A Comparison of Both Steady State Resonance and Transient Decay Methods of Determining Viscosity with a Vibrating Wire Viscometer: Results for Certified Reference Fluids for Viscosity that are Stagnant with Viscosity between (2.5 and 66) mPa·s and Flowing at Volumetric Flow Rates Below 50 $cm^3 \cdot s^{-1}$ and Viscosities Less than 34 mPa·s

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Flowing fluid may have a chemical composition that changes as a function of time, and this is referred to as slug-flow. To measure the viscosity of the fluid in this scenario requires an instrument with a measurement time less than the time required for one slug to pass through the viscometer. One viscometer that could be used for this purpose is based on determining the damping of the resonance frequency of a vibrating wire. The viscosity can be obtained from measurements of either steady state resonance or amplitude decay. In this article, we report both resonance (that required a data acquisition time of about 40 s) and transient (that required a data acquisition time of about 1 s) measurements obtained with a wire of radius about 0.075 mm immersed in both a stagnant fluid and also when subjected to volumetric flow rates up to 50 $cm^3 \cdot s^{-1}$. Certified reference materials N35 and S20 were used for these measurements. For both resonance and transient measurements, stagnant N35 was used at a pressure of 0.1 MPa and temperatures between (299.9 and 362.2) K over which the viscosity varied from (2.5 to 66) mPa·s. For flowing fluid, S20 was used at viscosities less than 35 mPa·s. The average absolute difference between the measured and cited values for all measurements was 3.2 %.

Introduction

Recently, Harrison et al.[1] described a vibrating wire operated in resonance mode to measure the viscosity of certified reference material S20 flowing at rates of (22, 44, and 66) $cm^3 \cdot s^{-1}$, which corresponds to a velocity less than 0.28 $m \cdot s^{-1}$, where the fluid viscosity was about 40 mPa·s. In these measurements with flowing fluid, neither additional noise nor systematic error in the viscosity was observed.[1] To obtain the viscosity from measurement of the resonance frequency required the acquisition of the complex voltage at discrete frequencies over the resonance with a lock-in amplifier. This process required a time that was determined by a combination of the post detection lock-in time constant and stabilization of the frequency after a frequency change (ring-down) that we found was in total no less than 40 s.[2] To perform the viscosity measurement required a homogeneous fluid of constant chemical composition for the time required of data acquisition. If the fluid is composed of slugs, each homogeneous but of different fluid phase or chemical composition, then these slugs must be longer than the wire and, when flowing, the product of the velocity and acquisition time. Thus, the data acquisition time of the resonance mode of the vibrating wire viscometer could place a severe constraint on the applications of the measurement technique as an in situ process monitor. However, the transient decay measurement requires a data acquisition time of about 0.1 s, and it will be no surprise, especially to those whom routinely used it for rapid measurement of viscosity of stagnant fluid,[3] that adopting this approach may improve the viability of an in situ viscosity measurement. Indeed, Caetano et al.[4] have operated a vibrating wire viscometer in both resonant and transient modes with fluids of viscosity < 3.3 mPa·s; however, to our knowledge, there is no reference of doing so while the fluid flows in the archival literature.

In this article, we report both steady state and transient decay measurements of viscosity with a wire of radius about 0.075 mm immersed in both a stagnant certified reference fluid for viscosity (CRMV) N25 and also when CRMV S20 was subjected to volumetric flow rates up to 50 $cm^3 \cdot s^{-1}$. The measurements were conducted at temperatures between (299.9 and 362.2) K and a pressure of 0.1 MPa over which the viscosity varied from (2.5 to 66) mPa·s.

Theory

The working equations used to determine the viscosity from measurements of the resonance bandwidth have been discussed in detail elsewhere[5–10] and were used without modification. For the transient method, the theoretical background is identical to that of the steady state for an exponentially damped sinusoid of simple damped harmonic motion that conforms to an induced voltage $V(t)$ given by[5,6]

$$V(t) = V_0 e^{-\Delta \omega t} \sin(\omega t + \phi) \quad (1)$$

where V_0 is the initial amplitude of the transient; Δ is the decrement linked to the damping experienced by the wire; ω is

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the angular resonance frequency; and ϕ is an unknown phase angle. In eq 1, the decrement Δ is related to the properties of both the wire and fluid that surrounds it by[5,6]

$$\Delta = \frac{(\rho/\rho_s)k' + 2\Delta_0}{2[1 + (\rho/\rho_s)k]} \tag{2}$$

where ρ and ρ_s are the density of fluid and wire, respectively; Δ_0 is the internal damping in a vacuum; and the quantities k and k' are defined by

$$k = -1 + 2\boldsymbol{T}(A) \tag{3}$$

and

$$k' = 2\boldsymbol{R}(A) + 2\Delta\boldsymbol{T}(A) \tag{4}$$

where $\boldsymbol{R}(A)$and $\boldsymbol{T}(A)$ are, respectively, the real and imaginary parts of the complex quantity A expressed by[5,6]

$$A = (\mathrm{i} - \Delta)\left[1 + \frac{2K_1[\{(\mathrm{i} - \Delta)\Omega\}^{\frac{1}{2}}]}{[(\mathrm{i} - \Delta)\Omega]^{\frac{1}{2}}K_0[\{(\mathrm{i} - \Delta)\Omega\}^{\frac{1}{2}}]}\right] \tag{5}$$

In eq 5, K_0 and K_1 are modified Bessel functions of the second order, and Ω is a modified Reynolds number (related to a Strouhal number) given by

$$\Omega = \frac{\omega\rho R^2}{\eta} \tag{6}$$

that characterizes the flow around the cylindrical wire of radius R at the resonance frequency ω immersed in fluid of viscosity η and density ρ.

In practice eq 1 must be modified to accommodate the finite impedance of the wire and connections to it with

$$V(t) = V_0 \mathrm{e}^{-\Delta\omega t}\sin(\omega t + \phi) + a + bt \tag{7}$$

where a and b are constants determined in the analysis.

The internal damping can also be determined from transient measurements in a vacuum and the radius from measurements in a calibration fluid for which the viscosity and density are known with sufficient accuracy. The decrement Δ which is the root of the nonlinear equation

$$\frac{(\rho/\rho_s)k' + 2\Delta_0}{2[1 + (\rho/\rho_s)k]} - \Delta = 0 \tag{8}$$

is determined by regression.[6]

A vibrating wire of known radius operated in transient mode and immersed in a fluid of known density is described by eqs 1 to 7, and the adjustable parameters are a, b, ϕ, and η that are adjusted to minimize the difference between the calculated and measured amplitude as a function of time.

Quality Factor and Resonant Frequency. For the steady state mode, the complex quantity $(f + \mathrm{i}g)$ where f is the frequency g, half the resonance line-width can be obtained directly from the measurements with the function reported by Mehl.[11] The quality factor is obtained from the definition

$$Q = f/(2g) \tag{9}$$

For the transient mode, the quality factor can also be calculated from the decrement Δ using

$$Q = (2\Delta)^{-1} \tag{10}$$

Alternatively, Q can be defined by

$$Q = \frac{k}{\boldsymbol{R}(D)f} \tag{11}$$

where k is the spring constant and $\boldsymbol{R}(D)$ is the real part of the drag per unit length D for a cylinder moving transverse to its axis as given by Stokes[12] of

$$D = \mathrm{i}\eta v\pi\gamma^2\left(1 + \frac{4K_1(\sqrt{\mathrm{i}}\gamma)}{\sqrt{\mathrm{i}}\gamma K_0(\sqrt{\mathrm{i}}\gamma)}\right) \tag{12}$$

In eq, 12 v is the velocity of the wire and $\gamma = \sqrt{\Omega}$ where Ω is defined by eq 6. Assuming the vibration wire acts like a damped harmonic oscillator, the k of eq 11 can be determined from the resonant frequency f_0 obtained in air and the mass m of the wire through $k = f_0{}^2m$.

The resonant frequency of the damped harmonic oscillator f can be obtained by determining the excitation frequency f_e that produces maximum amplitude $A(f_e)$ defined by

$$A(f_e) = \frac{F}{\{k - f_e{}^2\sigma - f\,\mathrm{Im}(D)\} + \mathrm{i}f_e\mathrm{Re}(D)} \tag{13}$$

where σ is the mass per unit length of the wire and F the driving force.[6,10] The resonance quality factor obtained from eqs 9 and 13 can be compared.

Apparatus and Experimental Procedures

Lundstrom et al.[13] described the vibrating wire viscometer formed from tungsten held taut along the cylindrical axis of an electrically isolating aluminum nitride cylinder. Ref 13 also describes the pressure vessel that held the vibrating wire viscometer and permitted fluid to flow through it and also separated the wire from the magnetic flux of about 0.4 T by a distance of about 2 cm. Rare earth permanent magnets were used as described in ref 13. The axis of the wire was essentially concentric with the tube through which fluid flowed at rates between (4 and 50) $\mathrm{cm}^3\cdot\mathrm{s}^{-1}$ within the apparatus reported by Harrison et al.[1] For steady state measurements, a lock-in amplifier (Stanford Research Systems model SRS-850) was used as described previously.[13–15] For the transient measurements, the wire was excited at a frequency close to resonance with a sine wave consisting of N ($>Q$) oscillations obtained from a function generator (Agilent model 33220A); $N > Q$ to attain about 96 % of the maximum amplitude while minimizing the temperature increment arising from resistive heating, and in these experiments, the viscosity varied from (2.5 to 66.5) mPa·s and Q varied from 4.0 to 26.9. The duration of this burst was approximately 50 ms, and the exact length of the burst depended upon the excitation frequency. The output of the function generator was amplified (with a Krohn Hite model number 7500) and passed through a 100 Ω resistor in series with the wire, resulting in a current of ≈1 A r.m.s. The measurements can be achieved with substantially reduced electrical current but were not in this work owing to the relatively low signal-to-noise ratio that we will discuss below. Data acquisition was triggered by a synchronization output of the function generator. A digital oscilloscope (Tektronix model TDS 3034B) acquired the motional emf for a time of about 0.1 s after amplification (Princeton Applied Research, preamplifier model 185) by a factor of about 500.

The measured and calculated amplitude decay determined as a function of time from preliminary experiments are shown in Figures 1 and 2 for the wire immersed in N35 at η(362 K) = 5.63 mPa·s and η(300 K) = 50.95 mPa·s, respectively. In both Figures 1 and 2, the top part of the figure shows the measured

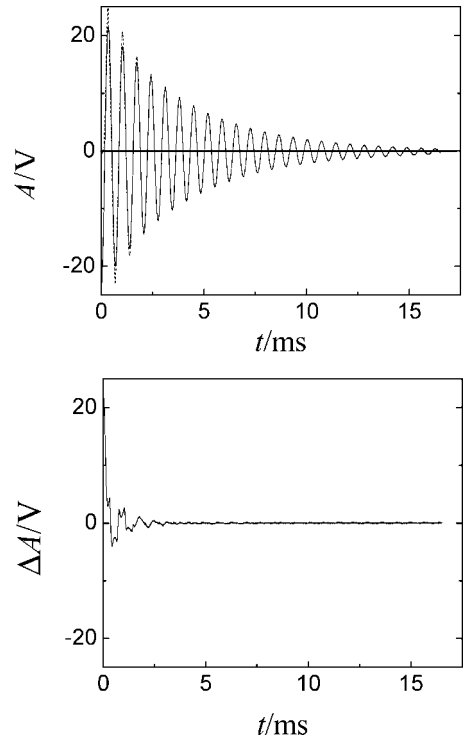

Figure 1. TOP: Amplitude A as a function of time t after extinction of the excitation for a vibrating wire immersed in certified reference material N35. BOTTOM: Difference $\Delta A = A(\text{exptl}) - A(\text{calcd})$ of the measured $A(\text{exptl})$ from the value obtained with eqs 1 to 7 and η(N35, 362 K) = 5.63 mPa·s, illustrating the distorted signal at $t < 1.7$ ms. —, measurements; - - - - -, eqs 1 to 7 with η(N35, 362 K) = 5.63 mPa·s.

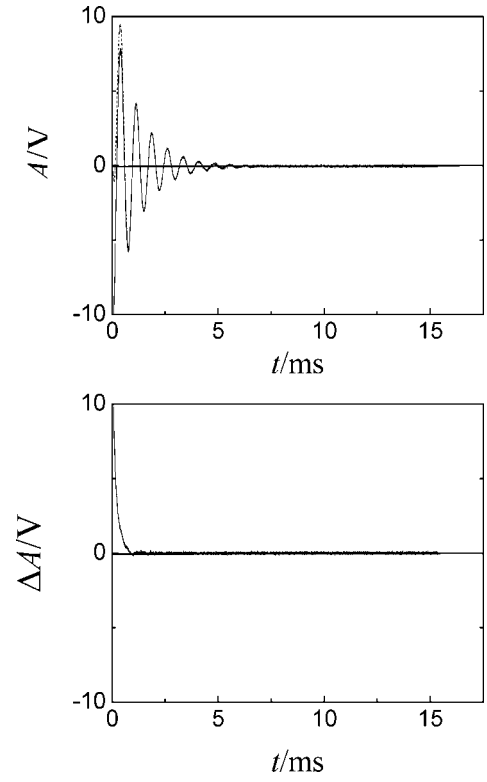

Figure 2. TOP: Amplitude A as a function of time t after extinction of the excitation for a vibrating wire immersed in certified reference material N35. BOTTOM: Difference $\Delta A = A(\text{exptl}) - A(\text{calcd})$ of the measured $A(\text{exptl})$ from the value obtained with eqs 1 to 7 and η(N35, 300 K) = 50.95 mPa·s, illustrating the distorted signal at $t < 1.7$ ms. —, measurements; - - - - -, eqs 1 to 7 with η(N35, 300 K) = 50.95 mPa·s.

and calculated decay as a function of time, and they appear essentially indistinguishable. The bottom panel of Figures 1 and 2 shows the difference between the measured and calculated decay and illustrates a distorted signal at $t < 1.7$ ms. The amplitude distortion shown in Figure 2 was the worst case, and the preponderance of the transient signals observed possessed only minor distortion at $t < 1.7$ ms. The origin of the signal distortion was not determined, but a plausible source is overloading of the preamplifier.

The amplitude determined as a function of time after excitation was removed is shown in Figure 3 for the wire immersed in S20, of viscosity 22 mPa·s, at a pressure of 0.1 MPa, and exposed to a flow rate of 45 $cm^3 \cdot s^{-1}$ where the resonance frequency was 1425 Hz. Four amplitude decay curves are shown in Figure 3, each obtained from the average of n measurements. For the sake of clarity, the decay curves shown in Figure 3 have been displaced on the ordinate by addition of a constant. The lowest curve (average voltage $<A>$ about 0) shows results obtained from one excitation that, after about 7 oscillations (corresponding $t \approx 6.5$ ms), had decayed to be equivalent to the amplitude of the noise. The decay curve displaced so that $<A> \approx 10$ V was obtained from the average of 2 measurements. That at $<A> \approx 20$ V was obtained from the average of 5 measurements, while that at $<A> \approx 30$ V from 10 measurements, which permitted identification of the oscillations to $t = 11.5$ ms. A plausible source for the reduced signal-to-noise ratio arises from the alignment of the wire with the axis of the tube that in the presence of flow that is turbulent imparts random forces to the wire resulting in perturbations to the wire's motion and ultimately additional electrical noise reducing the precision of the measured viscosity.[1] Signal averaging was important for the measurements, and the procedure necessarily increased the measurement time. Improvements in the electronics used would substantial increase the signal-to-noise ratio and decrease the reliance on averaging and the time required to acquire the viscosity.

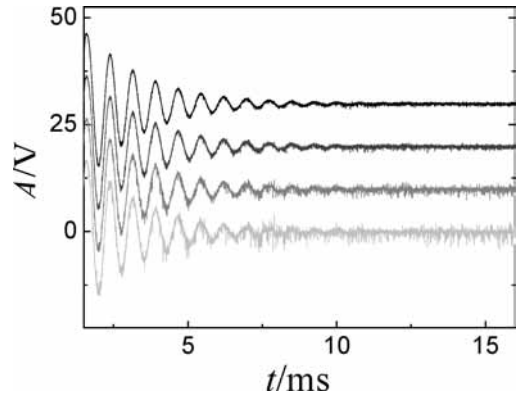

Figure 3. Amplitude A as a function of time t after extinction of the excitation and the number n of measurements averaged to obtain the decay curve for a vibrating wire immersed in certified reference material S20 flowing at a volumetric rate of 45 $cm^3 \cdot s^{-1}$ for which $\eta = 22$ mPa·s and $p = 0.1$ MPa and the resonance frequency is 1425 Hz. $<V> \approx 0$ and $n = 1$; $<V> \approx 10$ V and $n = 2$; $<V> \approx 20$ V and $n = 5$; and $<V> \approx 30$ V and $n = 10$. For the sake of clarity, the signals were displaced to these voltages by arbitrarily adding (10, 20, and 30) V, respectively, to the measured values.

Measurements were performed to determine the effect of parasitic signals on the transient method that might, for example, render it impossible to determine Δ and hence the viscosity η. Figure 4 shows the amplitude as a function of time when the wire was immersed in N35 with η(333 K) = 12.8 mPa·s after removal of the excitation signal. The data acquisition ceased after $t \approx 9$ ms. The decay curve shown in black at $A(t = 0) =$

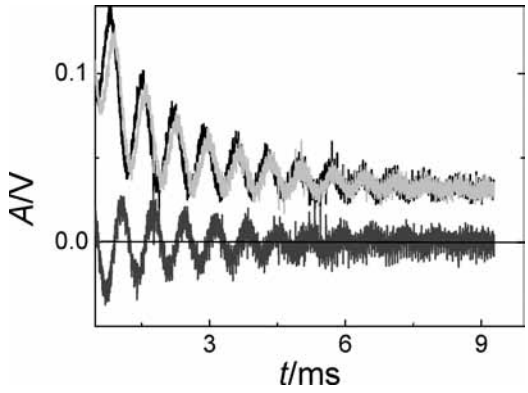

Figure 4. Amplitude A as a function of time t after extinction of excitation when the wire was immersed in certified reference material for viscosity N35 with cited η(333 K) = 12.8 mPa·s The data acquisition ceased at $t \approx$ 9 ms. The black decay curve is obtained from an excitation frequency of 1451 Hz superimposed upon a much lower-frequency exponential decay arising from saturation of a nonideal amplifier. The light gray signal with an excitation frequency of 1550 Hz is superimposed upon a much lower-frequency exponential decay arising from saturation of a nonideal amplifier that is at a frequency of 99 Hz, equal the bandwidth, above the black curve, and arbitrarily shifted to the right for the sake of clarity. The dark gray decay curve at $<A> \approx 0$ is the difference of these two signals whereby the parasitic exponential decay is removed and the data. The results can then be fit with eqs 1 to 7 and yield η(333 K) = 12.82 mPa·s which is within 0.16 % of the cited value and illustrates the success of our background subtraction strategy.

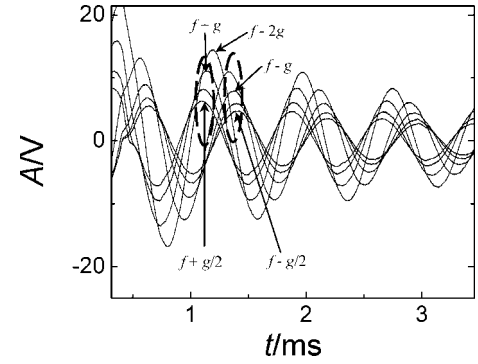

Figure 5. Amplitude A as a function of time t after extinction of excitation for the wire immersed in N35 where the cited η(334 K) = 12.2 mPa·s. The A of each of the eight transient decay curves was the difference of two data sets. The first consisted of a transient signal measured after excitation at the resonance frequency f, while the second was measured after excitation at a frequency slightly greater to or lower than the resonance frequency (referred to as background). For each, the average of 32 decay curves is shown. For the curve of largest amplitude, the excitation frequency is at $f - 2g$ and produces the largest signal. In the left ellipse, the three curves consist of excitation frequencies for the background from lowest to highest A of $f + g/2$, $f + 2g/3$, and $f + g$. In the right ellipse, the four curves consist of excitation frequencies for the background from lowest to highest A of $f - g/2$, $f - 2g/3$, $f - g$, and $f - 2g$ that produced a lower signal A and were deemed nonoptimal.

0.1 V was obtained at an excitation frequency equal to the resonance frequency $f = 1450$ Hz by superposition of a signal with an exponential decay time constant much greater than that of the period representing the damping of the wire oscillation. This scenario might result from saturation of nonideal amplification. The decay signal shown in Figure 4 in light gray also at $A(t = 0) = 0.1$ V is obtained with an excitation frequency of 1549 Hz obtained from $f + 2g$ where $2g = 99$ Hz is the resonance bandwidth. The second transient decay curve has the same frequency as the first but is phase shifted from the black curve of Figure 4 at $A(t = 0) = 0.1$ V. The difference between the two the two decay curves $A(t = 0) = 0.1$ V is, shown as dark gray at $A(t = 0) \approx 0$ in Figure 4, free of the low-frequency parasitic component arising from limitations in the electronics owing to the differences in the shifted phases. The data for the curve at $A(t = 0) \approx 0$ can then be fit with eqs 2 to 7 and provide η(333 K) = 12.82 mPa·s which is within 0.16 % of the cited value and illustrates the success of this background subtraction strategy. This experimentally determined background elimination scheme can be shown theoretically to be suitable for the removal of parasitic signals.

The optimum excitation frequency for the background elimination was determined by experiment for this particular wire, clamping arrangement, electronics, and interconnecting cables. Our methodology is illustrated in Figure 5 which shows eight transient curves obtained in N35, each being the difference of a first signal where the vibrating wire viscometer was excited at the resonant frequency and a second where the excitation was off-resonance (the latter is referred to as the background). For each curve, a different background signal was used comprising the average of 32 scans. Each curve's background was measured by excitation at a slightly different frequency from that of the resonance. For example, the background for the curve of largest amplitude (largest A near to the ordinate axis) was obtained by exciting the vibrating wire at a frequency equaling $f + 2g$. The ellipse at the left shows three curves where the excitation frequency of the background is greater than the resonance frequency, and the ellipse at the right shows three curves where the excitation frequency of the background is less than the resonance frequency. The curve corresponding to a background excitation frequency of $f + 2g$ had the largest amplitude, was deemed the most symmetric, and was chosen as the excitation frequency for the background elimination for all subsequent measurements.

When the vibrating wire is excited at a frequency close (within about 100 Hz) to the resonance, a transient decay signal is obtained. If this process is repeated, another frequency within 200 Hz of the previous excitation frequency, the same resonance frequency as that obtained from the first excitation frequency is obtained albeit with different phase and amplitude. The signal obtained from the difference between two transient decay signals consistently gave one amplitude and phase and was found to apply regardless of the chosen excitation frequencies provided they were close to that of the actual wire resonance frequency. Trigonometric identities show all sinusoidal waves of dissimilar amplitude and phase, but identical frequency, and can be combined. This is advantageous when the resonance frequency of the wire overlaps with the frequency of a source of noise because this procedure permits the reduction of the influence of the noise source.

The data acquisition procedure included the following four steps: (1) the ring-down was obtained from an average of about 12 measurements at the resonant frequency but only for times greater than about 1.7 ms after cessation of excitation because at $t < 1.7$ ms the oscillations were distorted; (2) the background noise was determined from the average of also about 12 measurements where the excitation was at a frequency between the resonance and 2 times the resonance line-width; (3) the amplitude decay after extinction of excitation was determined from the average of 12 measurements; and (4) the frequency for excitation was determined. At each temperature and pressure, items 2 and 3 required a total elapsed time of about 2.4 s for the determination of viscosity with the transient method but still a factor of 17 less than the resonance method. In ref 13, the steady state measurement required a time of 200 s, and the

transient mode is then 83 times faster. The time of 2.4 s could be reduced with improved electronics.

Over the range of the investigation, the Q of resonance and Δ of decay measurements are both power laws in viscosity: increasing viscosity results in a decrease in Q and an increase in Δ. The resonance frequency decreases from about 1450 Hz at $\eta \approx 1$ mPa·s to about 1300 Hz at $\eta \approx 100$ mPa·s.

For the fluid with viscosities between (4 and 70) mPa·s used in this work, the current did not impart a wire displacement amplitude that violated the assumptions used to derive the working equations. However, when the current was passed for a time not exceeding 10 s prior to transient data acquisition to a tungsten wire {c_p(W, 298 K) $\approx$ 0.133 kJ·kg^{-1}·K^{-1} and ρ(W, 298 K) $\approx$ 19300 kg·m^{-3}}, of $R \approx 0.075$ mm and mass $1.4 \cdot 10^{-5}$ kg, and resistance of order 1 Ω immersed in S20 {c_p(298 K) $\approx$ 2 kJ·kg^{-1}·K^{-1}, ρ(298 K) $\approx$ 840 kg·m^{-3} and $\kappa \approx 120$ mW·m^{-1}·K^{-1}}, the fluid temperature was estimated to rise by 0.12 K, assuming all electrical energy dissipated into the fluid volume enclosed by the wire holder (about $2 \cdot 10^{-6}$ m^3). The resulting worst case error in viscosity is about 0.2 % in our measurements, $|(\partial\eta/\partial T)_p| < 1.5$ mPa·s·K^{-1}, assuming infinite fluid thermal conductivity.

The fluid was displaced into an evacuated pressure vessel, and the pressure of it was controlled with a positive displacement pump (Isco model 65D) with a maximum operating pressure of 138 MPa. For the viscosity measurements obtained while flowing S20, the pressure of about 0.69 MPa was determined with the strain gauge transducer with an uncertainty of ± 0.02 MPa. For the measurements with N35, the pressure was maintained at 0.1 MPa. The temperature of the outer surface of the pressure vessel was determined with a K-type thermocouple with an uncertainty of ± 0.1 K. The largest source of uncertainty in our values of viscosity arises from the uncertainty in temperature. The estimated standard uncertainty in the measurements of viscosity with a vibrating wire, excluding the error in temperature measurements, is ± 1 %.[2,13,14,16] The flow rate was determined both with the positive displacement and gravimetrically.

Calibration. Steady state measurements in air at a pressure of 0.1 MPa were used to determine the internal damping Δ_0 (eq 8 of ref 1) of the wire and holder with the result $\Delta_0 = 0.000380 \pm 0.000020$ with the assumption this was equivalent to that determined under vacuum. The difference between Δ_0 obtained from measurements in air or vacuum results in an insignificant difference in the measured viscosity when the viscosity is on the order of 1 mPa·s or greater.[15] The wire was immersed in methylbenzene at a temperature of 298.15 K and a pressure of 0.1 MPa to determine the effective wire radius of (75.7 ± 0.1) μm. The viscosity of 0.555 mPa·s and density of 862.6 kg·m^{-3} were estimated from the correlation reported by Assael et al.[17] with our measurements of temperature and pressure. Values of Δ_0 and R determined with transient measurements agreed with the steady state values albeit with a standard deviation significantly greater owing to noise emanating from the measurement electronics.

Materials. Methylbenzene (CAS# 108-88-3) was provided by Chromasolv with stated mass fraction purity ≥ 0.999. Two certified reference materials for viscosity, N35 (Cannon, lot number 05301) and S20 (Cannon, lot number 05301), were used for these measurements with viscosities provided by the supplier that varied from (2.5 to 66.5) mPa·s. The supplier measured the kinematic viscosity at temperatures between (293 and 373) K using long (at least 400 mm) 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 expanded uncertainty in the kinematic viscosity was ± 0.25 % relative to water, for which the uncertainty at $T = 298$ K and $p = 0.1$ MPa is ± 0.25 %, and the uncertainty in the density was ± 0.02 %. When these uncertainties are combined in quadrature, the expanded uncertainty in the dynamic viscosity is ± 0.35 % assuming no additional uncertainty arises from the step-up procedure.[18,19] The N35 was used for measurements with stagnant fluid, while S20 was used for flowing fluid.

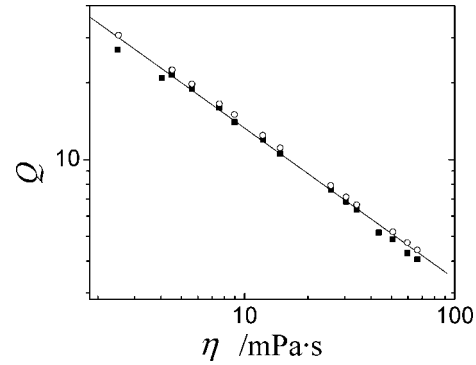

Figure 6. Resonance quality factor Q for the wire immersed in certified reference material N35 as a function of viscosity η between (2.5 and 66.5) mPa·s. ■, steady state measurement from eq 9; ○, Q estimated from eqs 12 and 11 for a vibrating wire undergoing damped harmonic motion; —, $Q = 51.476 \cdot \eta^{-0.5977}$.

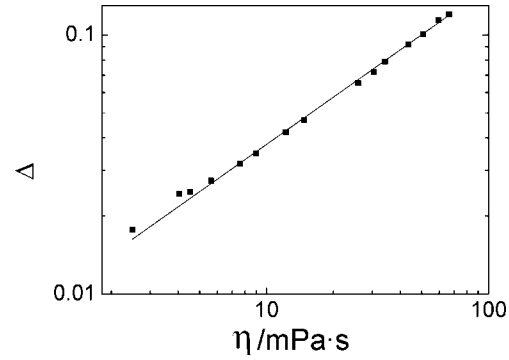

Figure 7. Decrement Δ for the wire immersed in certified reference material N35 as a function of viscosity η between (2.5 and 66.5) mPa·s. ■, transient measurement; —, $\Delta = 0.00936 \cdot \eta^{0.6064}$, which is consistent with eq 10.

Results and Discussion

The resonance quality factor Q obtained for steady state measurements from eq 9 are shown in Figure 6 as a function of viscosity that increased from (2.5 to 66.5) mPa·s as Q decreased from 26.9 to 4.0. The Q can be represented by $Q = 51.476 \cdot \eta^{-0.5977}$, and this empirical function is also shown in Figure 6 along with the Q estimated from eqs 12 and 11 for a vibrating wire undergoing damped harmonic motion. The resonant frequency in air was used to determine the spring constant for the wire, and this value was assumed to be equal to that when the wire was in vacuum. The decrement Δ obtained from transient measurements is shown in Figure 7 as a function of viscosity that increased from 0.120 to 0.018 with viscosity increasing from (2.5 to 66.5) mPa·s. The measured decrement of Figure 7 can be represented by $\Delta = 0.00936 \cdot \eta^{0.6064}$, consistent with the functional form of eq 10. The resonant frequency of the vibrating wire viscometer can be estimated from eq 13 and is found, as Figure 8 shows, in good agreement with the data using the same naïve model of a damped harmonic

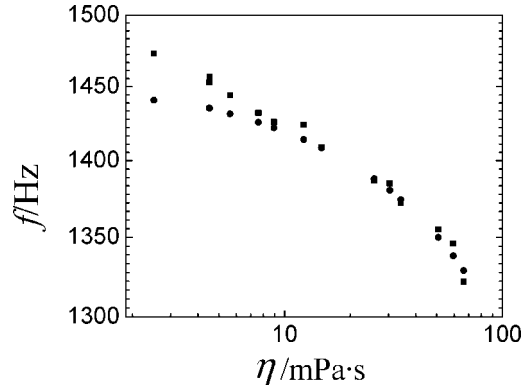

Figure 8. Resonance frequency f obtained from eq 13 for simple harmonic motion for the wire immersed in certified reference material N35 as a function of viscosity η between (2.5 and 66.5) mPa·s. ■, measured frequency; ●, calculated from eq 13.

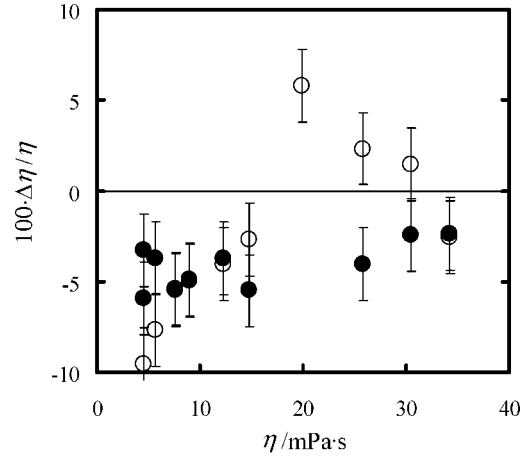

Figure 9. Fractional deviation $\Delta\eta/\eta = \{\eta(\text{exptl}) - \eta(\text{calcd})\}/\eta(\text{calcd})$ of the experimental viscosity obtained with the vibrating wire η(exptl) from the value η(calcd) cited by the supplier as a function of viscosity η for certified reference fluid N35. ●, transient measurement where each value was acquired in a time of about 2 s; ○, steady state measurement where each value was acquired in a time of about 40 s. The anticipated expanded uncertainty in each viscosity measurement is shown.

Table 1. Viscosity of N35 Cited by the Supplier η(Cited) with the Viscosity Determined from Steady State η(SS) and Transient η(Trans) Measurements at Temperature T

T/K	η(Cited)/mPa·s	η(SS)/mPa·s	η(Trans)/mPa·s
308.1	34.20	33.33	33.38
311.0	30.44	30.88	29.70
315.0	25.794	26.39	24.75
320.9	19.863	21.01	
328.9	14.783	14.38	13.97
334.4	12.236	11.74	11.78
344.6	8.947	8.51	8.50
350.6	7.586	7.18	7.17
362.4	5.626	5.19	5.42
372.1	4.528		4.381
372.2	4.512	4.081	4.246

oscillator except at viscosities less than about 10 mPa·s that probably originate from omission of intrinsic damping in our calculations.

The viscosities obtained from both the steady state and transient methods are shown relative to the cited values in Figure 9 and listed in Table 1 for N35 at temperatures between (295 and 372) K and pressures of 0.1 MPa that correspond to viscosities in the range (4.5 to 34) mPa·s. The four measurements at viscosities between (44 and 66) mPa·s, while adequate to demonstrate the versatility of the model based on damped

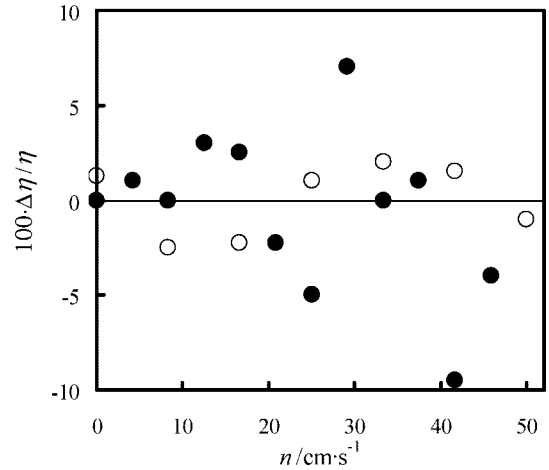

Figure 10. Fractional deviation $\Delta\eta/\eta = \{\eta(\text{exptl}) - \eta(\text{calcd})\}/\eta(\text{calcd})$ of the experimental viscosity obtained with the vibrating wire η(exptl) from the value η(calcd) cited by the supplier as a function of fluid flow rate n for certified reference fluid S20. ●, transient measurement where each value was acquired in a time of about 2 s; ○, steady state measurement where each value was acquired in a time of about 40 s.

harmonic motion, were subject to a significantly lower signal-to-noise ratio and were of insufficient precision to list. The cited values of viscosity, with an uncertainty of 0.35 %, were fit to an interpolating function that introduced an additional uncertainty of less than 0.3 %. At all temperatures, the differences are within ± 10 % of the cited values albeit with a systematic undulation. The most significant and quantifiable contribution to the uncertainties arises from $d\eta/dT$ owing to the uncertainty in our temperature measurements. For N35, the derivative was estimated from the cited values and the contribution to $\delta\eta$ from δT lying between (0.01 and 0.25) mPa·s {about (0.25 to 0.5) %} that decreased with increasing temperature. Perhaps of greater significance is the agreement between the viscosities obtained from both transient and steady state methods that are within less than two times the combined expanded uncertainty of 4 %. The differences shown in Figure 9 are comparable with those reported for measurements with certified reference materials for viscosity,[13,14,16] and it is plausible they arose from a chemical impurity, such as the presence of S20 or methylbenzene in the apparatus. No measurements were conducted to confirm either of these postulates.

We have measured the viscosity of stagnant S20 at a temperature of 297 K and pressure of 0.1 MPa and obtained a viscosity that differed by about 5 % from the cited value. The same vibrating wire was also used to measure the viscosity when immersed in S20 that was flowed at rates between (4 and 50) $cm^3 \cdot s^{-1}$. The tubular holder of the taut wire has an inner diameter of 5.5 mm, and at a volumetric flow rate of 50 $cm^3 \cdot s^{-1}$, the fluid has an average velocity of 0.21 $m \cdot s^{-1}$. The viscosities obtained in both flowing and stagnant conditions with both steady state resonance and transient decay methods are shown, as deviations from the correlation of ref 14, in Figure 10. The differences increase with increasing volumetric flow rate, and the plausible sources for these differences are axial alignment of the wire and the temperature variations arising from flow. Each will be briefly considered. However, the differences are equal to the uncertainty of ± 10 % considered adequate to guide value and exploitation calculations of a hydrocarbon-bearing formation with sufficient rigor.[20,21]

In ref 1, the effect of variations in axial alignment of the wire within the cylinder of $(2 \text{ to } 4) \cdot 10^{-3} \cdot \pi$ was investigated, and an off-axis wire resulted in a lower signal-to-noise ratio

than for the axial case but not a systematic error in viscosity. The conclusion was the wire must be aligned with the axis of the cylinder within $\pi \cdot 4 \cdot 10^{-4}$ degrees.

A mechanical pump was used to flow fluid through the vibrating wire and interconnecting tube. The temperature of the outer surface of the metallic pressure vessel containing the viscometer increased with increasing flow rate, and it is entirely plausible that the observed temperature fluctuations arose from the energy imparted to the system by the mechanical pump. At the highest flow rate of 50 $cm^3 \cdot s^{-1}$, the measured temperature increased by $\approx$ 9 K above the value measured for zero flow. As a result of the temperature fluctuations, the viscosity range varied from (33 to 21) mPa·s as the flow rate increased to 50 $cm^3 \cdot s^{-1}$. At each flow rate, sufficient time was permitted for the temperature to reach a steady state before data acquisition commenced so as to minimize the effect of these temperature variations on the measurements. In the absence of direct measurements of the fluid temperature and in view of the adopted procedures, we assume the uncertainty of the measured temperatures is a factor of 20 greater than the uncertainty of an individual measurement, and so $\delta T \approx 2$ K. On the basis of the $\eta(T, p)$ of stagnant S20 reported by Kandil et al.,[14] this δT gives rise to $\delta\eta/\eta \approx \pm$ 10 % consistent with the difference shown in Figure 10. If the fluctuations in measured viscosity are solely a result of the variation in temperature of <2 K, we conclude flowing fluid with $\eta \approx 0.25$ mPa·s at a rate less than 50 $cm^3 \cdot s^{-1}$ would not introduce a significant systematic error in the η obtained from an axially symmetric vibrating wire operated in either the steady state or transient decay modes. This result is perhaps not surprising for a wire orientated axial to a flowing fluid because there is a stagnant fluid layer on the wire of thickness about the same order as the amplitude of the wire motion (about 1 μm). It is a task for theoretical fluid mechanics to verify these results. The observed temperature fluctuations might have arisen from the energy imparted to the system by the mechanical pump used to flow the fluid through the vibrating wire and interconnecting tube.

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