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# Viscosity of Di-isodecylphthalate: A Potential Standard of Moderate Viscosity[1]

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The paper reports our first measurements of the viscosity of di-isodecylphthalate, which is a candidate for a reference material. At the same time it has a viscosity, which, at room temperature, is around 120 mPa · s, so that it can fulfill the need for a reference material more nearly matched to the needs of industry. The present measurements were carried out with a specially designed vibrating-wire viscometer over the temperature range 288–308 K and have an estimated uncertainty smaller than ±1.5%, following calibration against the viscosity of toluene. The instrument and results are presented here to encourage other measurements on the same material, by different techniques, which will lead eventually to the establishment of di-isodecylphthalate as a suitable reference material, as well as reference values for its viscosity.

**KEY WORDS:** DIDP; di-isodecylphthalate; reference material; vibrating-wire technique; viscosity.

## 1. INTRODUCTION

The viscosity of fluids is a property of major economic importance, e.g., for the design of separation processes, for process control, or for measurement of flow rate. Its measurement is also often required for quality assurance of many products. Most of the currently used techniques for

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measuring the viscosity of fluids demand a calibration with an appropriate reference fluid, at the measuring temperature and pressure [1]. This imposes a higher limit to the attainable accuracy, namely because of the scarcity of reference fluids. In fact, all accredited viscosity measurements must be traceable to the viscosity of water at 20°C, under normal pressure [2]. There has been considerable controversy about the standard reference value under these conditions, and several new determinations of the property have been carried out since the original 1952 measurement by Swindells et al. [3]. However, the value of the viscosity used as a reference has remained intact, although the uncertainty limits around the value have been increased [2].

The industry concern with high viscosity fluids implies the routine measurement of viscosities several orders of magnitude higher than the water primary reference point. The calibration of a viscometer for that purpose, involves a succession of transfers from the viscosity of water, using a series of capillary viscometers along overlapping ranges of viscosity. The high costs involved, as well as the lower accuracy, resulting from error propagation, attained by this process has enhanced the recognized need for the establishment of reference fluids with high viscosity [4]. The Bureau International des Poids et Mesures has promoted a search for a suitable reference material for such a high viscosity standard and the measurement of its viscosity. The former subcommittee on Transport Properties of IUPAC has participated in this study, and the present paper proposes one contribution to this search.

The choice of a suitable reference material should take into account characteristics such as water solubility, vapor pressure, purity, toxicity, availability, and cost. The dialkyl esters of orthophthalic acid are substances with low water solubility, low volatility and are liquid over wide ranges of temperature. Furthermore, because of their structure, the length of the side chains influences a number of relevant physical properties. Moreover, due to their industrial applications, the safety profile of long-chain alkyl esters, like di-isodecylphthalate, has been widely studied [5,6], which is thought to provide the necessary basis for a future decision on their adequacy for the present purposes.

## 2. THEORETICAL DESCRIPTION

### 2.1. Background

The working principle of vibrating-wire viscometers operated in a free-decay mode has been largely described [7,8], as well as its rigorous theory [9]. In our laboratories in Lisbon, we have developed a vibrating-wire technique, which has been successfully applied to perform the simultaneous measurement of the viscosity and density of pure liquids [10–13] and mixtures [14] over wide ranges of temperature and pressure. The instrument used has been operated in a forced mode, so that the frequency response of the sensor is obtained experimentally. The operation of the sensor lies on the rigorous description of the hydrodynamic effects of the fluid on the vibrating-wire motion [15], and on its use as a hydrostatic balance. Its operation is thus supported on two basic principles of measurement, namely, a rigorous description of the hydrodynamics involved and the hydrostatic weighing principle, and it possesses a complete set of working equations [16]. Furthermore, we have recently developed a vibrating-wire instrument [17–19], which can be operated either in a forced mode by sweeping a range of frequencies, or in free-decay where the sensor is initially deflected and left to perform its free decaying oscillations. Both modes of operation are theoretically described, and consequently the viscosity can be obtained from the analysis of the resonance curve or from the time response of the sensor. The use of this cell has so far been restricted to perform measurements of the viscosity alone, showing total consistency between the results obtained by both operation modes within their mutual precision [17].

For the present work a new sensor has been designed and built in order to perform viscosity measurements, ranging from 0.5 to 120 mPa · s. This purposely built instrument, dedicated to viscosity measurements, was operated in the forced mode; therefore, the experimental parameters are the resonant frequency and the half-width of the resonance curve.

## 2.2. Theoretical Model

The theoretical description for the forced mode of operation has been published by Pádua et al. [16], and just a brief description of the working equations is given here. The wire's velocity resonant frequency, $\omega_r$, and the half-width of a resonance curve, $\Delta\omega = \omega_+ - \omega_-$, are related to the cell parameters through Eqs. (1) and (2):

$$\frac{d}{d\tilde{\omega}}\left\{\tilde{\omega}^2\left(\beta' + 2\Delta_0\right)^2 + \left[\tilde{\omega}\left(1+\beta\right) - \frac{\tilde{\omega}_0^2}{\tilde{\omega}}\right]^2\right\} = 0 \tag{1}$$

$$\frac{\tilde{\omega}_\pm\left(\beta' + 2\Delta_0\right)}{\tilde{\omega}_\pm^2\left(\beta' + 2\Delta_0\right)^2 + \left[\tilde{\omega}_\pm\left(1+\beta\right) - \frac{\tilde{\omega}_0^2}{\tilde{\omega}_\pm}\right]^2} = \frac{1}{2}\frac{\tilde{\omega}_r^2\left(\beta' + 2\Delta_0\right)}{\tilde{\omega}_r^2\left(\beta' + 2\Delta_0\right)^2 + \left[\tilde{\omega}_r\left(1+\beta\right) - \frac{\tilde{\omega}_0^2}{\tilde{\omega}_r}\right]^2} \tag{2}$$

In the above equations, the tilde above a symbol indicates a corresponding dimensionless quantity [16]; $\omega_0$ represents the natural frequency (in total absence of damping), and $\Delta_0$ is the wire internal damping, assuming that the axial tension on the wire is the same as for the oscillation in the fluid. The oscillation characteristics of the vibrating-wire sensor are dependent on the density, $\rho$, and viscosity, $\eta$, of the surrounding fluid through the functions $\beta$ and $\beta'$, defined as

$$\beta = (\rho/\rho_s)\,k \text{ and } \beta' = (\rho/\rho_s)\,k' \tag{3}$$

with

$$k = -1 + 2\mathfrak{Im}\,(A) \text{ and } k' = 2\mathfrak{Re}\,(A) \tag{4}$$

and

$$A = j\left[1 + \frac{2K_1\left(\sqrt{j\Omega}\right)}{\sqrt{j\Omega}K_0\left(\sqrt{j\Omega}\right)}\right] \tag{5}$$

The quantities $K_0$ and $K_1$ are modified complex argument Bessel functions, and $\Omega$ is a dimensionless frequency related to the Reynolds number for the fluid motion around the wire:

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

The working equations of the instrument are based on Eqs. (1) and (2) and are fully described in Refs. 18 and 19.

## 3. VIBRATING-WIRE SENSOR

The novel vibrating-wire sensor has been developed in order to fulfill the following basic requirements: (i) a single sensor should be able to perform measurements of viscosity in the range $0.5 \leqslant \eta \leqslant 120\,\text{mPa}\cdot\text{s}$; and (ii) the measurement precision should be of the order of ±0.5% over the whole range of operation. For this purpose, simulation studies were performed in order to optimize the physical parameters of the cell, namely, the radius and length of the wire sensor, and to determine other operating conditions that ensure the necessary quality factor for the resonance curves.

These studies were complemented by exploratory experimental tests [20] performed with toluene ($\eta \approx 0.55\,\text{mPa}\cdot\text{s}$ near 20°C) and dibuthylphtalate at atmospheric pressure and temperatures from 268 to 298 K ($16 \leqslant \eta \leqslant 90$ mPa·s). In addition, some operating conditions were defined, namely, the tension applied to the sensor, the resonance frequency, and the imposed drive current. Subsequently, a novel measuring cell has been constructed, bearing in mind that the inevitable departures from the ideal model must be rendered small.

As a consequence of the theoretical model, as well as practical restrictions on the construction, there are several constraints related to both the linear behavior of the sensor and to the geometry of the whole assembly that have to be followed. In particular, to ensure that the end effects are small, the half-length of the sensor should be significantly larger than its radius, which is verified, since the ratio of these two quantities is of the order of 150. An additional condition to ensure the linear behavior of the sensor is given by the dimensionless amplitude of the oscillation, $\varepsilon$, defined as $\varepsilon = (y_0/R) \leqslant 0.01$, where $y_0$ represents the maximum displacement of the oscillation and $R$ is the radius of the sensor. Furthermore, from fluid mechanics analysis, the following condition must be verified [9]:

$$\varepsilon \ll \Omega = \frac{\omega \rho R^2}{\eta} \ll \frac{1}{\varepsilon^2} \tag{7}$$

Moreover, the compressibility effects can only be neglected if the Mach number is small, which is given by the condition,

$$Ma = \frac{\omega \varepsilon R}{c} \ll 1 \tag{8}$$

where $c$ is the speed of sound.

A detailed analysis of the previous conditions, as well as the exploratory tests performed, led to the definition of the essential cell parameters and operating conditions. Hence, in order to measure with a single sensor a range of viscosities from 0.5 to 120 mPa · s, it was concluded that the sensor should have a nominal radius of ca. 200 $\mu$m and length of about 0.06 m. Concerning the operating conditions, it was assumed that the vertical tension applied to the wire should not exceed 50% of the wire material yield strength, leading to a resonant frequency of the order of 1 kHz. Regarding the ancillary electronic equipment, it has been estimated that the drive current necessary would be less than 30 mA for the complete range of viscosity.

A further matter of concern to the design is the selection of the minimum distance from the oscillating wire at which boundaries to the fluid may be placed without affecting the operation of the instrument, since the mathematical model was developed for the ideal situation of a fluid of infinite extent [9]. On one hand, it is desirable to have the greatest possible magnetic field, and hence to keep the magnets as close as possible, whereas on the other hand, in order to reduce the outer boundary effect, any wall should be as far from the wire as possible. The problem of finite boundaries in the measurement of viscosity with vibrating-body instruments has been tackled by Chen et al. [21]. Oliveira [7] has subsequently studied this effect for several values of the ratio of the radius of the container to the radius of the vibrating-wire sensor, $\sigma^* = R_{\text{container}}/R_{\text{sensor}}$. The latter author has shown that, provided $\sigma^* > 45$, for values of $\Omega$ between 1 and 90, the boundary effect on the viscosity does not exceed 0.5%. Using the aforementioned treatment [7], it is possible to estimate the maximum effect of the outer boundary on the viscosity, once the relevant cell parameters are known. For the current measurements, the closest distance of a cell component from the wire is of the order of 50 times the wire radius, and, assuming a cylindrical wall around the wire with $\sigma^* \approx 50$, it is found that the maximum correction on the viscosity results would be of the order of −0.18%.

## 4. EXPERIMENTAL SETUP

### 4.1. Cell Description

The cell has a tungsten wire (supplied by Goodfellow Cambridge Limited, UK), with a purity of 99.95% and nominal radius of 190 μm. The wire is clamped at both ends to two Inconel® plates by means of chucks fabricated from the same material. The plates are kept parallel and rigidly fixed by two 4 mm diameter tungsten rod spacers. Electrical insulation of the wire is provided using Ertacetal® washers. The mechanical arrangement was designed in order to enable the adjustment of the vertical tension on the wire by means of a fine threaded nut without torsion of the wire. Similarly, the rotation of the chuck necessary to minimize any torsional stresses is made possible without changing the vertical tension.

The cell is mounted inside a custom-made 316 stainless steel vessel. The electrical connections of the vibrating-wire are made using four copper leads, two for each end of the wire, which pass through the cap of the vessel by means of a custom-made feedthrough.

The magnetic circuit is made of soft iron and is composed of four NdFeB permanent magnets supplied by Sura Magnets (Sweden). The magnetic circuit is placed outside the vessel, and it is mounted on a device that enables its partial rotation relative to the vessel. The magnetic induction in the center of the gap between the magnetic poles, where the vibrating-wire is located, is ca. 0.6 $T$.

### 4.2. Instrumentation

For the present viscosity measurements, the vibrating-wire sensor has been used in the force mode of operation. For this purpose, a drive alternate current is passed through the wire, sweeping a range of frequencies that includes the resonant frequency. As the wire is subject to a uniform magnetic field, an oscillatory motion is developed, which by itself initiates an additional induced current in the wire.

A lock-in amplifier (Perkin Elmer Instruments, Model 7225) was used both as a sinusoidal current generator with an amplitude of 1.0 V rms, and as a voltmeter, to measure the voltage drop at the wire ends. The signal magnitude measurements were performed in the differential mode. The vibrating-wire sensor was connected in series with a resistance, including a variable resistor, to provide a simple means of controlling the current through the sensor. After several tests, it was observed that a current of 15–20 mA through the sensor, when immersed in di-isodecylphthalate, yielded an adequate response regarding both the signal-to-noise ratio and the restrictions of the theoretical model. For the measurements in toluene aimed at determination of the wire radius, the current used was 4 mA. The equipment was controlled by a personal computer through a IEEE-488 bus, and the data for each resonance curve were acquired and recorded together with the fluid temperature, determined by means of a platinum resistance thermometer, for subsequent processing.

### 4.3. Cell Parameters

The hydrodynamic model equations, Eqs. (1)–(6), incorporate several parameters that are independent of the fluid, namely, $\Delta_0$, $R$ and the wire material density, $\rho_S$. Once these and the density of the fluid sample are known, the viscosity of the fluid can be obtained from the resonant frequency and the width of the resonance curve.

The parameter $\Delta_0$ is obtained experimentally from the resonance curve of the sensor under vacuum [10], and the density of the wire is taken from the literature [22]. For the present purposes the wire radius is advantageously determined in a single experimental run under thermodynamic conditions where the viscosity of a reference fluid is well known. Hence, a single experimental run in the forced mode, with toluene as a reference fluid, was performed near 298 K and 0.1 MPa in order to obtain an effective average radius for the wire sensor. The viscosity and density reference data for toluene were taken from Gonçalves et al. [23] and Kashiwagi et al. [24], respectively. Given that the current cell is dedicated to viscosity measurements, the only calibration parameter is the wire radius, which is essentially determined from the viscosity of the calibration fluid. The actual cell parameters for the present setup, at 298 K, are shown in Table I.

## 5. EXPERIMENTAL RESULTS

The sample of di-isodecylphthalate (Merck p.a.), with a nominal purity of 99.5% by GC, was dried using molecular sieves (Riedel-deHaën,

**Table I.** Cell Parameters at 298 K

| | | |
|---|---|---|
| Radius of the wire | $R$ | $197.96 \times 10^{-6}$ m |
| Internal damping | $\Delta_0$ | $2.0 \times 10^{-4}$ |
| Wire density | $\rho_s$ | 19,230 $\text{kg} \cdot \text{m}^{-3}$ |

0.4 nm), and subsequently used without further purification. The water content of the sample determined by a Karl-Fisher titration analysis prior to the measurements did not exceed 20 ppm. The toluene used for the determination of the effective average radius of the wire, (Aldrich HPLC grade) with a minimum purity of 99.8%, was dried as described for DIDP, and its maximum water content, obtained by Karl-Fischer titration, was less than 8 ppm. The liquid samples were previously degassed with helium and introduced in the measurement cell under vacuum.

The present measurements were carried out over the temperature range 288–308 K and have an estimated uncertainty smaller than ±1.5%, following calibration against the viscosity of toluene. In Table II the results of the present measurements for the viscosity of di-isodecylphthalate are shown for several nominal temperatures. The viscosity datum given for each temperature is the mean value of the results obtained, at the respective temperature, for a minimum of six experimental runs. The standard deviation of the mean values is also shown in the table.

It should be noted that, because of the lack of accurate density data for di-isodecylphthalate, experimental measurements that will be reported elsewhere were performed using an automatic Anton Paar densimeter (Model DMA 5000). These measurements were carried out over the same temperature range as the present viscosity results and have an estimated precision of ±0.01%. It should be pointed out that a sensitivity analysis has shown that an uncertainty of ±0.1% in the density yields an uncertainty of ±0.05% in the viscosity.

**Table II.** Experimental Viscosity Measurements for Di-isodecylphthalate

| $T$(K) | $\eta$(mPa · s) | $\sigma$(%) |
|---|---|---|
| 288.32 | 174.06 | 0.25 |
| 293.29 | 120.96 | 0.05 |
| 298.22 | 86.72 | 0.03 |
| 303.22 | 64.19 | 0.06 |
| 308.12 | 48.73 | 0.06 |

**Table III.** Fitting Parameters of Eq. (9)

| | |
|---|---|
| $A$ | −2.4469 |
| $B$(K) | 748.9464 |
| $C$(K) | −189.8620 |

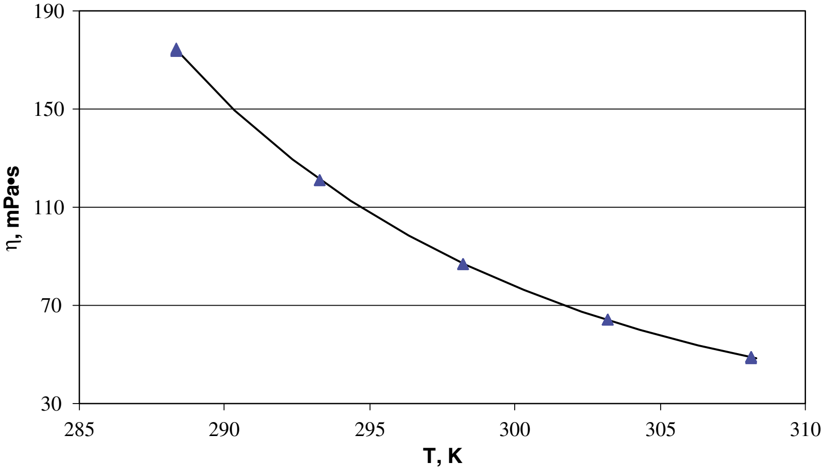

**Fig. 1.** Experimental viscosity data of di-isodecylphthalate, as a function of temperature. ▲ Experimental data; ——— Fitting equation (Eq. (9)).

The complete set of experimental data was fitted with an equation of the form,

$$\eta\,(\text{mPa}\cdot\text{s}) = \exp\left(A + \frac{B}{C+T}\right) \tag{9}$$

where $A$, $B$, and $C$ are empirically determined parameters. In Table III the values of the parameters of Eq. (9), obtained by a statistically weighted fitting procedure, are shown. The statistical weight of each datum has been assumed to be the inverse of the standard deviation for the corresponding nominal temperature, as shown in Table II.

Figures 1 and 2 show the viscosity of di-isodecylphthalate as a function of temperature, and the deviation plot of the complete set of experimental measurements from the fitting equation, Eq. (9), respectively. Comparison of the present results is hindered by the lack of published measurements. Nevertheless, it should be pointed out that H. Bauer, Physikalisch-Technische Bundesanstalt, Braunschweig, Germany, (pers. commun.) has performed some measurements of the viscosity of

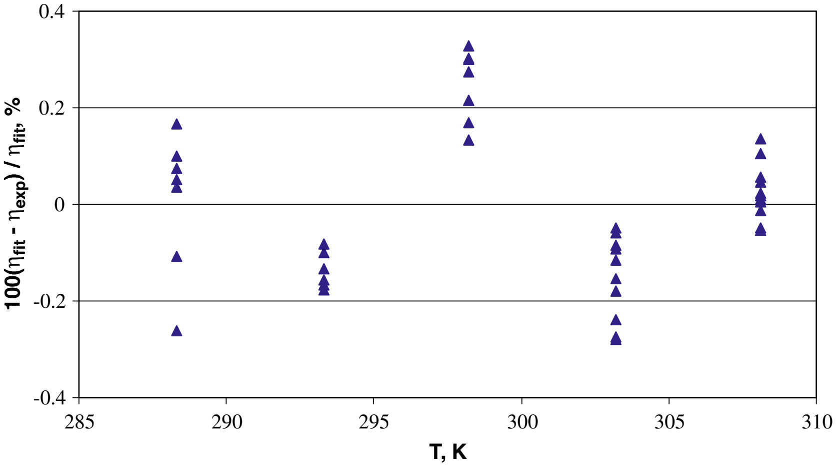

**Fig. 2.** Deviations of viscosity measurements from the fitting equation, Eq. (9).

di-isodecylphthalate at 20°C using capillary viscometers on a sample of the same origin as the one used in the present work (Merck p.a.), and the results obtained differ from the data correlation, Eq. (9), by +1%, which is within the estimated uncertainty of the measurements.

## 6. CONCLUSIONS

It should be remarked that the viscosity of di-isodecylphthalate at the lowest temperature significantly exceeds the upper limit of 120 mPa · s, which has been established as a design objective for the present instrument. Notwithstanding this point, the estimated precision of the measurements, even at such high viscosity, is still compatible with our design goals. The results obtained for the other temperatures show that the present instrument is capable of performing measurements of viscosity in the range $0.5 \leqslant \eta \leqslant 120\,\mathrm{mPa \cdot s}$ with a precision well within ±0.5%. It is expected that the overall uncertainty of the results obtained with this type of sensor can still be improved, in particular, when calibration against the primary reference point (water at 20°C) is made possible. Further experimental work on the same material, using different techniques, will be necessary regarding the establishment of di-isodecylphthalate as a suitable viscosity reference material.

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