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An Absolute Vibrating-Wire Viscometer for Liquids at High Pressures

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The design and operation of a new vibrating-wire viscometer for the measurement of the viscosity of liquids at pressures up to 100 MPa are described. The design of the instrument is based on a complete theory so that it is possible to make absolute measurements with an associated error of only a few parts in one thousand. Absolute measurements of the viscosity of *n*-hexane are reported at 298.15 K at pressures up to 80 MPa. The overall uncertainty in the reported viscosity data is estimated to be ±0.5%, an estimate confirmed by the comparison of values of viscosity of slightly inferior accuracy.

KEY WORDS: high pressure; *n*-hexane; vibrating wire; viscosity.

1. INTRODUCTION

Many classical methods for the measurement of the viscosity of liquids require a bulk motion of the fluid as well as the measurement of relatively small pressure differences. Whereas such techniques are simple near atmospheric pressure, they become increasingly inappropriate at high pressures due to the difficulties associated with the measurement of such small pressure differences in the pressence of a high total hydrostatic pressure. For this reason, high-pressure viscometry has made use of different techniques involving the motion of solid bodies through the fluid. The most popular of these techniques has been that of observing the time of fall of a body of revolution through the fluid under gravity. It is frequently difficult to ensure that such devices operate exactly in

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accordance with the available theory of them, so that although the precision of the measurements can be as good as ±0.1%, the uncertainty is often one order of magnitude worse.

An alternative type of viscometer makes use of the effect of the fluid on the oscillations of a body of revolution immersed in the fluid. For operation at high pressures, the most suitable geometry for such a device is that of a cylindrical wire performing transverse oscillations perpendicular to its length. This is because the volume of fluid required is small, the amplitude of motion of the solid material is of the order of a micrometer and the requisite measurement of the prime experimental quantities can be made with a high precision. Instruments of this kind have been employed successfully for measurements at the temperatures of liquid helium [1] and, independently, in gases at pressures up to 1000 MPa [2]. A recent reevaluation of the theory of the technique has enabled the working equations for the method to be refined [3] and, in particular, has established the criteria which it is necessary to satisfy in order that the instruments operate in a manner consistent with the theory. In this paper we describe an instrument of this type designed in accordance with theoretical constraints to perform viscosity measurements in liquids at pressures up to 100 MPa with an uncertainty of ±0.5%.

2. THE IDEAL MODEL

The ideal model of the viscometer is essentially that sketched in Fig. 1. A circular section rod of radius R and half-length L, clamped at both ends, is performing free oscillations in an initially stationary fluid of constant

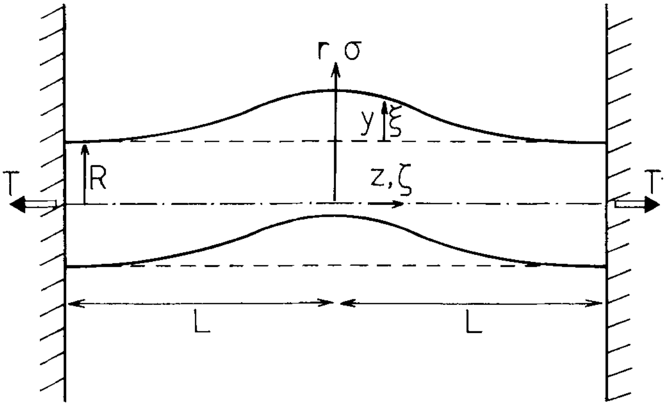

Fig. 1. The ideal model.

viscosity, μ, and density, ρ. The motion of the rod is initiated by providing transverse deflection $y_0 f(z)$ and releasing it. It can be shown that, provided the wire is sufficiently thin ($R \ll L$), the equation of motion for the rod can be written [3,4] as

$$EIy_{zzzz} - Ty_{zz} + (m_s + m_b)\, y_{tt} + (D_b + D_0)\, y_t = F(z, t) \tag{1}$$

where E represents the Young's modulus for the rod material, T the axial tension in the rod, and D_0 a coefficient of internal damping. The term F represents a force per unit length acting on the rod that arises from the initiation of motion in the fluid at $t = 0$. For long times this term becomes negligible and the motion of the rod and fluid is oscillating and isochronous.

The remaining parameters of Eq. (1) are

$$\begin{aligned} I &= (1/4)\pi R^4, & D_b &= \rho\pi R^2 \omega k' \\ m_s &= \rho_s \pi R^2, & m_b &= \rho\pi R^2 k \end{aligned} \tag{2}$$

and we write

$$D_0 = 2\rho_s \pi R^2 \omega \Delta_0 \tag{3}$$

for later convenience. Here, ρ_s is the density of the rod material and Δ_0 the logarithmic decrement of the oscillation in vacuo. The parameters k and k', which are functions of frequency, express the mass and damping added to the oscillating rod by the presence of the external fluid. It is preferred to analyze the mechanical motion of the rod without specifying the exact nature of k and k' and subsequently determine the later from an analysis of the fluid flow around the rod. At this stage of the analysis, ω represents a characteristic frequency yet to be determined.

As we are concerned with the transient decay of free oscillations of the rod, Eq. (1) is to be solved subject to the spatial boundary conditions [3, 4],

$$y = 0 \quad \text{and} \quad y_z = 0 \quad \text{at} \quad z = \pm L \tag{4}$$

and the initial conditions,

$$\begin{aligned} y(z, t) &= y_0 f(z) \\ y_t = 0 \quad &\text{at} \quad t = 0 \end{aligned} \tag{5}$$

where y_0 is the maximum initial displacement of the rod and f an arbitrary function of $z(|f| \leqslant 1)$.

The general solution of Eq. (1) is [3, 4]

$$\xi(\zeta, \tau) = \sum_{j=1}^{\infty} \Phi_j(\zeta)\, e^{(i-\Delta_j)\underline{\omega}_j \tau} + \sum_{m=1}^{\infty} \Phi_m(\zeta) e^{-\nu_m \underline{\omega}_m \tau} \tag{6}$$

where ξ is a dimensionless displacement from the rest position, ζ a dimensionless axial coordinate, τ a dimensionless time, and $\underline{\omega}_j$ a dimensionless angular frequency for the normal mode of oscilation Φ_j. These dimensionless quantities are defined [3] as

$$\begin{aligned} \xi &= y/y_0, & \tau &= t(EI/m_s L^4)^{1/2} \\ \zeta &= z/L, & \underline{\omega}_j &= \omega_j (m_s L^4/EI)^{1/2} \end{aligned} \tag{7}$$

where ω_j is the angular frequency in mode j in a fluid.

The second summation on the right-hand side of Eq. (6) represents a simply decaying displacement whose exact value depents on the initial conditions for the motion. In the present analysis these terms are not considered because they are ultimately unimportant to the evaluation of the viscosity [3]. The first summation contains a damped simple-harmonic oscillation for each mode of oscillation in which Δ_j characterizes the rate of damping.

The normal nodes of the wire, in the same dimensionless notation, are

$$\Phi_j = A_j \cos\ a_j^- \xi + B_j \cosh a_j^+ \xi \tag{8}$$

with the wave vectors given by the equation

$$a_j^{\pm} = \{[(\alpha^2/4) + n_j^2]^{1/2} \pm (\alpha/2)\}^{1/2} \tag{9}$$

with n_j determined as the solution of the equation

$$a_j^- \tan a_j^- + a_j^+ \tanh a_j^+ = 0 \tag{10}$$

and

$$\alpha = TL^2/EI \tag{11}$$

If we consider first the wire vibrating in vacuo, so that the fluid density is zero and the only damping is internal to the wire, then considering just one mode [3],

$$\Delta = \Delta_0 \tag{12}$$

and

$$\underline{\omega}_0 = n_j [1 + \Delta_0^2]^{-1/2} \tag{13}$$

When the liquid surrounds the wire, then the working equation for the viscometer, which is complex, can be written [3] as

$$\Delta = \frac{(\rho/\rho_s)k' + 2\Delta_0}{2[1 + (\rho/\rho_s)k]} \tag{14}$$

for the imaginary part, and

$$\frac{\omega^2}{\omega_0^2}\left[\left[1 + \frac{\rho k}{\rho_s}\right](\Delta^2 - 1) - \frac{\Delta \rho k'}{\rho_s} - 2\Delta_0\right] + 1 + \Delta_0^2 = 0 \tag{15}$$

for the real part.

In circumstances when $L \gg R$, the fluid motion will take place in planes normal to the axis of the wire, and provided that the amplitude of the motion, εR, is sufficiently small, it is possible to linearize the Navier–Stokes equations. It can thus be shown [3] that the parameters k and k' are given by

$$k = -1 + 2\,\mathrm{Im}(A) \tag{16}$$

and

$$k' = 2\,\mathrm{Re}(A) - 2\Delta\,\mathrm{Im}(A) \tag{17}$$

where

$$A = (i - \Delta)\left\{1 + \frac{2K_1[[(i-\Delta)\Omega]^{1/2}]}{[(i-\Delta)\Omega]^{1/2}\,K_0[[(i-\Delta)\Omega]^{1/2}]}\right\} \tag{18}$$

The parameter Ω in the above equation is defined as

$$\Omega = \rho \omega R^2/\mu \tag{19}$$

and represents the appropriate Reynolds number with μ the fluid viscosity, while K_0 and K_1 are modified Bessel functions.

The above relationships are valid provided [3] that

$$\varepsilon \ll \Omega \ll 1/\varepsilon^2 \tag{20}$$

and

$$\omega \varepsilon R/C \ll 1 \tag{21}$$

where C is the sonic velocity in the fluid.

In principle, either Eq. (14) or Eq. (15) may be used to obtain the viscosity but they are not equivalent since they differ in their sensitivity to the measured variables. In practice Eq. (14) will always be prefereable because it does not require a knowledge of ω_0 and because Eq. (15) requires a far greater precision in the measurement of frequency than is attainable.

Thus, Eq. (14) together with Eqs. (16)–(19) forms a consistent set of equations from which the viscosity of the liquid can be calculated based on the measurements of the logarithmic decrement and frequency of oscillation in the liquid and the measurement of the logarithmic decrement in the vacuo.

3. EXPERIMENTAL

In any practical realization of a vibrating-wire viscometer it is necessary to add additional design criteria. First, in the present arrangement in order to preserve the precision in the viscosity measurement, it is necessary to contain the logarithmic decrement in a range

$$0.005 < \Delta < 0.1 \tag{22}$$

so that it is sufficiently large to be measured with a high precision but sufficiently small that a number of cycles of oscillation are observed. Second, the theory outlined above presumed that the liquid was of infinite extent in the radial direction. In practice, the liquid must be confined in a cylinder of radius R_c so that it is necessary to amend the results for k and k' to allow for this. An analysis performed by Chen et al. [5] has shown that provided that

$$R_c/R > 30 \tag{23}$$

the correction to the viscosity value calculated by the theory described above is less than 0.1 %.

The combination of these constraints together with those given earlier defines uniquely the design parameters of a viscometer for application to a particular liquid. For the present application to simple hydrocarbons at temperatures above ambient and pressures up to 100 MPa, the application of the design criteria result in the instrument shown in Fig. 2, while in Fig. 3 the assembled viscometer in the pressure vessel is shown.

The vibrating wire is made of 100-μm-diameter tungsten wire with a length of 54 mm and a frequency in vacuo of about 1 kHz. The wire is placed between two chucks. The upper chuck, 1, is insulated from its support plate, 2, by PTFE washers, while support plate 2 is connected to support 3 that screws under the upper closure of the pressure vessel—the complete assembly shown in Fig. 3. At its lower end, the wire carries a second chuck, 4, connected to a central weight made of tungsten, 5, that ensure constant tension in the wire. However, changes in the density of the surrounding liquid would result in changes of the buoyancy force on this weight and thus produce variable tension on the wire. To avoid this effect a second weight, 6, made of stainless steel is used in conjunction with a balancing mechanism, 7, shown in detail in Fig. 2. The balancing mechanism, also made of stainless steel, acts like a "seesaw" for the two weights, while small rubis at the tip of each cone ensure minimum friction. The volumes of the two weights are chosen so that the net effect of changing the density of the surrounding liquid results in a negligible effect upon the frequency of oscillation.

At the same time, the inertia of the suspended weights is such that the lower point of attachment to the wire remains a node. These arrangements prevent the large frequency changes that would otherwise result from the

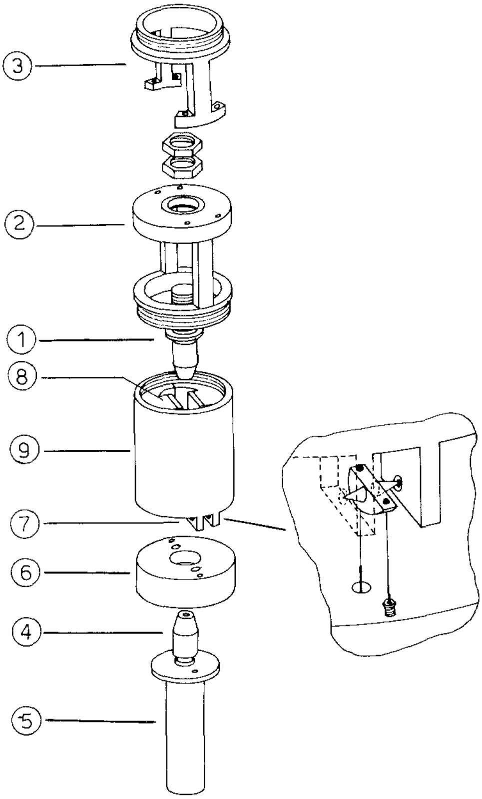

Fig. 2. Schematic drawing of the viscometer.

effects of buoyancy on an uncompensated weight or the clamping of the wire at both ends in a frame whose dimensional changes under high pressure are different from those of the wire and unpredictable.

The top electrical connection is made between the two nuts on the upper insulated chuck, while the bottom conection is on the bottom chuck. Both electrical connections are led out of the pressure vessel through an appropriate fitting. The oscillations of the wire are induced electromagnetically and detected in a similar fashion. The magnets, 8, used for both of these purpose are mounted in a cage, 9, surrounding the wire. The magnets, made from samarium-cobalt, produce a field of about 1 Tesla at the wire. Finally, stainless-steel pieces (not shown in Fig. 2) are placed in the upper two supports so as to reduce the volume of the liquid required.

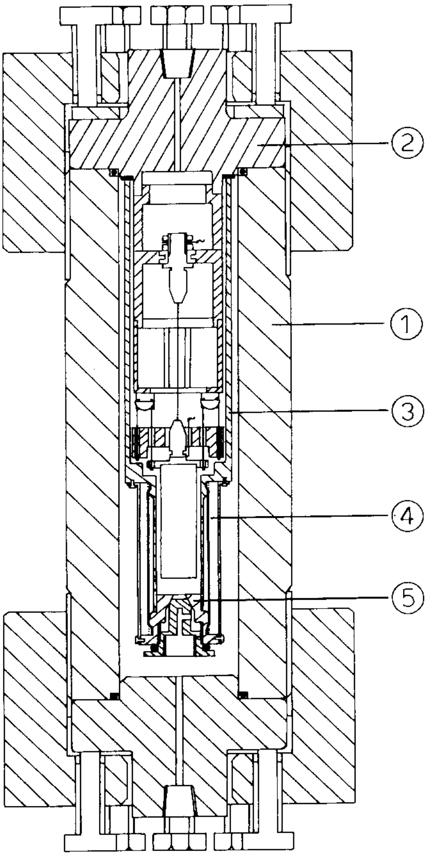

Fig. 3. The viscometer assembly.

The assembled instrument is shown in Fig. 3. The pressure vessel, 1, is made of steel 4340 and the viscometer hangs from the upper closure, 2, of the pressure vessel. A thin-walled stainless-steel inner vessel, 3, separates the liquid under investigation from the pressure pump oil. At its bottom a thin cylindrical PTFE sleave, 4, is used to transmit the pressure from the oil to the liquid. In the lower part of this thin-walled inner vessel, an arrangement, 5, supported by two metal strips, is available for the filling in vacuo of this inner vessel with the liquid. The pressure vessel is connected at its bottom with the pressure system, consisting of a hand-operated oil pump and a Budenberg calibrated pressure gauge. At the top of the pressure vessel the two electrical connections come out. The temperature of the pressure vessel is recorded by two calibrated platinum resistance thermometers placed in small holes on its two cups. The pressure vessel is finally placed in a 150-lt oil bath (Shell, Thermia B) capable of maintaining the temperature stable and uniform with an accuracy of ±10 mK.

The oscillations of the wire are initiated by applying two pulses of current opposite sign to the wire. The initial motion then contains a number of harmonics of the fundamental frequency which decay rapidly compared with the decay of the fundamental. It has been found that this symmetric method of initiation is essential to ensure that the zero point of the oscillation is coincident with the rest position of the wire. Following initiation of the motion, the signal induced in the vibrating wire is observed with a bridge in which the wire forms one arm. The out-of-balance signal, amplified by 30,000 times, is then observed with an A/D converter coupled to a microcomputer through Direct Memory Access. This configuration enables sampling of the oscillating signal at a rate of 50 kHz with a resolution of 12 bits. Since the frequency of the oscillation is about 1 kHz, one obtains roughly 50 points per cycle of the wire's motion. This information is stored for subsequent analysis.

4. CONFIRMATION OF OPERATION ACCURACY

The recorded data from a single transient decay should, if the theory is consistent with the operation of the instrument, conform to the equation

$$y = y_0 e^{(i - \Delta)\omega t} \tag{24}$$

that represents Eq. (6) for the fundamental mode of oscillation. Thus values of Δ and ω may be derived by fitting the above equation to the experimental data. This can be readily achieved with the aid of a nonlinear least-squares fitting procedure. Figure 4 contains the first 2000 points accumulated in a typical run in toluene at 304.7 K and atmospheric pressure. The deviation plot shown in the same figure illustrates the magnitude of the deviation of the experimental points from the fit of Eq. (24) in this run. It is clear that there are no systematic effects and that Eq. (24) represents the data within the random noise level. This result indicates that the instrument operates in accordance with the theoretical model of it. In the case of the measurement in the fluid the decrement Δ has a value of about $\Delta \approx 0.012$, whereas in vacuo $\Delta_0 \approx 5 \times 10^{-5}$. The uncertainty in the calculation of the decrement is better than 0.1%, while for repeated measurements under the same conductions in the fluid, its reproducibility was found to be beter than ±0.1%. The uncertainty and reproducibility of the frequency of oscillation are ±0.2%. Of course, the precision of the measurement of Δ_0 is inferior but its contribution to the final viscosity is small so that this is unimportant. It is worthwhile recording here that the buoyancy compensation mechanism has proved successful because the change of resonant frequency of the wire with the weights immersed in air or the fluid does not exceed ±0.1%.

The final viscosity value is obtained from Eq. (14) and Eqs. (16)–(19). In these equations, the calculation of the modified Bessel functions can be achieved with a very high accuracy [6–8], while the uncertainty of the

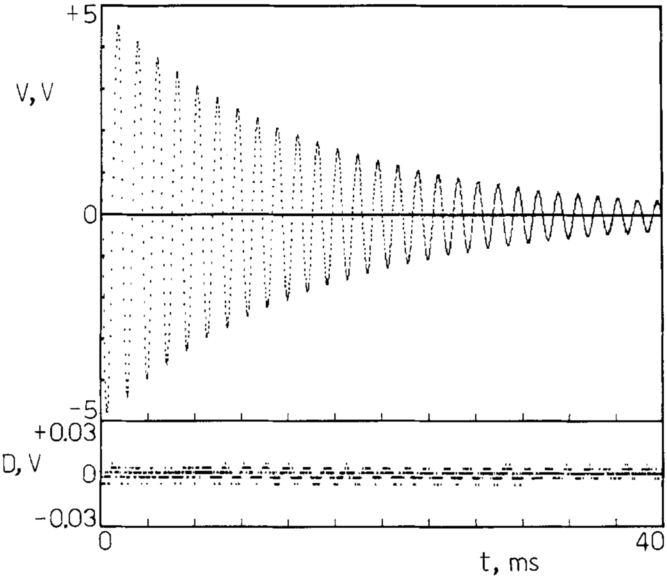

Fig. 4. Voltage values, V, obtained in toluene at 304.7 K and atmospheric pressure, and their deviations, D, from Eq. (24) as a function of the sampling time, t.

decrement and the frequency of oscillation as well as of the density of the liquid is less than a few parts in a thousand. Thus the uncertainty of the viscosity value is related to the uncertainty of the density of the wire ρ_s and its radius R. It has not, however, yet been possible to measure accurately the density of the wire sample, while its radius was found to be $50.05 \pm 0.03\ \mu$m. The combined uncertainty in these two quantities produces an uncertainty in the absolute value of the viscosity of about ±1%. To reduce this uncertainty of the viscosity further we have adopted the following procedure.

We have assumed that the wire diameter was exactly 100.1 μm and the density of the wire equal to that given by Barrett [9] for pure tungsten. We have subsequently performed a set of viscosity measurements for toluene at atmospheric pressure as a function of temperature. The sample of toluene used was supplied by Aldrich and has a purity of 99.9% (HPLC). We have consequently altered slightly the value of the wire density (<1%), so that these measurements coincide exactly with the measurements of Goncalves et al. [10], performed in an Ubbelohde capillary viscometer with an uncertainty of ±0.3%. In Table I, our values for the viscosity of toluene and the values obtained by Gonçalves et al. [10] are shown. The value of the density of the wire obtained in this way was $19090\ \mathrm{kg \cdot m^{-3}}$ at 273.15 K. It is thus estimated that the uncertainty of the present measurements is ±0.5%, while the precision and reproducibility are better than ±0.1%.

5. RESULTS

In Table II the present measurements of *n*-hexane at 298.15 K and pressures up to 80 MPa are shown. The density of *n*-hexane used in these measurements was obtained from those represented by Li [11] and

Table I. The Viscosity of Toluene as a Function of Temperature at Atmospheric Pressure

Temperature (K)	Viscosity (μPa · s)		Deviation (%)
	Present work	Ref. 10	
304.72	513.8	513.7	+0.02
312.52	470.6	471.2	−0.12
322.24	426.0	425.6	+0.09
334.69	376.9	376.7	+0.05

Table II. The Viscosity of *n*-Hexane at 298.15 K as a Function of Pressure

Pressure (MPa)	Density ($kg \cdot m^{-3}$)	Viscosity ($\mu Pa \cdot s$)
0.1	655.2	298.0
5.4	660.3	314.5
10.5	665.1	331.4
15.5	669.5	347.8
20.6	673.8	364.1
25.4	677.7	379.1
30.7	681.8	396.5
35.8	685.6	412.4
41.3	689.5	430.9
45.9	692.6	446.5
50.9	695.9	462.9
55.9	699.2	479.7
60.9	702.2	496.6
66.0	705.2	513.5
70.6	707.9	529.6

Dymond et al. [12], with an uncertainty better than ±0.1 %. The value of the viscosity of *n*-hexane obtained at atmospheric pressure (280.0 $\mu Pa \cdot s$) agrees with that obtained by Knapstad et al. [13] (294.9 $\mu Pa \cdot s$), in an absolute oscillating-cup viscometer with a quoted uncertainty of ±0.5 %, within the uncertainty of the two instruments. As this instrument is the only other absolute viscometer, this comparison confirms the uncertainty quoted for our instrument.

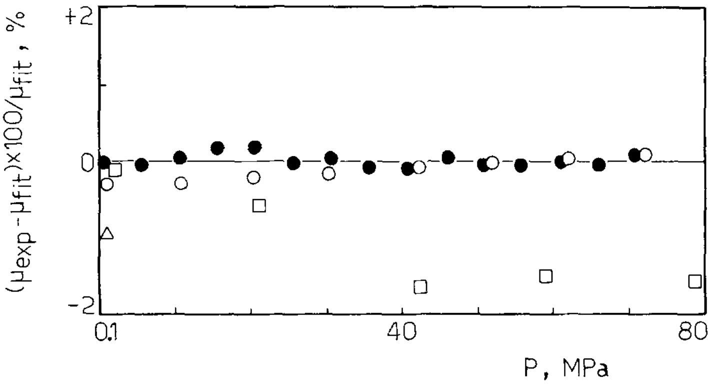

Fig. 5. Deviations of experimental values of the viscosity of *n*-hexane at 298.15 K and up to 80 MPa, from Eq. (25). (●) Present work; (□) Ref. 12; (△) Ref. 13; (○) Ref. 14.

For comparison purposes, we have used a Tait equation-based relation [14] to correlate the present measurements as

$$\ln\left[\frac{\mu}{\mu_0}\right] = E \ln\left[\frac{D+P}{D+0.1}\right] \tag{25}$$

where μ_0 represents the experimental viscosity at atmospheric pressure (298.04 μPa · s). The values of E and D, obtained by a nonliniear least-squares procedure, were found to be $E = 1.142$ and $D = 108$ MPa. In Fig. 5 the deviations of the present experimental measurements from the above equation are shown. It can be seen that the maximum deviation is less than 0.20%, while the standard deviation of the fit is ±0.08%. In the same figure the deviations of the measurements of two other investigators are also shown. The measurements of Kashiwagi and Makita [14] were performed in a torsionally vibrating crystal instrument on a relative basis and with a quoted uncertainty of ±2%. This set of measurements agrees with the present values within ±0.3%, which is well within the mutual uncertainty of the two instruments. The second set of measurements is that of Dymond et al. [12] performed in a self-centering falling-body viscometer on a relative basis with a quoted uncertainty of ±2%. The maximum deviation of these measurements from the above equation is ±1.7%, which again is well within the mutual uncertainty of the two instruments.

6. CONCLUSION

A new vibrating-wire viscometer for viscosity measurements in liquids at high pressures has been developed. The results presented in the paper show that the instrument operates in accordance with the theoretical description of it. Measurements of the viscosity of *n*-hexane are presented at 298.15 K and up to 80 MPa pressure, with an estimated absolute uncertainty of ±0.5%, an estimate confirmed by the comparison of laterature values of inferior accuracy.

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