# Viscosity Measurements of Diisodecyl Phthalate Using a Vibrating Wire Instrument Operated In Free Decay Mode: Comparison with Results Obtained with the Forced Mode of Operation[†]

**J. L. Correia da Mata,[‡] Fernando J. P. Caetano,[§] Carla M. B. P. Oliveira,[§] and João M. N. A. Fareleira***

Centro de Química Estrutural, Instituto Superior Técnico, Universidade Técnica de Lisboa, Av. Rovisco Pais,
1049-001 Lisbon, Portugal

Recently, several authors described measurements of liquid viscosities higher than 100 mPa·s, using the vibrating wire technique in the forced oscillation mode of operation. The use of a vibrating wire instrument to measure increasingly higher viscosities poses experimental difficulties due to the consequent decrease of the quality factor of the resonance. This problem affects both modes of operation: in the steady-state, forced oscillation mode, there is a loss of definition of the resonance curve, and in the transient, free decay mode, there is an increase of the decrement of the sinusoidal time response of the vibrating wire. In the present work, we have measured the viscosity of diisodecyl phthalate (DIDP) at 0.1 MPa with a vibrating wire of nominal radius of 190 $\mu$m using the free decay mode of operation. The measurements covered a range of viscosities from (64 to 265) mPa·s. The results agreed with those we have obtained with a vibrating wire instrument operated in the forced mode and with the literature data, within the estimated experimental uncertainty ($k = 2$) of ± 2 %. The comparisons indicate that the use of the free decay mode of operation does not necessarily imply a significant increase of uncertainty of the viscosity results at moderately high viscosities.

## Introduction

Vibrating wire viscometers operated in the steady-state, forced mode of oscillation, rather than in the transient, free-decay mode, have received much attention in recent publications,[1−6] in particular, for measurements of high viscosity. A summary of the expansion of the upper limit of the viscosity determined with vibrating wire instruments before 2005 has been provided by Kandil et al.[4]

The most relevant advantages of vibrating wire viscometers are (i) the existence of theoretically based rigorous working equations[7,8] and (ii) the simplicity of the calibration procedure, as it only requires the determination of the wire radius at one temperature and pressure, in addition to the internal damping, $\Delta_0$. Regarding the former, the variation of the cylindrical wire radius and material density with temperature and pressure can be estimated from the physical properties of the wire material, which essentially avoids the need to perform any further calibrations for various temperatures and pressures. These two characteristics make the vibrating wire viscometer particularly suited to many industrial applications.

In vibrating wire instruments, currently in use for the measurement of the viscosity of liquids, the sensor is a metallic wire subject to an axial tension, placed within a magnetic field, and can be operated in either free decay or forced oscillation modes. In the former mode, the wire is disturbed from its equilibrium position, and the damped transverse oscillations in the magnetic field originate an electromotive force in the wire that gives rise to an electric current, according to Faraday's law of induction. This time response is used to obtain the viscosity, through the hydrodynamic model,[8] provided the density of the fluid and the average radius, material density, and internal damping of the wire are known. This transient mode of operation has been used for the measurement of the viscosity of several fluids. Application of the technique, using the hydrodynamic model described in ref 8, for the measurement of liquids is described in several measurements carried out by Assael et al.[9,10] and Oliveira and Wakeham[11] in the early 1990s.

In the forced mode of operation, a sinusoidal current is fed to the wire in a range of frequencies including its resonance frequency. The characteristics of the resulting resonance curve are related to the viscosity,[12] through the corresponding hydrodynamic model.[7] In the early 1990s, this steady-state mode was proposed for the measurement of density,[13,14] and soon afterward its use was extended to perform simultaneous measurement of both viscosity and density over wide ranges of temperature and pressure.[15−21]

More recently, the use of the forced mode of operation is gaining great popularity for the measurement of viscosity alone.[1−5,22−27] This surge of interest may presumably be the result of experimental difficulties related to the operation of vibrating-wire instruments in free decay mode with fluids of viscosity significantly higher than that of water, due to an increase of the decrement of the free wire oscillations with increasing fluid viscosity. It should however be made clear that the forced mode of operation also becomes more difficult to use as the viscosity increases because the quality factor of the resonance circuit that models the measuring cell decreases.[1,12] An increase of the fluid viscosity is therefore reflected experimentally by an increase of the width of the resonance curve in the forced mode and a higher damping (an increase of the

---

* To whom correspondence should be addressed. E-mail: j.fareleira@ist.utl.pt.

[†] Part of the "William A. Wakeham Festschrift".

[‡] And Academia Militar, Paço da Rainha, 29, 1150-244 Lisbon, Portugal.

[§] And Universidade Aberta, R. da Escola Politécnica, 147, 1269-001 Lisbon, Portugal.

10.1021/je900113f CCC: $40.75

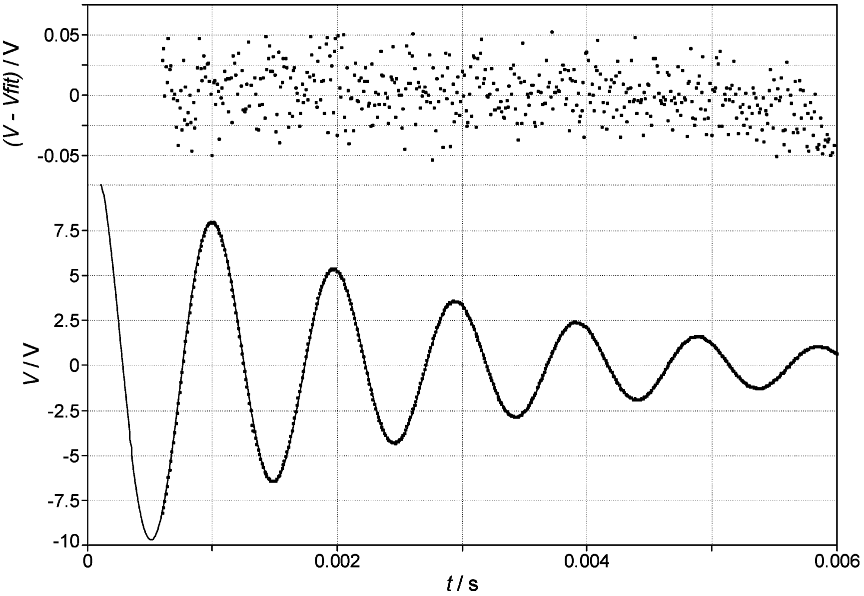

**Figure 1.** Fitting and deviation plot (made with Table Curve 2D) of experimental points, corresponding to a typical free oscillation decay response of the sensor obtained with DIDP at 293.15 K and atmospheric pressure. The fitting curve (eq 1) is represented by the line.

decrement of the sinusoidal time response of the wire) in the free-decay mode of operation.

One chief advantage of the forced mode of operation is the possibility to easily filter the electric signal from the vibrating wire sensor. In the free decay mode of operation, filtering the signal by electronic hardware is much more difficult, and it usually is replaced by repetition of the measurements and averaging of the results. Notwithstanding this, a drawback of the forced mode of operation lies in the time taken by the data acquisition for completion of a measurement. In fact, the time required for one viscosity measurement can be of great importance, for instance, in situations where the composition of the sample can vary along the time.[28] To the knowledge of the authors, until recently, the minimum reported time for the forced mode of operation was about 200 s.[5,6] Having it in view to tackle situations where the measurement time is a crucial parameter, Etchart et al.[28] claim measurement times for the transient and the steady-state modes of operation of (2.4 and 40) s, respectively. In any case, one is to expect that forced mode measurements will take at least about 1 order of magnitude longer than the corresponding free decay mode of operation. The same authors also compare steady-state and transient viscosity measurements of a standard reference sample in the range (4 to 34) mPa•s. The reported agreement[28] between the results obtained by the two methods is within 8 %, which the authors claimed to be two times the combined expanded uncertainty of the measurements.

In our previous work,[1] we have shown that it was possible to use the transient mode at viscosities from 0.55 mPa•s to about 3.3 mPa•s, without a significant reduction in the measurement precision. The main purpose of the present work is to extend the range of viscosities studied to an upper limit of about 265 mPa•s and, by comparing both operation modes, give evidence that they can, in principle, be used at moderately high viscosities ensuring a commensurate level of performance.

An oral description of part of the present work has been communicated to the 18th European Conference on Thermophysical Properties.[29]

## Measurement Technique

The hydrodynamic theory of vibrating wire viscometers operated in transient or free decay mode of oscillation was developed by Retsina et al.[8] and ultimately relates the time response characteristics of the sensor to the viscosity of the fluid surrounding it.

A typical time response of a vibrating wire immersed in DIDP at a temperature of 293.15 K and pressure of 0.1 MPa is shown in Figure 1, where $V(t)$ is the induced voltage at the wire terminals due to its damped, free decay oscillation, represented by

$$V(t) = V_0 \exp(-\Delta\omega t)\cos(\omega t + \varphi) + V_1 \qquad (1)$$

where $\omega$ is the frequency of the transverse oscillations; $V_0$ is the initial amplitude of the induced voltage; $\Delta$ is the logarithmic decrement; $t$ is the time; and $V_1$ and $\varphi$ are the signal amplitude and phase offsets, respectively.

The working equations of the vibrating wire method are a complete set that relate the experimentally obtained characteristics of the free decaying transverse oscillations of the wire, namely, its frequency, $\omega$, and logarithmic decrement, $\Delta$, with the viscosity of the fluid where the sensor is immersed. For this purpose, the density of the fluid is required, along with the radius and the density of the wire, and the logarithmic decrement in vacuum. The working equations used in the present work are described by Retsina et al.,[8] and their applicability are subject to the constraints reported in the literature.[8,10,11,30]

The time response of the sensor is described by eq 1 only after the initial transient terms of the oscillation have decayed.[8] In the present work, the initial transient data that were discarded corresponded to times from (0.6 to 1) ms, i.e., from about (0.6 to 1) periods of the wire oscillations, as the frequency was about 1 kHz. On the other hand, the data acquisition should end when the signal-to-noise ratio becomes too low. In the present measurements, the upper time limit for the data acquisition was between (6.3 and 7.0) ms. Both upper and lower time limits have been determined by the standard deviation of the fit of eq 1 to the experimental data.

## Experimental Setup

The transient vibrating wire measurements were conducted with the apparatus previously used[3] to determine the viscosity of DIDP with forced (or steady-state) mode of oscillation. The main difference between the experimental setups consists of the

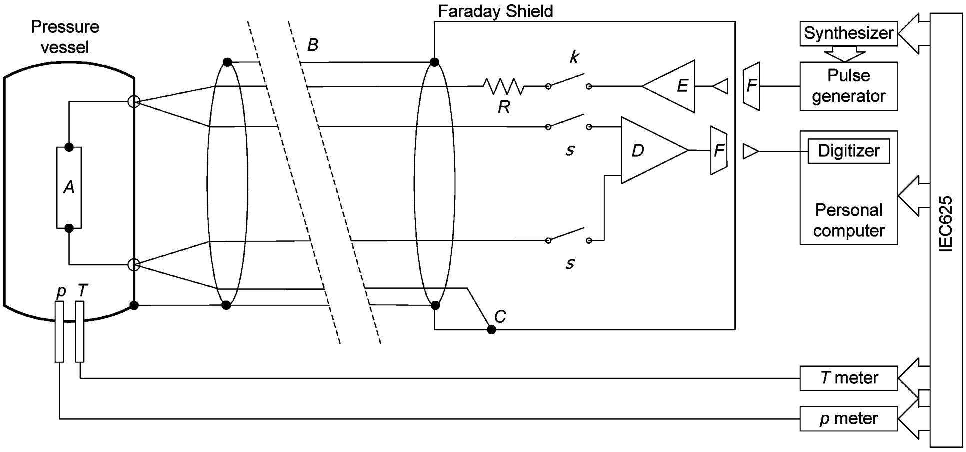

**Figure 2.** Data acquisition system.

electronic control and data acquisition system, which is imposed by the diverse nature of the experimental procedures of the two modes of operation, and this will be discussed below.

***Vibrating Wire Viscometer.*** The present measurements have been carried out with a vibrating-wire sensor that has been described previously by Caetano et al.,[2,3] and only a brief description will be given here. The vibrating wire is made of tungsten (supplied by Goodfellow Cambridge Limited, U.K.), with a purity of 99.95 % and a nominal radius of 190 $\mu$m. The wire is clamped at both ends to two Inconel plates that are kept parallel and rigidly fixed by two 4 mm diameter tungsten rod spacers. The tungsten wire is electrically isolated from the support by plastic washers machined from Ertacetal rods (supplied by DSM Engineering Plastic Products, The Netherlands). The wire holder is attached to the cap of a pressure vessel, fabricated from 316 stainless steel, that, when assembled, is mounted between two neodymium−iron−boron permanent magnets supplied by Sura Magnets (Sweden) that generate a magnetic induction of about 0.6 T at the center of the gap between the magnetic poles. Within the pressure vessel, the tungsten wire is connected by four copper wires, two for each end of the wire, to an electrical feedthrough in the pressure vessel cap.

The pressure vessel and surrounding magnets are placed in a stirred fluid thermostatic bath, controlled by a combination of Hart Scientific temperature controller (model 2100), a platinum resistance thermometer, and recirculating immersion cooler. The temperature of the thermostat was stable to within ± 0.003 K for a time of about 30 min. The temperature of the fluid was determined from the resistance of a four-wire platinum resistance thermometer of nominal resistance 100 Ω as measured by a digital multimeter (Prema model 6001) with an uncertainty estimated to be ± 0.01 K.

***Control and Data Acquisition System.*** In the transient mode, the tungsten wire, which is within a permanent magnetic field, is forced into motion by passage of one period of a square wave at a frequency close to that of the fundamental wire resonance. The subsequent free oscillations give rise to an induced voltage with the exponential sinusoidal decay dependent on the viscosity of the medium in which the wire is immersed.

The control and data acquisition system, shown in Figure 2, is essentially the same as used for measurements of the viscosity of toluene at low temperatures.[1] The purpose of the control and acquisition system is 2-fold: to generate the symmetric pulse that stimulates the vibrating wire and to acquire and store the voltage arising from the wire movement.

The square symmetric current pulse is obtained from a frequency synthesizer (Stanford Research Systems DS345) that is fed into a power operational amplifier *E*, connected in series with a switch *k* and resistor *R* that acts as a current limiter. The amplifier *D* collects and amplifies the transient voltage resulting from the free decaying oscillations of the wire. The cell response is subsequently recorded by an Advantech Ltd., PC_Labcard, model PCL-318, 12 bit, $10^5$ samples·$s^{-1}$ digitizer. During the application of the current pulse two reed relays, the switches *s* are kept open to prevent the input stage of the amplifier *D* from saturating. Subsequently, they are closed when the vibrating wire starts its decaying oscillation. The switch *k* opens after the end of the current pulse to guarantee that the resistor *R* and the output of the voltage amplifier do not offer a path for any currents, which, circulating through the vibrating wire, would give rise to false readings. The *D* and *E* amplifiers are connected to the outside of this module through optical isolators, which prevent the flow of noise currents and allow the ground node to float and be connected to a Faraday shield that encloses the whole circuit and is connected to the external wall of the measuring cell, providing a screen against external noise. The system is controlled by a computer through an IEC625 bus.

## Experimental Details

***Fluids.*** The diisodecyl phthalate (DIDP) (CAS Registry No. 26761-40-0) used for this work was from the same batch as that used for the viscosity measurements reported previously[3] with a vibrating wire viscometer operated in forced mode. This sample was obtained from Merck KGaA as “for analysis” grade from lot no. 328 with a certificate of quality (1.03622.1000 diisodecyl phthalate GR acc. to DIN 752001, batch K22132622) stating a minimum purity of 99.8 % as determined by GC. The sample was subjected to the same treatment described in ref 3; in particular, the sample was dried over 0.4 nm molecular sieves (Riedel-deHaën), and the subsequent water content was determined by Karl Fisher coulometric titration (Aquapal, model III, UK) to be less than 20 mg·$kg^{-1}$.

***Cell Parameters.*** The measuring cell used in the free decay experiments of the present work is the same as the one utilized to measure DIDP in the forced mode of operation.[3] Consequently, the cell parameters ($\Delta_0$, the logarithmic decrement in vacuum, the wire average radius, the wire density, and $\Delta_0$) are the same as were used in the measurements in forced mode of operation.[3] The wire radius was determined by calibration with water at a temperature of 293.15 K and a pressure of 0.1 MPa,

**Table 1. Experimental Results, $\eta_{exp}$, of the Viscosity of DIDP Obtained Using a Vibrating Wire Technique Operated in Free Decay Mode[a]**

| $T$/K | $\eta_{exp}$/(mPa·s) | $\sigma$/% | $N_p$ |
|---|---|---|---|
| 283.03 | 264.88 | 0.52 | 15 |
| 288.36 | 173.92 | 0.75 | 15 |
| 288.23 | 176.35 | 0.50 | 8 |
| 293.93 | 116.51 | 0.80 | 15 |
| 293.23 | 122.34 | 0.26 | 12 |
| 298.13 | 87.76 | 0.20 | 8 |
| 298.58 | 85.30 | 0.22 | 15 |
| 303.18 | 64.51 | 0.11 | 12 |
| 303.50 | 63.25 | 0.13 | 12 |

[a] The data are mean values of sets of at least eight measurements with standard deviation, $\sigma$. Information is also given on the number of points entering each set of data, $N_p$.

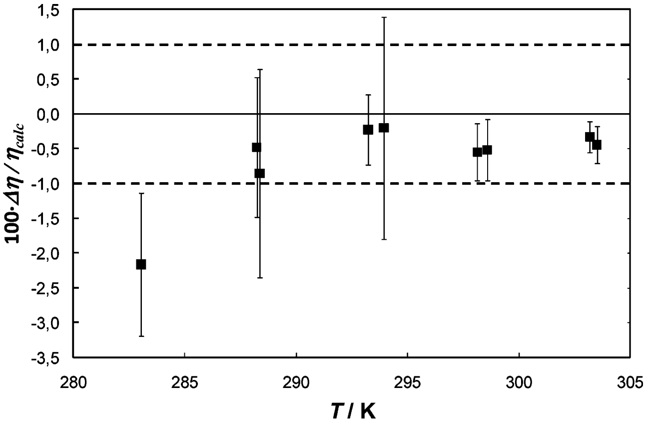

**Figure 3.** Relative deviations, $\Delta\eta/\eta_{calc} = [\eta_{expt} - \eta_{calc}]/\eta_{calc}$, of the present transient results, $\eta_{expt}$, from the viscosity calculated from eq 2 of ref 3, $\eta_{calc}$, that represents the viscosity of DIDP obtained in forced mode as a function of temperature. The error bars for the transient measurements are two times the standard deviations listed in Table 1.

**Table 2. Fitting Parameters of the Vogel−Fulcher−Tammann[37] Type Correlation Equation of Selected Literature Viscosity Results at Temperatures Between (283.15 and 308.15) K, with the Corresponding Relative Root Mean Square Deviation, rmsd, and the Bias of the Data from the Equation[a]**

| | |
|---|---|
| $A$ | −2.8656 |
| $B$/K | 843.21 |
| $C$/K | −183.38 |
| rmsd/% | 0.26 |
| bias/% | −0.01 |

[a] The selected data have all been obtained with DIDP samples of purity greater than 99.8 % and were taken from data sets shown in refs 3 and 31 to 36.

the primary standard for viscosity. The internal damping, $\Delta_0$, was obtained from the resonance curve of the wire under vacuum.[15]

## Results and Comparisons

The viscosity of DIDP was obtained at temperatures between (283.15 and 303.15) K and a pressure of 0.1 MPa. The measurements have been grouped in sets of $N_p$ = (8 to 15) points at each of the temperatures as shown in Table 1. Also, the mean viscosity determined from the $N_p$ measurements of each set is given, as well as the corresponding standard deviation, $\sigma$. It should be noted that the data deviating by more than twice the standard deviation from the mean were not included.

Figure 3 shows the relative deviations of the viscosity obtained by the present transient measurements from the correlation equation of the data obtained operating the viscometer in forced mode (eq 2 with parameters in Table 4 of ref 3). The error bars shown in Figure 3 are two times the standard deviation, listed in Table 1. The overall uncertainty of the measurements obtained in the forced mode of operation is estimated to be ± 1 % for temperatures lower than 293 K and ± 0.8 % for the other temperatures. This comparison enables a direct assessment of the consistency of the results obtained in both modes of operation using the same cell. The deviations of the present free decay measurements from the correlation are less than ± 1 %, except for the highest viscosity measured, at $T$ = 283.03 K where the absolute value of the deviation is greater than 2 %. The agreement between the viscosity obtained with the forced and transient methods is therefore compatible with a rough estimate, based on the highest standard deviation shown in Table 1, of the expanded ($k$ = 2) uncertainty being better than ± 2 % for the present transient measurements. It should be remarked that no general systematic relation of the deviations with temperature (or viscosity) is apparent. However, the coincidence of the highest deviation observed with the lowest temperature may be an indication that the uncertainty may increase for higher viscosities, using the present experimental arrangement.

To compare the viscosity listed in Table 1 with values reported in the literature, an interpolating equation is required. In this work, we used the data chosen to define the reference values for the viscosity of DIDP,[3,31−36] presented in the article that proposed that fluid to be an industrial reference standard for viscosity.[31] However, instead of using the correlation equation published with that proposal,[31] which is restricted to the temperature range (288.15 to 308.15) K, we have selected, from the same data sets,[3,31−36] the 29 viscosity results obtained at temperatures within the range (283 to 304) K. Those data were used to obtain the parameters of a Vogel−Fulcher−Tammann-type equation[37]

$$\eta/(\text{mPa·s}) = \exp\left(A + \frac{B}{C + T}\right) \tag{2}$$

The parameters that fit eq 2 to the mentioned literature data are shown in Table 2, together with the root-mean-square deviation, rmsd, and bias, defined as, respectively

$$\text{rmsd} = \left[\frac{1}{N}\sum_{i=1}^{N}\left(\frac{\eta_i - \eta(T_i)}{\eta(T_i)}\right)^2\right]^{1/2} \tag{3}$$

and

$$\text{bias} = \frac{1}{N}\sum_{i=1}^{N}\left(\frac{\eta_i - \eta(T_i)}{\eta(T_i)}\right) \tag{4}$$

where $\eta_i$ is the $i^{th}$ viscosity value obtained from refs 3 and 31 to 36 at temperature, $T_i$; $\eta(T_i)$ is the corresponding calculated value of the viscosity; and $N$ is the number of experimental data used to define the correlation equation.

The viscosities listed in Table 1 are shown as deviations from eq 2 in Figure 4 along with the reference DIDP viscosity values[31] at temperatures of (293.15, 298.15, and 303.15) K. The values reported by Al Motari et al.[38] at $p$ = 0.1 MPa obtained with DIDP samples of nominal purity greater than 99.8 % are also shown in the same figure. All viscosity results obtained from the transient mode of operation agree with the literature values within an interval of ± 2 %, which is within the estimated uncertainty of the measurements. As in Figure 3, no systematic trend with temperature is found, although the highest absolute deviation occurs for the lowest temperature (highest viscosity).

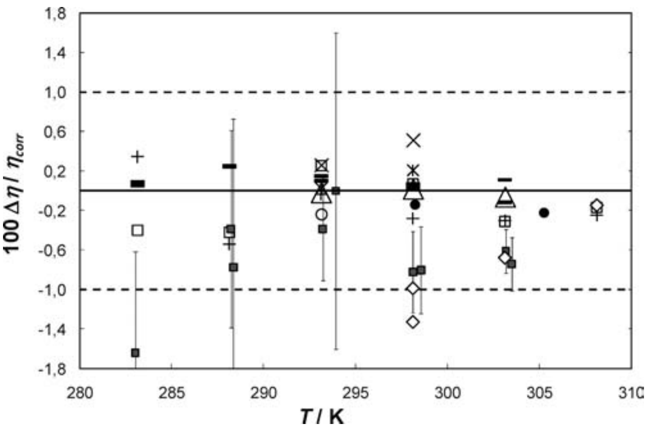

**Figure 4.** Relative deviations, $\Delta\eta/\eta_{\mathrm{corr}} = [\eta - \eta_{\mathrm{corr}}]/\eta_{\mathrm{corr}}$, of the present measurements and of literature data, $\eta$, from the correlation equation (eq 2), $\eta_{\mathrm{corr}}$, obtained from literature values, in the temperature range (283.15 to 308.15) K. +, Caetano et al. (vibrating wire in forced mode);[3] △, viscosity reference data;[31] □, Fröba and Leipertz;[32] —, Harris and Bair;[33] *, Caetano et al. (capillary, DIDP 99.8 % from Merck KGaA);[34] ×, Caetano et al. (capillary, DIDP 99.8 % from Fluka);[34] ○, Bauer;[35] ●, Peleties and Trusler;[34,36] ◇, Al Motari et al.;[38] ■, present work.

## Discussion

The design of vibrating wire sensors for any particular application must fulfill the theoretical requirements of the hydrodynamic model.[7,8] Furthermore, the viscosity range and the measurement uncertainty level sought require the optimization of physical dimensions, like the wire radius and length, to ensure the necessary quality factor[23] and the establishment of appropriate operating conditions, in particular, those determining the signal-to-noise ratio.

The resonance quality factor $Q$ is defined by

$$Q = \frac{\omega_{\mathrm{res}}}{\omega_{-}^{+}} \tag{5}$$

where $\omega_{\mathrm{res}}$ is the resonance frequency and $\omega_{-}^{+}$ is the width of the resonance curve, measured between the frequencies at which the dissipated power is half of the maximum.[7,12]

As mentioned above, it is well-known that, as the viscosity increases, the quality factor of a certain resonance cell decreases, and Lundstrom and co-workers[5] have indicated a lower limit of $Q = 2.0$ for the practical measurement of viscosity.

For certain applications, like online measurements of flowing fluids[28] with varying properties, additional constraints must be imposed. Namely, the time required to complete a measurement must be sufficiently small to prevent introduction of uncertainties arising from significant variations in chemical composition or temperature or pressure of the flowing fluid. As has been mentioned in the Introduction, the time required for a viscosity measurement with a vibrating wire sensor operated in the transient mode is at least 1 order of magnitude smaller than that required for the steady-state mode. Therefore, for many possible applications, it is important to determine the convenience of using the former mode rather than the latter. Regarding those kinds of applications, therefore, the maximum time allowable for a measurement along with the required signal-to-noise ratio will determine the mode of operation and thus the upper measurable viscosity, for a certain level of uncertainty.

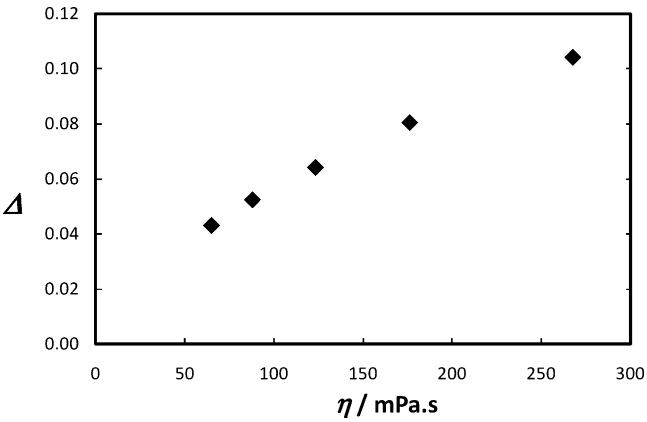

**Figure 5.** Approximate average decrement, Δ, as a function of viscosity, $\eta$, for the present transient mode measurements.

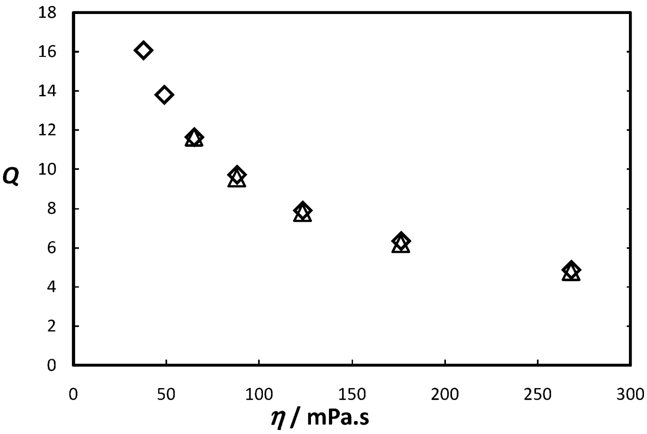

**Figure 6.** Quality factor, $Q$, of DIDP viscosity measurements: ◇, forced mode of oscillation; △, free decay mode of oscillation.

For the present free decay mode measurements, listed in Table 1, Figure 5 shows the logarithmic decrement, Δ, as a function of viscosity. As expected, Δ increases monotonically with viscosity. For comparison with the forced mode measurements, Δ may be related to the quality factor through the relation[28]

$$Q = \frac{1}{2\Delta} \tag{6}$$

Figure 6 shows the quality factor, $Q$, obtained from eq 5 for the forced mode measurements of DIDP[3] and from eq 6 for the transient mode, and in both cases, the values are essentially dependent on the viscosity alone.

For a viscometer, there is a minimum value of $Q$, below which the uncertainty in the measured viscosity increases significantly. This minimum threshold is in part determined by the requirement to achieve an acceptable signal-to-noise ratio. To ensure a value of $Q$ that provides an acceptable signal-to-noise ratio, when immersed in liquids with increasingly higher viscosity, it is necessary to use wires with correspondingly larger diameter, as shown by Caetano et al.[1,2] and by Harrison et al.[39]

It is possible, despite the reduction in $Q$, to retain a similar uncertainty of the viscosity obtained from either mode of operation, provided $Q$ is maintained greater than a minimum value. The uncertainty of the viscosity results is directly related to the root-mean-square deviation, rmsd, of the experimental points to the fitted curves, as predicted by the theoretical models used—for the present measurements, this would be eq 1. When the sensor is operated in the forced mode, the increase in viscosity, and therefore the decrease in $Q$, may be overcome, in principle, by an enlargement of the spanned frequency range. This may be illustrated by our measurements,[2] using the same sensor in the forced mode of operation, of the viscosity of water

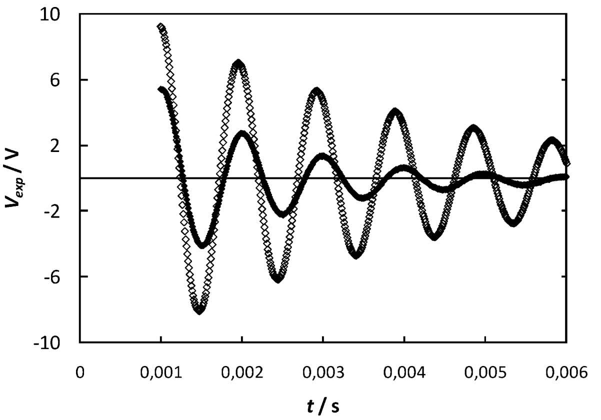

**Figure 7.** Experimental free decay curves obtained in the present viscosity measurements of DIDP at: ◇, 303.15 K ($\Delta = 0.0429$); and ◆, 283.15 K ($\Delta = 0.105$).

($\eta \approx 1.002$ mPa·s) and of a certified reference specimen PTB 100B (Physikalisch-Technische Bundesanstalt, Braunschweig, Germany) with a viscosity about $\eta \approx 125$ mPa·s, at 20 °C. In typical resonance curves, as shown in Figures 3 and 4 of ref 2, the quality factors were 112.1 and 7.9, for water and PTB 100B, respectively. Notwithstanding this difference, the relative rmsd's of the experimental impedance points from the theoretical resonance curve are of comparable magnitude (less than 0.1 %) for both water and PTB100B. Apart from the driving current, which was necessarily different for both experiments, the main difference of those measurements was the frequency range spanned, as shown in those figures.[2]

A comparison of the present transient measurements for $T = 283$ K (for which $Q = 4$) with those obtained in forced mode of operation[3] suggests that a lower signal-to-noise ratio in the free decay experiments may have determined a $Q$ threshold higher than the one observed in our steady-state measurements. It is expected that the electrical noise level of the detected signal will determine in practice the threshold value for $Q$. It is important to note that, while in the forced mode of operation, the decrease of $Q$ with increasing viscosity can be compensated by enlarging the frequencies spanned for acquiring the resonance curve, and an analogous approach cannot be adopted for the transient mode. This limitation is illustrated in Figure 7, where two decay curves obtained with DIDP, at $T = (283.15$ and $303.15)$ K, are shown. The values of the logarithmic decrement are $\Delta = (0.105$ and $0.0429)$, respectively. The decaying signal at the highest viscosity (at $T = 283.15$ K) approaches the baseline at a rate such that extending the signal acquisition beyond about 6 ms would impair the precision of the determination of the viscosity. The augmentation of data points, without loss of precision, would require an improved instrumentation.

The choice of one or the other mode of operation of the vibrating wire technique seems, therefore, to require, for each application, a consideration of several factors, including the uncertainty level required for the results, the upper time limit of measurement, and the signal-to-noise ratio attainable.

## Conclusions

New results for the viscosity of DIDP obtained with a vibrating wire technique operated in the transient mode have been presented. The measured viscosities are in the range (63 to 265) mPa·s. The results were compared to high quality measurements performed with a vibrating wire instrument operated in the forced mode. The comparisons indicate that the use of the free decay mode of operation did not imply a serious increase of uncertainty of the results, the deviations never exceeding ± 1 %, except at the lowest temperature, where the deviation amounts to the order of −2 %.

The present work shows that both transient and steady-state methods can be used in extended ranges of viscosity. The comparisons made indicate that preference of one mode of operation over the other will ultimately require the consideration of a number of factors, namely, the uncertainty level required for the results, the upper time limit of measurement, and the signal-to-noise ratio that can be reached in each of the experimental methods.

## Acknowledgment

Part of this work has been presented in an oral communication to the 18th European Conference on Thermophysical Properties, Pau, France, 31 Aug.−4 Sept. 2008, where the discussion has started.

## Literature Cited

(1) Caetano, F. J. P.; Correia da Mata, J. L.; Fareleira, J. M. N. A.; Oliveira, C. M. B. P.; Wakeham, W. A. Viscosity measurements of liquid toluene at low temperatures using a dual vibrating-wire technique. *Int. J. Thermophys.* **2004**, *25*, 1–11.

(2) 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 of 0.5 to 135 mPa·s. *J. Chem. Eng. Data* **2005**, *50*, 201–205.

(3) Caetano, F. J. P.; Fareleira, J. M. N. A.; Oliveira, C. M. B. P.; Wakeham, W. A. New measurements of the viscosity of diisodecyl phthalate using a vibrating wire technique. *J. Chem. Eng. Data* **2005**, *50*, 1875–1878.

(4) Kandil, M. E.; Marsh, K. N.; Goodwin, A. R. H. 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 232) mPa·s at temperatures between (298 and 373) K and pressures below 40 MPa. *J. Chem. Eng. Data* **2005**, *50*, 647–655.

(5) Lundstrom, R.; Goodwin, A. R. H.; Hsu, K.; Frels, M.; Caudwell, D. R.; Trusler, J. P. M.; Marsh, K. N. 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. *J. Chem. Eng. Data* **2005**, *50*, 1377–1388, 1787.

(6) Kandil, M. E.; Harris, K. R.; Goodwin, A. R. H.; Hsu, K.; Marsh, K. N. Measurement of the viscosity and density of a reference fluid, with nominal viscosity at $T = 298$ K and $p = 0.1$ MPa of 29 mPa·s, at temperatures between (273 and 423) K and pressures below 275 MPa. *J. Chem. Eng. Data* **2006**, *51*, 2185–2196.

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

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

(9) Assael, M. J.; Papadaki, M.; Wakeham, W. A. Measurements of the Viscosity of Benzene, Toluene and Meta-Xylene at Pressure up to 80 MPa. *Int. J. Thermophys.* **1991**, *12*, 449–457.

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

(11) Oliveira, C. M. B. P.; Wakeham, W. A. The Viscosity of 5 Liquid Hydrocarbons at Pressures up to 250 MPa. *Int. J. Thermophys.* **1992**, *13*, 773–790.

(12) 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.

(13) Dix, M.; Fareleira, J. M. N. A.; Takaishi, Y.; Wakeham, W. A. A Vibrating-wire Densimeter for Measurements in Fluids at High-Pressure. *Int. J. Thermophys.* **1991**, *12*, 357–370.

(14) Pádua, A. A. H.; Fareleira, J. M. N. A.; Calado, J. C. G.; Wakeham, W. A. A Vibrating-Wire Densimeter for Liquids at High-Pressures - The Density of 2,2,4-Trimethylpentane from 298.15 to 348.15 K and up to 100 MPa. *Int. J. Thermophys.* **1994**, *15*, 229–243.

(15) Pádua, A. A. H.; Fareleira, J. M. N. A.; Calado, J. C. G.; Wakeham, W. A. Validation of an accurate vibrating-wire densimeter: Density and viscosity of liquids over wide ranges of temperature and pressure. *Int. J. Thermophys.* **1996**, *17*, 781–802.

(16) 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 to 298 K and up to 100 MPa. *J. Chem. Eng. Data* **1996**, *41*, 731–735.

(17) Pádua, A. A. H.; Fareleira, J. M. N. A.; Calado, J. C. G.; Wakeham, W. A. Density and viscosity measurements of 2,2,4-Trimethylpentane (Isooctane) from 198 to 348 K and up to 100 MPa. *J. Chem. Eng. Data* **1996**, *41*, 1488–1494.

(18) Gourgouillon, D.; Avelino, H.; Fareleira, J. M. N. A.; da Ponte, M. N. Simultaneous viscosity and density measurement of supercritical CO2-saturated PEG 400. *J. Supercrit. Fluids* **1998**, *13*, 177–185.

(19) Avelino, H. M. N. T.; Fareleira, J. M. N. A.; Wakeham, W. A. Simultaneous Measurement of the Density and Viscosity of Compressed Liquid Toluene. *Int. J. Thermophys.* **2003**, *24*, 323–336.

(20) Caudwell, D. R.; Trusler, J. P. M.; Vesovic, V.; Wakeham, W. A. The viscosity and density of n-dodecane and n-octadecane at pressures up to 200 MPa and temperatures up to 473 K. *Int. J. Thermophys* **2004**, *25*, 1339–1352.

(21) Audonnet, F.; Pádua, A. A. H. Simultaneous measurement of density and viscosity of n-pentane from 298 to 383 K and up to 100 MPa using a vibrating-wire instrument. *Fluid Phase Equilib.* **2001**, *181*, 147–161.

(22) Avelino, H. M. N. T.; Fareleira, J. M. N. A.; Oliveira, C. M. B. P. Viscosity of compressed liquid 1,1,1-trifluoroethane (HFC-143a) and pentafluoroethane (HFC-125). *J. Chem. Eng. Data* **2006**, *51*, 1672–1677.

(23) Caetano, F. J. P.; Fareleira, J. M. N. A.; Oliveira, C. M. B. P.; Wakeham, W. A. Viscosity of di-isodecylphthalate: A potential standard of moderate viscosity. *Int. J. Thermophys* **2004**, *25*, 1311–1322.

(24) Avelino, H. M. N. T.; Fareleira, J. M. N. A.; Oliveira, C. M. B. P. Viscosity measurements of compressed liquid refrigerant blend R-507A, using a vibrating-wire technique. *J. Chem. Eng. Data* **2008**, *53*, 53–56.

(25) Len, C. W.; Trusler, J. P. M.; Vesovic, V.; Wakeham, W. A. The viscosity of organic liquid mixtures. *Int. J. Thermophys.* **2006**, *27*, 48–65.

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

(27) Etchart, I.; Jundt, J.; Harrison, C.; Goodwin, A. R. H.; Hsu, K. Operation of a vibrating wire viscometer with a wire radius of 0.207 mm in a fluid with nominal viscosity, at $T = 289.1$ K, of 1.581 Pa·s at temperatures between (289.1 and 420.7) K and a pressure of 0.1 MPa. *J. Chem. Eng. Data* **2007**, *52*, 1494–1496.

(28) Etchart, I.; Sullivan, M.; Jundt, J.; Harrison, C.; Goodwin, A. R. H.; Hsu, K. 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 $\mathrm{cm^3 \cdot s^{-1}}$ and viscosities less than 34 mPa·s. *J. Chem. Eng. Data* **2008**, *53*, 1691–1697.

(29) Correia da Mata, J. L.; Caetano, F. J. P.; Fareleira, J. M. N. A.; Oliveira, C. M. B. P. *Measurements of the Viscosity of Diisodecyl Phthalate (DIDP) with a Vibrating Wire Instrument Operated in Free Decay Mode of Oscillation*, 18th European Conference on Thermophysical Properties, Pau, France, 31 Aug.−4 Sept. 2008; in Book of Abstracts, pp 199−200.

(30) Oliveira, C. M. B. P. Viscosity of Liquid Hydrocarbons at High Pressure, PhD Thesis, Imperial College of Science, Technology and Medicine, London, United Kingdom, 1991.

(31) Caetano, F. J. P.; Fareleira, J. M. N. A.; Fröba, A. P.; Harris, K. R.; Leipertz, A.; Oliveira, C. M. B. P.; Trusler, J. P. M.; Wakeham, W. A. An industrial reference fluid for moderately high viscosity. *J. Chem. Eng. Data* **2008**, *53*, 2003–2011.

(32) Fröba, A. P.; Leipertz, A. Viscosity of diisodecyl phthalate by surface light scattering (SLS). *J. Chem. Eng. Data* **2007**, *52*, 1803–1810.

(33) Harris, K. R.; Bair, S. Temperature and pressure dependence of the viscosity of diisodecyl phthalate at temperatures between (0 and 100) °C and at pressures to 1 GPa. *J. Chem. Eng. Data* **2007**, *52*, 272–278.

(34) Caetano, F. J. P.; Fareleira, J. M. N. A.; Fröba, A. P.; Harris, K. R.; Leipertz, A.; Oliveira, C. M. B. P.; Trusler, J. P. M.; Wakeham, W. A. An Industrial Reference Fluid for Moderately High Viscosity - Supplementary Information. *J. Chem. Eng. Data:* **2008**, *53*, 2003–2011.

(35) Bauer, H. *Physikalisch-Technische Bundesanstalt (PTB)*; Braunschweig: Germany; cited in ref 31.

(36) Peleties, F. Advanced Fluid Property Measurement for Oilfield Applications, PhD Thesis, University of London, 2008.

(37) Poling, B. E.; Prausnitz, J. M.; O'Connell, J. P. *The Properties of Gases and Liquids*, 5th ed.; McGraw-Hill: NY, 2001. Original references: (a) Vogel, H. Das Temperaturabhängigkeitgesetz der Viskosität von Flüssigkeiten (The temperature dependence of the viscosity of liquids). *Physik. Z.* **1921**, *22*, 645–646. (b) Fulcher, G. S. Analysis of recent measurements of the viscosity of glasses. *J. Am. Ceram. Soc.* **1925**, *8*, 339–355. (c) Tammann, G.; Hesse, W. Die Abhängigkeit der Viskosität von der Temperatur bei unterkühlten Flüssigkeiten (The dependence of the viscosity on temperature for super-cooled liquids). *Z. Anorg. Allg. Chem.* **1926**, *156*, 245–257.

(38) Al Motari, M. M.; Kandil, M. E.; Marsh, K. N.; Goodwin, A. R. H. Density and viscosity of diisodecyl phthalate C6H4(COOC10H21)(2), with nominal viscosity at $T = 298$ K and $p = 0.1$ MPa of 87 mPa·s, at temperatures from (298.15 to 423.15) K and pressures up to 70 MPa. *J. Chem. Eng. Data* **2007**, *52*, 1233–1239.

(39) Harrison, C.; Sullivan, M.; Godefroy, S.; Matsumoto, N.; Goodwin, A. R. H.; Hsu, K. Operation of a vibrating wire viscometer at viscosities greater than 0.2 Pa·s: Results for a certified reference fluid with nominal viscosity at $T = 273$ K and $p = 0.1$ MPa of 0.652 Pa·s while stagnant and a fluid of nominal viscosity of 0.037 Pa·s while flowing. *J. Chem. Eng. Data* **2007**, *52*, 774–782.

Received for review January 28, 2009. Accepted April 20, 2009. This work was partially funded by the Pluriannual Funding to Centro de Química Estrutural from Fundação para a Ciência e a Tecnologia (FCT), Portugal, and is the continuation of the work developed under Project POCTI/34951/EQU/2000 that was supported by FCT, under Programa Operacional "CIÊNCIA, TECNOLOGIA, INOVAÇÃO" (POCTI), with European Union funds (FEDER) and National funds.

JE900113F