New Measurements of the Viscosity of Diisodecyl Phthalate Using a Vibrating Wire Technique

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Diisodecyl phthalate (DIDP) has been proposed as a suitable reference material for industrial application in the region of moderately high viscosity. The paper reports a new set of viscosity measurements of a 99.5 % GC sample of this substance, which are directly traceable to the primary standard reference value—the viscosity of water at 293.15 K. The present measurements, performed with a vibrating-wire sensor, were carried out at atmospheric pressure over the temperature range (283 to 313) K. Over this temperature range, the viscosity varies from approximately (37 to 267) mPa·s. The measurements have been carried out with an instrument that has already been the subject of improvement since the first measurements were performed, and it relies upon calibration exclusively against the primary standard of viscometry. The estimated overall uncertainty of the results does not exceed ± 1 %, over the whole range of the measurements and, for the results obtained at temperatures in the vicinity of 293 K, is ± 0.8 %. The higher quality of the present measurements, and their direct traceability to the primary reference value for viscosity, justifies the replacement of our earlier set of preliminary data on DIDP viscosity.

Introduction

In an earlier publication,[1] we drew attention to the need for a reference fluid with moderately high viscosity, in large measure to avoid the step-up procedures for calibrating capillary viscometers, which are currently inevitable owing to the existence of a single primary reference value for viscosity, water at 293.15 K. Diisodecyl phthalate (DIDP) possesses good general characteristics to be such a new reference fluid,[1] with viscosity around 120 mPa·s at room temperature. Among these are its low vapor pressure, low water solubility, and an extensive liquid-phase stability temperature range. Moreover, due to their many special industrial applications, the safety profile of long-chain alkyl esters, like DIDP, has been widely analyzed,[2,3] which will certainly provide the necessary basis for a future decision on the adequacy of DIDP to be a reference fluid with respect to safety requirements. In a previous article,[1] we reported a set of preliminary measurements of the viscosity of DIDP that were performed using a vibrating-wire instrument designed to operate over a large range of values of the viscosity. Following this initial set of measurements, the apparatus and the experimental technique were developed,[4] in order to improve the overall uncertainty of the measurements and to expand the available range of viscosity. The performance of the instrument was assessed[4] by means of a program of measurements of certified reference materials with viscosity around 100 mPa·s and of a liquid (2,2,4-trimethylpentane) with viscosity around 0.5 mPa·s at room temperature, after calibration with water at 293.15 K. Those tests have spanned a range of viscosity $0.5 \leq \eta \leq 135$ mPa·s and gave indication that the overall uncertainty is of the order of ± 0.8 %. One of the major improvements made to the experimental technique since the first measurements[1] resides in the direct traceability of the measurements to the water standard reference value, water at 293.15 K.[5,6] The significantly higher quality of the measurements performed with this improved technique justifies the publication of the new set of results, taking into account the ultimate purpose of the range of studies carried out with DIDP.

Experimental Section

Fluid Samples. The samples of DIDP used for the viscosity measurements with the vibrating-wire technique were obtained from Merck, with the grade "for analysis" (CAS Registry No. 26761-40-0), lot no. 328. The respective quality certificate (1.03622.1000 diisodecyl phthalate GR acc. to DIN 752001, batch K22132622) indicates a minimum purity of 99.8 % by GC and states that the IR spectrum conforms to the identity of the product. The samples were previously dried with molecular sieves (Riedel-deHaën, 0.4 nm) and subsequently used without further purification. The water content of the samples was monitored by Karl-Fisher coulometric titration, both before and after the measurements, being less than 20 mg/kg in both instances. Further viscosity studies[7] have shown that, at around room temperature, an increase of the sample's water content, by a factor of 5 leads to a decrease of about 0.5 % in its viscosity. Therefore, it is deemed that the amount of water present in the sample used does not contribute significantly to the uncertainty of the viscosity results. The samples were previously degassed with helium and introduced in the measurement cell under vacuum.

It is noteworthy that products with the designation DIDP are available commercially under two CAS Registry Nos.[8]—068515-49-1 (1,2-benzenedicarboxylic acid, di-C9−

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11-branched alkyl esters, C10-rich), and 026761-40-0 (diisodecyl phthalate or di-"isodecyl" phthalate). Identification of both products as a mixture of isomers can be found in the literature.[8] In particular, diisodecyl phthalate has been described as a mixture of isomers (e.g., by Earls et al.[9] and by Gómez-Hens and Aguilar-Caballos[10]). Aiming at a more complete characterization of its purity, the sample used in the present work was further analyzed using analytical facilities of Centro de Química Estrutural. The techniques employed were ^{1}H NMR, ^{13}C NMR, and gas chromatography−mass spectroscopy (GC−MS). In particular, the conformity of the ^{1}H NMR spectrum with the molecular structure attributed to DIDP (CAS Registry No. 026761-40-0)[11] has been verified, which corresponds to bis(8-methylnonyl) phthalate. However, the ^{13}C NMR spectrum obtained with our sample seems to evidence the presence of impurities, which we could not identify but are possibly isomers. No analysis of ^{13}C NMR spectra of DIDP has been found in the literature for comparison. The GC−MS analysis carried out for the present sample is compatible with the presence of the substance with the structural formula indicated above[11] for DIDP, but the presence of isomers in significant amounts cannot be excluded. In particular, the chromatogram obtained shows a broad peak which, in accordance with the observation of Earls et al.,[9] suggests the presence of a mixture of isomers.

From the point of view of a standard reference material and the standard values of the viscosity, the purity of the sample is rather less important than the fact that the impurities present do not affect the viscosity of the sample by an amount greater than the uncertainty in the reference value of viscosity, even if the impurities vary from sample to sample. Other studies conducted in our group seem to indicate that the ester content as indicated by GC analysis has a significant effect on the viscosity of the DIDP samples. Further work on characterizing our sample and tests upon samples of similar purity grade obtained from different suppliers is ongoing in our group. It is hoped to demonstrate that DIDP samples from a number of different sources with possibly different impurities or different distribution of isomers have essentially the same viscosity within the tolerance of the standard reference value. It is this evidence that will finally confirm the suitability of DIDP as a standard reference material.

To further characterize the sample, its refractive index was measured using an Abbe 60/ED refractometer with a sodium lamp. The instrument was calibrated using a test plate ($n_D^{20} = 1.51628$), with monobromonaphthalene as the contact liquid. The refractive index obtained at 293.15 K was 1.4845, in good agreement with the value supplied in the Merck Technical Data Sheet[12] at the same temperature (namely, 1.485).

Vibrating-Wire Cell Parameters. The present instrument has been modified in order to improve its performance. As described elsewhere,[4] simplifications were introduced in the electrical circuitry that increased the accuracy of the evaluation of the resonance curve parameters and the reduction of the electrical noise of the measurements. Also the limitation on the accuracy imposed by the choice of the calibration fluid has been surmounted by calibrating the instrument with water at 20 °C, the primary reference value for viscosity. The apparatus and the technique used as well as its operation in the forced mode have been abundantly described in the literature.[4,13−15] The cell parameters for the present measurements are shown in Table 1. They are the internal damping coefficient (Δ_0) of the vibrating wire, obtained from experiments under vacuum, the density,[16] and the radius of the wire. As explained before,[4] the wire radius of the vibrating-wire sensor was obtained by calibration against water at 293.15 K from a series of reference experiments. The water used in these measurements was previously distilled and deionized by a Millipore system (Milli-Q Plus). The value of the wire radius shown in Table 1 is the mean of the results obtained in nine experiments with a standard deviation of 0.01 %. The sensitivity of the viscosity results to the uncertainties of the cell parameters has been addressed previously.[4] The most important parameter concerning the overall uncertainty of the viscosity measurements is the wire radius—an uncertainty of ± 0.1 % in the radius alone leads to an uncertainty of ± 0.2 % in the viscosity.[4] The present measurements of the viscosity of DIDP were carried out at atmospheric pressure over the temperature range of (283 to 313) K.

Table 1. Cell Parameters at 293.15 K

radius of the wire	R	199.45 μm
internal damping	Δ_0	1.8×10^{-4}
wire density	ρ_s	19.23×10^3 kg·m^{-3}

Table 2. Fitting Parameters of Equation 1

A_0/(kg·m^{-3})	1464.5011
A_1/K^{-1}	−3.6265
A_2/K^{-2}	0.009768
A_3/K^{-3}	-1.09×10^{-5}

Results

The evaluation of the viscosity of a test fluid from measurements of the resonance of the vibrations of the wire has been carried out as described earlier.[1,4] In view of the lack of literature density data for diisodecyl phthalate, experimental measurements 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 repeatability of ± 0.01 %. The complete set of experimental data was fitted to an equation of the form:

$$\rho/(\mathrm{kg\cdot m^{-3}}) = \sum_{i=0}^{3} A_i T^i \qquad (1)$$

with a standard deviation of ± 0.002 %. The empirically determined parameters, A_i, are shown in Table 2. These results have been compared with measurements kindly provided by Bauer,[17] Physikalisch-Technische Bundesanstalt, Germany (at 293.15 K), and by Fröba and Leipertz (at 278.15 ≤ T ≤ 323.15 K),[18] which were personally communicated to the authors. The results obtained by those authors at temperatures within the temperature interval of the current measurements do not in any case deviate by more than ± 0.01 % from the values obtained in this work. It should be noted that the samples used by those authors were of the same purity grade as the samples used in the present work—Merck "for analysis"—but were used without any treatment.

The overall uncertainty of the present density measurements is estimated not to exceed ± 0.1 %. A sensitivity analysis[1] indicated that, as a consequence of this uncertainty, the corresponding propagated uncertainty to the viscosity measurements should be less than ± 0.05 %. Previously,[4] we have shown that the instrument is able to perform viscosity measurements up to 135 mPa·s with an uncertainty better than ± 0.8 % where the uncertainty of the primary reference point for viscosity is taken into

Table 3. Experimental Viscosity Measurements of Diisodecyl Phthalate as Function of Temperature under Atmospheric Pressure along with Values of Density (ρ) Determined by Equation 1 and with Values of Standard Deviation for Viscosity

T/K	ρ/kg·m^{-3}	η/mPa·s	σ/%
283.16	973.52	267.36	0.12
288.26	969.85	176.04	0.22
293.21	966.38	123.07	0.10
293.21	966.38	122.75	0.07
298.24	962.82	87.797	0.12
303.21	959.30	64.838	0.16
308.20	955.78	48.728	0.08
313.21	952.22	37.571	0.12

Table 4. Fitting Parameters of Equation 2

A	−2.623
B	786.74
C	−187.38

account. It is reasonable therefore to assert that the measurements of viscosity up to this value, carried out in the present work, have an estimated overall uncertainty of approximately ± 0.8 % where, naturally, no account is made of the uncertainty due to the impurity of the sample. This upper viscosity limit is determined by the certified viscosity values provided for the standard reference fluids used in our previous work and do not stem from any inherent limitation of the instrument. Thus, as stated before,[4] the utilization of the instrument at somewhat higher viscosity is expected to be possible without a serious loss of precision. The increase in the uncertainty of the present results, due to an increase in the viscosity of the samples, is primarily caused by a concomitant loss of the quality factor of the frequency response of the sensor. Therefore, this increased uncertainty in the viscosity results is easily estimated by a simple error propagation analysis of the uncertainty of the parameters of the model working equation, mainly owing to the increased uncertainty of the half-width of the experimental resonance curve. Upon such an analysis it is deemed that the overall uncertainty is ± 1 % for the highest value of viscosity measured in the present work. The repeatability of the present results is estimated to be of the order ± 0.5 % at a 95 % confidence level.

Table 3 contains the results of the present measurements for the viscosity of diisodecyl phthalate at several nominal temperatures and under atmospheric pressure as well as the fitted density values. The corresponding viscosity values vary from (37 to 267) mPa·s. 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 (σ), which is commensurate with the reproducibility of the measurements, is also shown on the same table.

The complete set of experimental viscosity data was fitted to an equation of the form:

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

with a standard deviation of ± 0.38 %. The fitting parameters A, B, and C are shown in Table 4. Figure 1 shows the deviation plot of the complete set of experimental measurements from the fitting equation (eq 2). Comparison of the present results with earlier data is hindered by the lack of published measurements. For comparison purposes, we make use of the data obtained by Bauer[17] with a capillary viscometer (Physikalisch-Technische Bundesanstalt, Germany) and data by Fröba and Leipertz[18] obtained by surface light scattering technique, which have been personally communicated to the authors. As stated above, the samples of DIDP used by those authors were of the same purity grade as the one used in the present work (Merck for analysis). However, those authors did not subject their samples to any treatment. As a consequence, a deviation of their results from the present work may be expected on account of the different water content of the samples. On the basis of an experimental study referred above,[7] this deviation is deemed not to exceed −0.5 %.

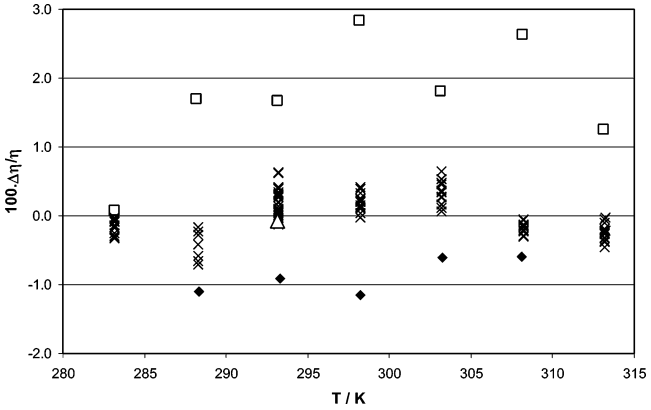

Figure 1. Deviation, $\Delta\eta/\eta$, of the viscosity measurements of DIDP from fitting equation (eq 1). ×, this work; △, data obtained by Bauer;[17] □, data obtained by Fröba and Leipertz;[18] ◆, data from previous work.[1]

Table 5. Comparison of DIDP Viscosity Measurements at 293.15 K, Obtained with Different Techniques[a]

method	η/mPa·s	±100·u[b]	$100\Delta\eta/\eta_{exp}$[c]
present work	123.28	0.8	
capillary[d]	123.19	0.31	+0.08
SLS[e]	125.34	1.5	+1.67
capillary[f]	121.71	1.5	−1.27

[a] All the measurements were made with samples of identical purity grade. [b] Uncertainties (u) as cited by the authors of original work. [c] $\Delta\eta/\eta$ is defined as $(\eta - \eta_{exp})/\eta_{exp}$. [d] Data obtained by Bauer.[17] [e] Data obtained by Fröba and Leipertz.[18] [f] Measurements performed[7] with a suspended level capillary viscometer, calibrated with certified reference specimen PTB100B.[4]

In Figure 1 the deviations of those data from the correlation of the present results are included. Table 5 summarizes the available viscosity data, at 293.15 K and at atmospheric pressure, on this grade DIDP (CAS Registry No. 26761-40-0, diisodecyl phthalate GR acc. to DIN 752001, batch K22132622). Included in this table is a set of measurements performed with a suspended level capillary viscometer, to be reported elsewhere.[7] An analysis of Figure 1 and Table 5 reveals that all the reported data differ from the present correlation by less than the nominal mutual uncertainty of the measurements. It is noteworthy the excellent agreement with the accurate datum obtained by Bauer, the deviation being less than 0.1 %.

Conclusions

The paper provides new data on the viscosity and density of liquid DIDP near room temperature and at atmospheric pressure. It should be remarked that the viscosity of the measured sample of DIDP at the lowest temperature is approximately twice the upper limit of 120 mPa·s, which has been established as a design objective for the present instrument.[1,4] Notwithstanding this point, the estimated precision of the measurements, even at such high viscosity, is compatible with our design goals. The overall uncertainty

of the results obtained with this type of sensor was improved when calibration against the primary reference point (water at 293.15 K) was made possible. The results obtained for the temperature interval covered shows that the present instrument is capable of performing measurements of viscosity in the range ($0.5 \leq \eta \leq 270$) mPa·s with a precision within ± 0.5 % and an overall uncertainty less than ± 1 %. The agreement with the scarce experimental data available with the present results is well within the nominal mutual uncertainty of the measurements. Further experimental work on the same material, using different techniques, will be necessary regarding the establishment of DIDP as a suitable viscosity reference material, in addition to the study of the effect of different impurities, or different distribution of C10 branched alkyl ester isomers on the viscosity of the sample.

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