pressure of 69 MPa) that when calibrated against a dead weight gauge with a precision of better than ±0.001 MPa was found to have an uncertainty of δp/MPa = ±(0.001p + 0.028).

The viscometer apparatus was filled with each fluid at T = 373 K, the highest temperature, and cooled to the lowest temperature while continuously oscillating the piston, before commencing measurements.

Materials and Measurements. Three fluids were used for the measurements. Methylbenzene from Merck BDH Ltd had a mass fraction greater than 0.99917. The two certified reference materials for viscosity N10 and S20 {with nominal viscosities of (16 and 29) mPa·s, respectively, at T = 298 K and p = 0.1 MPa} were obtained from Cannon Instruments with assigned lot numbers of 3201 and 3401, respectively. The supplier measured the kinematic viscosity for both N10 and S20 at temperatures between (293 and 373) K using long-capillary Master viscometers according to ASTM D 2164. The supplier also provided density values at all temperatures measured in accordance with ASTM D 1480. The uncertainty in the kinematic viscosity was ±0.25 % relative to water, and the uncertainty in the density was ±0.02 %.

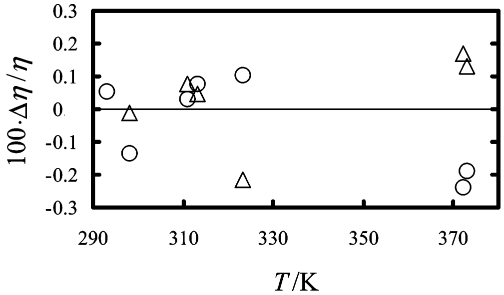

Figure 5. Fractional deviation $\Delta\eta/\eta = \{\eta(\text{exptl}) - \eta(\text{calcd})\}/\eta(\text{calcd})$ of the viscosity cited by the supplier η(exptl) from the value η(calcd) determined with eq 5. ○, Certified reference fluid N10; △, certified reference specimen S20.

Table 5. Coefficients of the Tait Equation (Eq 7) and Eq 8 for Certified Reference Specimens N10 and S20 with Number of Measurements *N*, Average Deviation $\delta = \{|\Delta\rho|/\rho\rangle$, and Maximum Deviation $\delta_{\max} = |\Delta\rho_{\max}|/\rho$

fluid	N	C	A_0/MPa	A_1/MPa·K^{-1}	10^3A_2/MPa·K^{-2}	$10^2\delta$	$10^2\delta_{\max}$
N10	14	0.21	270.927	−0.4678	0	0.022	0.063
S20	29	0.21	799.004	−3.3352	3.84159	0.042	0.177

For N10, measurements were performed at temperatures of (298 and 333) K, whereas for S20, measurements were performed at five temperatures in the range of (298 to 393) K; for both fluids, pressures between (0.1 and 55) MPa were investigated. The supplier cited values of both density and viscosity at a pressure of 0.1 MPa and seven temperatures of (293.15, 298.15, 310.93, 313.15, 323.15, 372.04, and 373.15) K. Our measurements of density and viscosity at temperatures of 298.15 K and 313.15 K corresponded to temperatures at which certified reference values were provided by the supplier. To obtain values of viscosity and density at our other experimental temperatures, we fit the reference values to empirical functions. Using the rule of Vogel,[54] the reference values of viscosity were represented by

$$\ln\left(\frac{\eta}{\eta^\circ}\right) = e + \frac{f}{g + T} \tag{5}$$

where η° = 1 mPa·s. The constants e, f, and g of eq 5 for N10 and S20 were obtained by a nonlinear adjustment and are listed in Table 1, and the relative differences of the reference values from eq 5 are shown in Figure 5, where the average deviation is 0.05 % and the maximum deviation is 0.2 %, both of which are within the 0.25 % uncertainty cited by the supplier. The seven cited values of density were fit to

$$\rho = h[(T/\text{K}) - 273.15] + j \tag{6}$$

with the parameters h and j listed in Table 1 for N10 and S20 adjusted to represent the cited values. The maximum difference between the cited density and that determined from eq 6 was 0.006 %, a factor of about 3 less than the cited uncertainty, and the average deviation was about 0.001 %. We conclude that eqs 5 and 6 introduced a negligible additional uncertainty into the values of density and viscosity calculated at other temperatures within the range of (293.15 to 373.15) K and an indeterminate uncertainty at our highest temperature of 398.15 K. Table 3 lists the density and viscosity of N10 and S20 at our experimental temperatures and includes the values cited by the supplier at 298.15 K and 313.15 K and values interpolated and extrapolated with eqs 5 and 6.

Results and Discussion

The viscosity of N10 and S20 obtained with both the vibrating wire and the oscillating sinker viscometers are listed in Table 4 along with the density determined with the vibrating tube at temperatures between (298 and 393) K at a pressure up to 55 MPa. Small corrections have been applied to the reported viscosity and density to reduce all values to the stated temperature for each isotherm. The uncertainties, listed in Table 4, are at a confidence interval of 0.995 (k = 2) and were obtained by combining in quadrature uncertainties arising from the uncertainty of the instrument with dη/dT and dη/dp for viscosity and dρ/dT with dρ/dp for density. For both viscosity and density, the major source of uncertainty (by at least a factor of 5) arises from the uncertainty of the viscometer and densimeter calibration. For viscosity values obtained from the vibrating wire viscometer, the uncertainty is, based on the work reported in refs 27 and 31, assumed to be ±1 %, whereas the viscosities obtained with the oscillating sinker

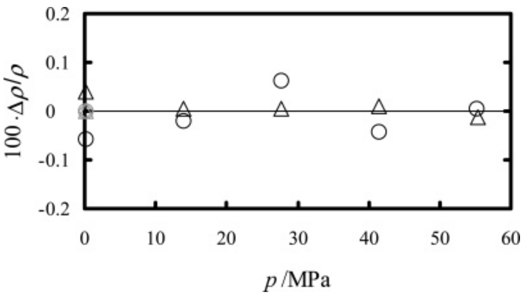

Figure 6. Fractional deviation $\Delta\rho/\rho = \{\rho\ (\mathrm{exptl}) - \rho(\mathrm{calcd})\}/\rho$ (calcd) of the density in either Table 3 or Table 4 ρ(exptl) from the value ρ(calcd) obtained from a combination of eqs 7 and 8 with coefficients listed in Table 5 for certified reference material N10. ○, Vibrating tube at $T = 298$ K from Table 4; gray ○, value cited by the supplier at $T = 298$ K from Table 3; △, vibrating tube at $T = 333$ K from Table 4; gray △, eq 6 with coefficients of Table 2 at $T = 333$ K from Table 3; gray □, value cited by the supplier at $T = 313$ K; and gray ◇, value cited by the supplier at $T = 323$ K.

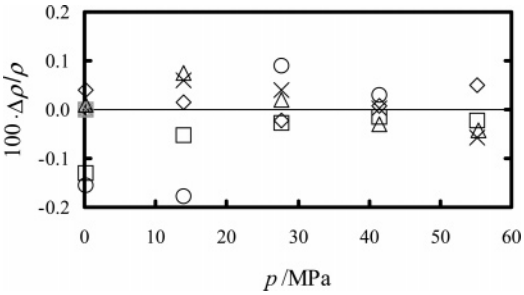

Figure 7. Fractional deviation $\Delta\rho/\rho = \{\rho\ (\mathrm{exptl}) - \rho(\mathrm{calcd})\}/\rho$ (calcd) of the density in either Table 3 or Table 4 ρ(exptl) from the value ρ(calcd) obtained from a combination of eqs 7 and 8 with coefficients listed in Table 5 for certified reference material S20. The scale of the ordinate axis is equal to the expanded uncertainty of Table 4. ○, Vibrating tube at $T = 298$ K from Table 4; gray ○, value cited by the supplier at $T = 298$ K from Table 3; □, vibrating tube at $T = 313$ K from Table 4; □, gray value cited by the supplier at $T = 313$ K from Table 3; △, vibrating tube at $T = 333$ K from Table 4; gray △, eq 6 with coefficients of Table 2 at $T = 333$ K from Table 3; ◇, vibrating tube at $T = 353$ K from Table 4; gray ◇, eq 6 with coefficients of Table 2 at $T = 353$ K from Table 3; ×, vibrating tube at $T = 393$ K from Table 4; and gray ×, eq 6 with coefficients of Table 2 at $T = 393$ K from Table 3

were uncertain by ±2 % based on the calibration. For density, the uncertainty was ±0.1 %, as determined by calibration. The next most significant and quantifiable contribution to the uncertainties arises from $\mathrm{d}\eta/\mathrm{d}p$ for viscosity and $\mathrm{d}\rho/\mathrm{d}p$ for density. These derivatives were estimated from a combination of our results and the δp listed in Table 4. For N10, the contribution to $\delta\eta$ from δp lies between (0.002 to 0.2) mPa·s {about (0.09 to 0.35) %}, which decreased with increasing temperature while the density error $\delta\rho$ from δp varied from (0.06 to 0.2) kg·m^{-3} {about (0.01 to 0.02) %}. For the certified reference specimen S20, the $\delta\eta$ arising from δp covered the range of (0.04 to 0.14) mPa·s {about (0.09 to 0.25) %}, and the $\delta\rho$ estimated from δp varied from (0.06 to 0.2) kg·m^{-3} {about (0.01 to 0.02) %}. The contribution to the uncertainty from either $\mathrm{d}\eta/\mathrm{d}T$ or $\mathrm{d}\rho/\mathrm{d}T$ was estimated from a combination of our results and the δT listed in Table 4. For N10, the contribution to $\delta\eta$ from δT was (0.0002 to 0.009) mPa·s {about (0.007 to 0.06) %} and $\delta\rho \approx 0.01$ kg·m^{-3} (about 0.001 %), whereas for S20, $\delta\eta$ arising from δT covered the range of (0.0003 to 0.022) mPa·s {about (0.007 to 0.07) %} and $\delta\rho \approx 0.01$ kg·m^{-3} (about 0.001 %). Clearly, for our measurements the uncertainty with which the pressure is measured is more significant for N10 and S20 than the uncertainty in temperature. In the absence of a chemical analysis for these fluids, the contribution to the uncertainty arising from the uncertainty in composition was assumed to be 0. For both certified reference materials at a certain temperature and pressure, the viscosities obtained with both the vibrating wire and the oscillating sinker agreed within the combined expanded uncertainty given in Table 4 except for S20 at a temperature of 393 K and pressures of (41.5 and 55.3) MPa, where the values were within the combined uncertainty at a confidence level 0.999. The worst case was for S20 at $T = 393$ K at $p = 55.3$ MPa for which the vibrating wire gave $\eta = 4.4$ mPa·s and the oscillating sinker gave $\eta = 4.8$ mPa·s. The latter is close to the lower end of the operating range for the oscillating sinker and at a viscosity of about 2 mPa·s below the calibration with S60. Our measurements with S6 at a viscosity of about 1.8 mPa·s suggest that the uncertainty of the viscosities obtained from the oscillating sinker increased to 7 % and, in the absence of other measurements, if we assume that this uncertainty also gives an upper bound error at a viscosity of 4 mPa·s then the results from both instruments agree within the combined expanded uncertainty. At three viscosities of η(S20, 298 K, 27 MPa) ≈ 54 mPa·s, η(N10, 298 K, 55 MPa) ≈ 59 mPa·s, and η(S20, 298 K, 41 MPa) ≈ 76 mPa·s, the oscillating sinker was operated above 45 mPa·s, the upper limit of the calibration with S60. At viscosities of 54 mPa·s and 59 mPa·s, the values obtained from the oscillating sinker agreed with the values obtained with the vibrating wire to within ±4 % of the uncertainty assigned to the sinker results, whereas at a viscosity of 73 mPa·s the sinker provided a value about 4.4 % below the vibrating wire; when the sinker was immersed in certified reference material N35 at a viscosity of about 58 mPa·s, the oscillating sinker provided values 7 % above an interpolation of the certified viscosity. Nevertheless, the agreement for the viscosities obtained from two experimental techniques that utilize different principles, and thus suffer from quite different sources of systematic error, is considered to be remarkable. In Table 4, we also give the weighted-average viscosity determined from the oscillating sinker and vibrating wire viscometers along with the weighted uncertainty.[55]

To represent the densities ρ, we used the modified Tait equation[56] in the form

$$\frac{\rho(p) - \rho_{\mathrm{r}}(p_{\mathrm{r}})}{\rho(p)} = C \log\left(\frac{B + p}{B + p_{\mathrm{r}}}\right) \tag{7}$$

where B is a function of temperature given by

$$B = A_0 + A_1 T + A_2 T^2 \tag{8}$$

In eq 7, $p_{\mathrm{r}} = 0.1$ MPa and $\rho_{\mathrm{r}}(p_{\mathrm{r}})$ is the density of the certified reference material cited by the supplier and listed in Table 3 at each of our experimental temperatures. The $\rho_{\mathrm{r}}(p_{\mathrm{r}})$ values were combined with the density values obtained with the vibrating tube from Table 4 to determine adjustable parameters A_0, A_1, and A_2. The regression was constrained with $C = 0.21$, reported by Dymond and coworkers,[57–59] for hydrocarbons to reproduce the density listed in Table 3 exactly. Because our measurements of the density of N10 were limited to temperatures of 298.15 K and 333.15 K, A_2 of eq 8 was 0, and we also included in the analysis ρ(313.15 K, 0.1 MPa) = 868.8 kg·m^{-3} and ρ(323.15 K, 0.1 MPa) = 862.2 kg·m^{-3} provided by the

Table 6. Coefficients of Equation 9 for Certified Reference Specimens N10 and S20 with Number of Measurements N, Average Deviation $\delta = \langle|\Delta\rho|/\rho\rangle$, and Maximum Deviation $\delta_{\max} = |\Delta\rho_{\max}|/\rho$

fluid	N	k	l/K	M/K	10^4n/MPa^{-2}	10^8q/K^{-1}·MPa^{-2}	$10^2\delta$	$10^2\delta_{\max}$
N10	12	−4.9297	161.76	−160.83	2.3483	−75.2606	0.268	0.881
S20	29	−4.6000	68.6397	−217.853	0.2118	−12.0786	0.487	2.270

supplier. The coefficients of eqs 7 and 8 so determined for certified reference materials N10 and S20 are listed in Table 5 together with the average percentage deviation, which never exceeds 0.04 %, and the maximum deviation from the experimental densities. We speculate, on the basis of the reported international consistency of these fluids,[21] that adopting this formalism might allow small but still significant differences between values of $\rho_r(p_r)$ to be accommodated solely by substituting values of $\rho_r(p_r)$ obtained either from other lots of the same supplier or from an alternative supplier of certified reference materials N10 and S20. No experiments have been performed to confirm this conjecture.

The densities from Tables 3 and 4 are shown relative to smoothing eqs 7 and 8 in Figures 6 and 7 for certified reference materials N10 and S20, respectively. The scale of the ordinate axis of Figures 6 and 7 is equal the expanded uncertainty given in Table 4. At pressures greater than 0.1 MPa, the densities obtained for N10 and S20 deviate from eqs 7 and 8 by less than ±0.2 % and are within the expanded uncertainty of our measurements (about 0.2 %).

There are numerous models, some with a theoretical basis, that have been used to represent the viscosity of liquids and, excluding that reported by Allal et al.,[60,61] have been reviewed in ref 62. One method in ref 62 uses a semiempirical equation based on the hard-sphere theory of transport properties in dense fluids. This scheme was developed and applied successfully by Assael et al.[13] to n-alkanes and their mixtures[63] and aromatic hydrocarbons[14,64] and by others to refrigerants.[65,66] Unfortunately, in the absence of the chemical composition for each certified reference material and therefore knowledge of both the molar mass and the characteristic molar volume we were unable to utilize this method or that reported in refs 60 and 61; other methods that are similarly constrained, and excluded, have been reported by Huber et al.[67] Thus, to correlate the viscosities for each certified reference material, we used an empirical method and represented the average viscosities of Table 4 combined with the values of Table 3 by

$$\ln\left[\frac{\eta(T,p)}{\eta_r(T,p_r)}\right] = \exp\left(k + \frac{l}{m+T}\right)\frac{(p-p_r)}{p^\circ} + (n+qT)(p-p_r)^2 \quad (9)$$

where $p_r = 0.1$ MPa, the pressure of the certified reference value given by $\eta_r(T, p_r)$, and $p^\circ = 1$ MPa; this regression was constrained, as it was for eqs 7 and 8, to reproduce the values of viscosity listed in Table 3 exactly. The coefficients of eq 9 are listed in Table 6 for N10 and S20 together with the average percentage deviation, which never exceeds 0.6 %, and the maximum deviation from the experimental viscosities. In view of the reported international consistency of these fluids,[21] adopting this formalism might allow small differences between values of $\eta_r(p_r)$ to be accommodated by solely substituting values of $\eta_r(p_r)$ obtained from either other lots of the same supplier or an alternative supplier of certified reference materials N10 and S20. Again, no experiments have been performed to confirm this conjecture.

The viscosities from Tables 3 and 4 are shown relative to eq 9 in Figures 8 and 9 for certified reference materials N10 and S20, respectively, where the dashed lines represent the expanded uncertainty of the measurements. At p = 0.1 MPa, the viscosities of Table 3 for both N10 and S20 are, as shown in Figures 8 and 9, in excellent agreement, deviating from the smoothing equation (eq 9) by less than 0.09 %, which is within the uncertainty cited by the supplier of the reference fluids (±0.25 %) and also within the expanded uncertainty (about 1.8 %). At pressures greater than 0.1 MPa, the results for N10 agree with eq 9 within ±1 %, about a factor of 2 lower than the expanded uncertainty of the measurements, whereas for S20 our average viscosities are consistent with eq 9 within the expanded uncertainty of the measurements except for η(298.15 K, 13.92 MPa) = 41.2 mPa·s, which lies 2.3 %

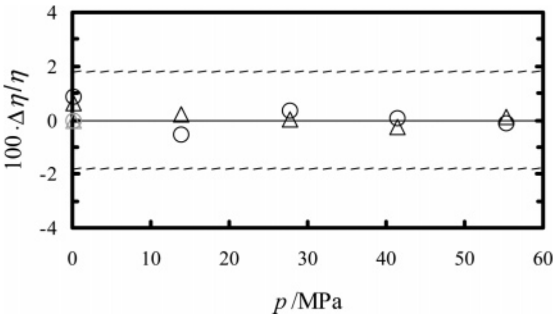

Figure 8. Fractional deviation $\Delta\eta/\eta = \{\eta(\text{exptl}) - \eta(\text{calcd})\}/\eta(\text{calcd})$ of the viscosity in either Table 3 or Table 4 η(exptl) from the value η(calcd) obtained from a combination of eq 9 with coefficients listed in Table 6 for certified reference material N10. The dashed lines are the expanded uncertainty of Table 4. ○, T = 298 K from Table 4; gray ○, value cited by the supplier at T = 298 K from Table 3; △, T = 333 K from Table 4; and gray △, eq 5 with coefficients of Table 1 at T = 333 K from Table 3.

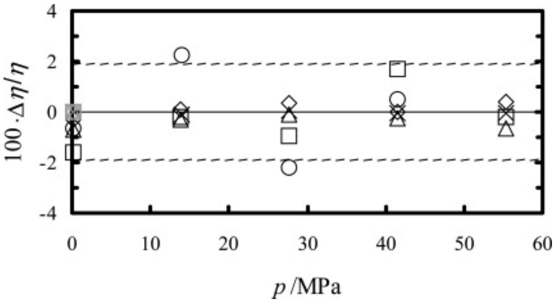

Figure 9. Fractional deviation $\Delta\eta/\eta = \{\eta(\text{exptl}) - \eta(\text{calcd})\}/\eta(\text{calcd})$ of the viscosity in either Table 3 or Table 4 ρ(exptl) from the value η(calcd) obtained from a combination of eq 9 with coefficients listed in Table 6 for certified reference material S20. The dashed lines are the expanded uncertainty of Table 4. ○, T = 298 K from Table 4; gray ○, value cited by the supplier at T = 298 K from Table 3; □, T = 313 K from Table 4; gray □, value cited by the supplier at T = 313 K from Table 3; △, T = 333 K from Table 4; gray △, eq 5 with coefficients of Table 1 at T = 333 K from Table 3; ◇, T = 353 K from Table 4; gray ◇, eq 5 with coefficients of Table 1 at T = 353 K from Table 3; ×, T = 393 K from Table 4; and gray ×, eq 5 with coefficients of Table 1 at T = 393 K from Table 3.

above eq 9, and η(298.15 K, 27.7 MPa) = 54.1 mPa·s, which deviates from eq 9 by −2.2 %.

To our knowledge, there are no values of either the density or viscosity of certified reference materials N10 and S20 at pressures greater than 0.1 MPa reported in the archival literature with which to compare our results.

Literature Cited

(1) International Union of Pure and Applied Chemistry. Commission on Physico-Chemical Symbols and Terminology. *Manual of Symbols and Terminology for Physicochemical Quantities and Units*Pergamon Press: Oxford, U.K., 1979; Appendix II, Part I.13. See also *Pure Appl. Chem.* **1979**, *51*, 1213.

(2) Swindells, J. F.; Coe, J. R.; Godfrey, T. B. Absolute Viscosity of Water at 20 °C. *J. Res. Natl. Bur. Stand. (U.S.)* **1952**, *48*, 1−31.

(3) ISO/TR 3666. *Viscosity of Water*; 1998.

(4) Künzel, W.; van Wijk, H. F.; Marsh, K. N. *Viscosity* in *Recommended Reference Materials for the Realization of Physicochemical Properties*; Marsh K. N., Ed.; for International Union of Pure and Applied Chemistry, Blackwell Scientific: Oxford, U.K., 1987; pp 45−72.

(5) Wakeham, W. A.; Nagashima, A.; Sengers, J. V. *Reference Data* in *Experimental Thermodynamics* Wakeham, W. A., Nagashima, A., Sengers, J. V., Eds.; for International Union of Pure and Applied Chemistry, Blackwell Scientific: Oxford, U.K., 1991; Vol. III, Chapter 13, pp 442−443.

(6) Nagashima, A. Viscosity of water substance - new international formulation and its background. *J. Phys. Chem. Ref. Data* **1977**, *6*, 1133−1166.

(7) Kestin, J.; Sololov, M. Wakeham, W. A. Viscosity of liquid water in the range −8 °C to 150 °C. *J. Phys. Chem. Ref. Data* **1978**, *7*, 941−948.

(8) James, C. J.; Mulcahy, D. E.; Steel, B. J. Viscometer Calibration Standards: Viscosities of Water between 0 and 60 °C and of Selected Aqueous Sucrose Solutions at 25 °C from Measurements with a Flared Capillary Viscometer. *J. Phys. D: Appl. Phys.* **1984**, *17*, 225−230.

(9) Collings A. F.; Bajenov, N. A High Precision Capillary Viscometer and Further Relative Results for the Viscosity of Water. *Metrologia* **1983**, *19*, 61−66.

(10) *Revised Release on the IAPS Formulation 1985 for the Viscosity of Ordinary Water Substance*; International Association of the Properties of Water and Steam, August 2003, available from http://www.iapws.org/.

(11) Sengers J. V.; Kamgar-Parsi, B. Representative equations for the viscosity of water substance. *J. Phys. Chem. Ref. Data* **1984**, *13*, 185−205.

(12) Bauer, H.; Meerlender, G. Precise viscosity measurements of Newtonian liquids with ν >1 mm^2/s for the selection of suitable standards. *Rheol. Acta* **1984**, *23*, 514.

(13) Assael, M. J.; Avelino, H. M. T.; Dalaouti, N. K.; Fareleira J. M. N. A.; Harris, K. R. Reference Correlation for the Viscosity of Liquid Toluene from 213 to 373 K at Pressures to 250 MPa. *Int. J. Thermophys.* **2001**, *22*, 789−799.

(14) Assael, M. J.; Dymond, J. H.; Papadaki, M.; Patterson, P. M. Correlation and Prediction of Dense Fluid Transport Coefficients. I. *n*-Alkanes. *Int. J. Thermophys.* **1992**, *13*, 269−281.

(15) Assael, M. J.; Oliveira, C. P.; Papdaki, M.; Wakeham, W. A. Vibrating-Wire Viscometers for Liquids at High Pressures. *Int. J. Thermophys.* **1992**, *13*, 593−615.

(16) Cibulka, I.; Hnedkovský, L. Liquid Densities at Elevated Pressures of *n*-Alkanes from C_5 to C_{16}: A Critical Evaluation of Experimental Data. *J. Chem. Eng. Data* **1996**, *41*, 657−668.

(17) Cibulka, I. Saturated liquid densities of 1-alkanols from C_1 to C_{10}, and *n*-alkanes from C_5 to C_{16}: a critical evaluation of experimental data. *Fluid Phase. Equilib.* **1993**, *89*, 1−18.

(18) Caetano, F. J. P.; Fareleira, J. M. N. A.; Oliveira C. M. B. P.; Wakeham, W. A. The Viscosity of Diisodecylphthalate a Potential Standard of Moderate Viscosity. *Int. J. Thermophys.* **2004**, *25*, 1311−1322.

(19) ISO, International Standard 3105, 1976.

(20) Daborn, J. E. The Viscosity Scale of the NPL. *Metrologia* **1975**, *11*, 79−84.

(21) Daborn J. E.; Kuhlborsch, G. *Report on the Second BCR Viscosity Audit*; Commission of The European Communities, BCR Information Report EUR 8359 EN, 1983.

(22) Johnson, J. F.; Martin, J. R.; Porter, R. S. *Physical Methods of Chemistry*; Weissberger, A. L., Rossiter, B. W., Eds.; Interscience: New York; 1977; Pt. VI, p 63.

(23) Nieuwoudt, J. C.; Shankland, I. R. Oscillating-Body Viscometers. In *Experimental Thermodynamics*; Wakeham, W. A., Nagashima, A., Sengers J. V., Eds.; for International Union of Pure and Applied Chemistry, Blackwell Scientific: Oxford, U.K., 1991; Vol. III, Chapter 2, pp 9−48.

(24) Kawata, M.; Kurase, K.; Nagashima, A.; Yoshida, K. Capillary Viscometers. In *Experimental Thermodynamics*; Wakeham, W. A., Nagashima, A., Sengers J. V., Eds.; for International Union of Pure and Applied Chemists, Blackwell Scientific: Oxford, U.K., 1991; Vol. III, Chapter 3, pp 51−75.

(25) Kawata, M.; Kurase, K.; Nagashima, A.; Yoshida, K.; Isdale, J. D. Falling-Body Viscometers. In *Experimental Thermodynamics*; Wakeham, W. A., Nagashima, A., Sengers J. V., Eds.; for International Union of Pure and Applied Chemists, Blackwell Scientific: Oxford, U.K., 1991; Vol. III, Chapter 5, pp 97−110.

(26) Diller D. E.; van der Gulik, P. S. Vibrating Viscometers. In *Experimental Thermodynamics*; Wakeham, W. A., Nagashima, A., Sengers J. V., Eds.; for International Union of Pure and Applied Chemists, Blackwell Scientific: Oxford, U.K., 1991; Vol. III, Chapter 4, pp 79−94.

(27) Kandil, M.; Marsh, K. N.; Goodwin, A. R. H. A Vibrating Wire Viscometer with Wire Diameters of (0.05 and 0.15) mm: Results for Methylbenzene and two Fluids with Nominal Viscosities at T = 298 K and p = 0.01 MPa of (14 and 240) mPa·s at Temperatures between (298 and 373) K and Pressures below 40 MPa. *J. Chem. Eng. Data* **2005**, *50*, 647−655..

(28) Charles, E.; Molenat, J.; Abachi, H.; Michel, J.; Malbrunot, P. The Use of a Vibrating Wire Viscometer in Liquids. *J. Phys. E: Sci. Instrum.* **1980**, *12*, 829−835.

(29) Gourgouillon, D.; Avelino, H. M. N. T.; Fareleira, J. M. N. A.; Nunes da Ponte, M. Simultaneous Viscosity and Density Measurement of Supercritical CO_2-saturated PEG-400 *J. Supercrit. Fluids* **1998**, *13*, 177−185.

(30) Caudwell, D. Viscosity of Dense Fluid Mixtures. Ph.D. Thesis, Imperial College London, 2004.

(31) Caetano, F. J. P.; Fareleira, J. M. N. A.; Oliveira, C. M. B. P.; Wakeham, W. A. Validation of a Vibrating Wire Viscometer: Measurements in the Range 0.5 to 135 mPa·s. *J. Chem. Eng. Data* **2005**, *50*, 201−205.

(32) Wagner, W.; Kleinrahm, R.; Lösch, H. W. Watson, J. T. R.; Majer, V.; Pádua, A. A. H.; Woolf, L. A.; Hoslte, J. C.; de Figueiredo Palavara, A. M.; Fujii K.; Stansfeld, J. W. Density. In *Experimental Thermodynamics*; Goodwin, A. R. H., Marsh, K. N., Wakeham W. A., Eds.; for International Union of Pure and Applied Chemistry, Elsevier: Amsterdam, 2003; Vol. VI, Chapter 5, pp 127−235.

(33) Tough, J. T.; McCormick, W. D.; Dash, J. D. Vibrating Wire Viscometer. *Rev. Sci. Instrum.* **1964**, *35*, 1345−1348.

(34) Goodwin, J. M. A Vibrating Wire Viscometer for Measurements at Elevated Pressure. *J. Phys. E: Sci. Instrum.* **1973**, *6*, 452−456.

(35) Bruschi, L.; Santini, M. Vibrating Wire Viscometer. *Rev. Sci. Instrum.* **1975**, *46*, 1560−1568.

(36) Retsina, T.; Richardson, S. M.; Wakeham, W. A. The Theory of a Vibrating-Rod Viscometer. *Appl. Sci. Res.* **1986**, *43*, 127−158.

(37) Retsina, T.; Richardson, S. M.; Wakeham, W. A. The Theory of a Vibrating-Rod Viscometer. *Appl. Sci. Res.* **1987**, *43*, 325−346.

(38) Mostert, R.; van Der Gulik, P. S.; van den Berg, H. R. The Working Equations of a Vibrating Wire Viscometer. *Physica A* **1989**, *156*, 909−920.

(39) Pádua, A. A. H.; Fareleira, J. M. N. A.; Calado, J. C. G.; Wakeham, W. A. Electromechanical Model for Vibrating-Wire Instruments. *Rev. Sci. Instrum.* **1998**, *69*, 2392−2399.

(40) Caudwell, D.; Goodwin, A. R. H.; Trusler, J. P. M. A robust vibrating wire viscometer for reservoir fluids: results for toluene and n-decane *J. Pet. Sci. Eng.* **2004**, *44*, 333−340.

(41) Wilhelm, J.; Vogel, E.; Lehmann, J. K.; Wakeham, W. A. A Vibrating-Wire Viscometer for Dilute and Dense Gases. *Int. J. Thermophys.* **1998**, *19*, 391−401.

(42) Oliveira, C. M. B. P. Viscosity of Liquid Hydrocarbons at High Pressure. Ph.D. Thesis, Imperial College of Science, Technology and Medicine, London, 1991.

(43) Kratky, O.; Leopold, H.; Stabinger, H. Dichtemessungen an Flüssigkeiten und Gasen auf 10^{-6} g/cm^3 bei 0,6 Präparatvolumen. *Z. Angew. Phys.* **1969**, *27*, 273−277.

(44) Laznickova, R.; Huemer, H. Investigations on the Limits of Uncertainty of Gas Density Measurements with Vibrating Tube Densimeters. *Meas. Sci. Technol.* **1998**, *9*, 719−733.

(45) Chang, R. F.; Moldover, M. R. High-temperature high-pressure oscillating tube densimeter. *Rev. Sci. Instrum.* **1996**, *67*, 251−256.

(46) Majer, V.; Pádua, A. A. H. Measurement of Density with Vibrating Bodies. In *Experimental Thermodynamics*; Goodwin, A. R. H., Marsh, K. N., Wakeham W. A., Eds.; for International Union of Pure and Applied Chemistry, Elsevier: Amsterdam, 2003; Vol. VI, Chapter 5, pp 158−168.

(47) Bernhardt, J.; Pauly, H. Pycnometric vs. Densimetric Measurements of Highly Viscous Protein Solutions. *J. Phys. Chem.* **1980**, *84*, 158−162.

(48) Ashcroft, S. J.; Booker, D. R.; Turner, J. C. R. Density Measurements by Oscillating Tube Effects of Viscosity, Temperature, Calibration and Signal Processing. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 145−149.

(49) Private communication. Anton Paar, Gmbh, Austria, 2005.

(50) Chen, S. S.; Wambsganss, M. W.; Jendrzejczyk, J. A. *Trans. ASME: J. Appl. Mech.* **1976**, *43*, 325−329.

(51) Jakeways, C. V.; Goodwin, A. R. H. The Viscosity and Density of 1-Propene,1,1,2,3,3,3-hexafluoro-oxidized-polymd and Polydimethylsiloxane at Temperatures from 313 K to 373 K and a Pressure of 0.1 MPa. *J. Chem. Thermodyn*. Article in press doi: 10.1016/j.jct.2005.01.012.

(52) Span, R.; Wagner, W. Equations of State for Technical Applications. II. Results for Nonpolar Fluids. *Int. J. Thermophys.* **2003**, *24*, 41−109.

(53) Wagner W.; Pruss, A. The IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use. *J. Phys. Chem. Ref. Data* **2002**, *31*, 387−535.

(54) Vogel, H. The law of the relation between the viscosity of liquids and the temperature *Phys. Z.* **1921**, *22*, 645−646.

(55) Bevington, P. R.; Robinson, D. K. *Data Reduction and Error Analysis for the Physical Sciences*; McGraw-Hill: Boston, 1992; pp 59−61.

(56) Hayward, A. T. J. Compressibility equations for liquids: a comparative study. *Br. J. Appl. Phys.* **1967**, *18*, 965−977.

(57) Dymond, J. H.; Malhotra, R. Densities of *n*-Alkanes and Their Mixtures at Elevated Pressures. *Int. J. Thermophys.* **1987**, *8*, 541−555.

(58) Dymond, J. H.; Malhotra, R. The Tait Equation: 100 Years On. *Int. J. Thermophys.* **1988**, *9*, 941−951.

(59) Assael, M. J.; Dymond, J. H.; Exadaktilan, D. An Improved Representation for *n*-Alkane Liquid Densities. *Int. J. Thermophys.* **1994**, *15*, 155−164.

(60) Allal, A.; Boned, C.; Baylaucq, A. Free-volume viscosity model for fluids in the dense and gaseous states. *Phys. Rev. E* **2001**, *64*, 011203.

(61) Allal, A.; Moha-Ouchane, M.; Boned, C. A new free volume model for dynamic viscosity and density of dense fluids versus pressure and temperature. *Phys. Chem. Liq.* **2001**, *39*, 1−30.

(62) *Transport Properties of Fluids: Their Correlation, Estimation and Prediction*; Millat, J., Dymond, J. H., Nieto de Castro, C. A., Eds.; Cambridge University Press: Cambridge, U.K., 1996; p 483.

(63) Assael, M. J.; Dymond, J. H.; Papadaki, M.; Patterson, P. M. Correlation and Prediction of Dense Fluid Transport Coefficients. III. *n*-Alkane Mixtures. *Int. J. Thermophys*. **1992**, *13*, 659−669.

(64) Assael, M. J.; Dymond, J. H.; Patterson, P. M. Correlation and Prediction of Dense Fluid Transport Coefficients. V. Aromatic Hydrocarbons. *Int. J. Thermophys*. **1992**, *13*, 895−905.

(65) Oliveira, C. M. B. P.; Wakeham, W. A. The viscosity of liquid R134a. *Int. J. Thermophys*. **1993**, *14*, 33−44.

(66) Pádua, A. A. H.; Fareleira, J. M. N. A.; Calado, J. C. G.; Wakeham, W. A. Density and Viscosity Measurements of 1,1,1,2-Tetrafluoroethane (HFC-134a) from 199 K to 298 K and up to 100 MPa. *J. Chem. Eng. Data* **1996**, *41*, 731−735.

(67) Huber, M. L.; Laesecke, A.; Xiang, H. W. Viscosity correlations for minor constituent fluids in natural gas: n-octane, n-nonane and n-decane. *Fluid Phase Equilib.* **2004**, *224*, 263−270.

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