Viscosity of Diisodecyl Phthalate by Surface Light Scattering (SLS)

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Surface light scattering (SLS) has been used for the measurement of the viscosity of diisodecyl phthalate (DIDP), a potential candidate for an industrial reference material in the moderate- to high-viscosity region from (0.01 to 1) Pa•s. The investigations reported here were stimulated by recent research activities of the International Association for Transport Properties (IATP), which aim at evaluating a recommendation concerning standard reference values for DIDP at moderately high viscosity at room temperature. For this purpose, the measurement of the viscosity of DIDP using viscometers of different types and operating principles was encouraged. Even though in the case of high-viscosity fluids reference data for the interfacial tension are needed for data evaluation, the integration of the SLS method within this project is particularly interesting. In contrast to conventional viscometers, SLS allows the determination of viscosity in macroscopic thermodynamic equilibrium. Furthermore, whereas almost all conventional methods determine the viscosity in a relative manner, for the SLS technique no calibration procedure using a fluid of known viscosity is needed. In the present work, for temperatures between (283.15 and 313.15) K, corresponding to a viscosity range of about (250 to 50) mPa•s, an expanded uncertainty ($k = 2$) of less than ±1.4 % could be achieved for the viscosity of DIDP by carrying out a data evaluation procedure based on an exact description of the hydrodynamic capillary wave problem for a free liquid surface.

Introduction

For performing accredited and/or accurate viscosity measurements on liquids, the majority of viscometers need to be calibrated or verified with an adequate certified reference material.[1,2] Many national metrology institutes or certified producers provide a great assortment of reference liquids with Newtonian behavior, corresponding to a viscosity range generally extending from (0.001 to 1000) Pa•s. The calibration traceability of all reference fluids is based on a kinematic viscosity of $\nu = 1.0034\ \mathrm{mm^2 \cdot s^{-1}}$, which corresponds to water at $T = 293.15$ K and atmospheric pressure and represents, until now, the only internationally agreed value in accordance with ISO/TR 3666-1998.[3,4] Starting from the viscosity of water, the viscosity of a reference liquid is determined using a series of master capillary viscometers along overlapping ranges of viscosity. Not only the number of single steps, and by this the costs, but also the uncertainty associated with this so-called “step-up” procedure increases from the low- to the high-viscosity region. The relative uncertainty of the viscosity of reference liquids provided by the national metrology institutes, for example, the Physikalisch-Technische Bundesantalt (PTB) in Germany, is typically between (0.2 and 1.0) % of their value.[5,6] Provided that the reference materials are handled with special care, as stipulated in their certificates, the viscosity values stated therein are typically valid for time periods varying between 2 and 12 months. The more or less limited minimum durability of reference materials, for example, petroleum oils, polyisobutenes, silicone oils, and undefined polymers, is particularly founded in their indeterminate composition changing with time.[1]

The high costs resulting from the time-consuming calibration procedure of the reference fluids and their limited shelf life have stimulated the search for an alternative reference fluid in the moderate-viscosity region (100 mPa•s), which can be used for industrial purposes and simply purchased from chemical suppliers. Of course, such an alternative reference fluid can never substitute for internationally agreed upon standardization procedures associated with the measurement of viscosity, yet it could result in a readily available working reference material, which may simplify the calibration and performance check of instruments in industrial practice. Within recent research activities of the International Association for Transport Properties (IATP), diisodecyl phthalate (DIDP) was suggested as a potential candidate for an industrial standard of moderately high viscosity.[7] Besides having a viscosity of about 125 mPa•s at a temperature of 293.15 K, the most advantageous characteristics of DIDP can be summarized as follows. DIDP is a chemically stable material with low vapor pressure; it is nontoxic, relatively inexpensive, and available throughout the world. However, the fact that DIDP can be very likely purchased from suppliers only as an isomeric mixture could hinder its establishment as a future reference material, as recently revealed by Caetano[8] and Harris and Bair.[9] They have shown that DIDP samples from different commercial sources are actually mixtures of phthalate esters of a wide range of isomers of isodecyl alcohol. Different grades with differences in purity and/or composition, including differences in the distribution of isomers, can result in differences in the viscosity. Nevertheless, DIDP may still be a potential moderate- to high-viscosity calibrant for industrial viscometers, provided that one grade from one source is agreed upon for this purpose. Apart from studying the effect of impurities and/or composition on the viscosity, under the auspices of IATP, investigations carried out in several laboratories throughout the world[10] concentrated mostly on a selected batch of DIDP from Merck KGaA, Darmstadt, Germany (grade for analysis according to DIN 75201, ordering no. 1.03622.1000, batch no. K22132622), with a nominal purity of higher than 99.5 %. By

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a gas chromatography assay of this selected batch a purity of higher than 99.8 % was certified.

Within the past 3 years, the same material was also the subject of our individual research activities at the Department of Engineering Thermodynamics (LTT) in Erlangen. These were motivated by the desire both to contribute to the verification and improvement of the recommendation of DIDP as a future industrial reference material and to test the surface light scattering (SLS) technique. Research based on the latter is the subject of two forthcoming publications. One is dedicated to the accurate determination of dynamic viscosity of high-viscosity fluids[11] and the other to the simultaneous determination of viscosity and interfacial tension, passing the critical damping of surface waves, which has been demonstrated for DIDP at temperatures between (323.15 and 433.15) K.[12] The present paper, on the other hand, summarizes all of our SLS investigations of the viscosity of DIDP carried out within a temperature range between (273.15 and 323.15) K, whereas three independent measurement series were performed for the same sample, yet under different experimental conditions with regard to its water content and preparation procedure.

In the following experimental section, only some characteristics of the SLS method, especially with regard to its application to high-viscosity fluids, and some special features of the SLS experiment are noted, with which the dynamics of surface fluctuations may be analyzed with high accuracy. The experimental conditions and the sample preparation procedure are described in detail. The latter was different for the three independent SLS measurement series performed in the years 2003, 2005, and 2006 for the same DIDP sample from Merck KGaG, Darmstadt, Germany (see above) in the temperature range between (273.15 and 323.15) K. The uncertainties and experimental conditions for the complementary measurements techniques used within this work for the determination of density and interfacial tension are briefly stated. Subsequently, the results of the three independent experimental runs will be compared. Finally, for a specific run, the data for the viscosity of DIDP will be compared to data originating from other techniques. In comparison to these, the main advantage of the SLS technique relies on the possibility of determining the viscosity in macroscopic thermodynamic equilibrium, in an absolute way, without the need of any calibration procedure involving a fluid of known viscosity.

Experimental Section

Surface Light Scattering. Here, a more specific treatment of the theory of SLS was used, by inspecting the hydrodynamic capillary wave problem in the limiting case of a free liquid surface, neglecting the presence of a second fluid phase. For the present investigations of a phase boundary between DIDP and air at atmospheric pressure, this can be done without any significant loss of accuracy because the vapor properties are very small compared to the respective liquid quantities.[11] In this case, the decay dependence on time t of a particular surface mode of the form ex[[i$\vec{q}\vec{r}$ + iαt], with a wave vector $\vec{q}$ at a given point $\vec{r}$, is obtained from the dispersion equation[13]

$$\left(\mathrm{i}\alpha + \frac{2\eta q^2}{\rho}\right)^2 + \frac{\sigma q^3}{\rho} + gq - \frac{4\eta^2 q^4}{\rho^2}\sqrt{1 + \frac{\mathrm{i}\alpha\rho}{\eta q^2}} = 0 \qquad (1)$$

where g is the acceleration of gravity and η, σ, and ρ are the dynamic viscosity, interfacial tension, and density of the liquid, respectively. In general, two physical solutions for the temporal decay of surface fluctuations and thus for the complex frequency α have to be considered. In the case of low viscosity and/or large interfacial tension, surface fluctuations show an oscillatory behavior corresponding to the complex frequency $\alpha_{1,2} = \pm\omega_q + \mathrm{i}\Gamma$, where the real part represents the frequency ω_q and the imaginary part the damping Γ of the surface mode observed. In the case of high viscosity and/or low interfacial tension, as was relevant within this work, surface fluctuations are overdamped and do not propagate ($\omega_q = 0$). In this case, the complex frequency is associated with two different damping rates, $\alpha_{1,2} = \mathrm{i}\Gamma_{1,2}$. As a first-order approximation, the complex frequency can be represented by

$$\alpha_{1,2} \approx \pm\sqrt{\frac{\sigma q^3}{\rho} + gq} + \mathrm{i}\frac{2\eta q^2}{\rho} \qquad (2)$$

or

$$\alpha_1 \approx \mathrm{i}\frac{q}{2\eta}\left(\sigma + \frac{g\rho}{q^2}\right) \quad \text{and} \quad \alpha_2 \approx \mathrm{i}\ 0.9\frac{\eta q}{\rho} \qquad (3)$$

assuming that the decay of surface waves is oscillatory or overdamped, respectively. In principle, for both cases viscosity and interfacial tension can be determined simultaneously by probing frequency and/or damping of surface fluctuations within the SLS experiment. Whereas in the case of an oscillatory behavior this is a straightforward task and, meanwhile, the SLS technique is well-established for measuring viscosity and surface tension with high accuracy,[14] in the overdamped case only under special conditions can both properties be accessed simultaneously.[12] For the present investigations of DIDP over the temperature range of (273.15 to 323.15) K, however, from the two modes decaying at different rates, only that one associated with α_1 could be resolved. By this, as a first-order approximation and neglecting the forces of inertia, cf. eq 3, SLS gives only access to the ratio of dynamic viscosity η to interfacial tension σ. For this purpose the decay behavior or mean lifetime $\tau_{C,1}$, $\tau_{C,1} = 1/\Gamma_1 \approx 2\eta/(\sigma q)$, of surface fluctuations at a given wave number q is analyzed. For a detailed and comprehensive description of the fundamentals and methodological principles of SLS, the reader is referred to the specialized literature.[13−17]

The experimental setup used here for the investigation of DIDP is the same as that employed in our former SLS investigations for numerous pure refrigerants,[18] refrigerant mixtures,[19,20] and reference fluids[14,21] and includes a laser (Coherent, Verdi-2V; laser wavelength in vacuo $\lambda_0 = 532$ nm; operated at 100 mW), correlator (ALV, Fast-Corr 6/256), optical and electro-optical parts, sample cell (aluminum; inner diameter, 70 mm; volume, 150 cm^3), and thermostat. Scattered light is detected in the forward direction near refraction perpendicular to the surface plane at variable and relatively high wavenumbers. For this arrangement, the modulus of the wave vector, $q = 2\pi/\lambda_0 \sin(\Theta_E)$, of the observed surface vibration mode can be deduced as a function of the easily accessible angle of incidence, Θ_E. For the experiment, the angle of incidence Θ_E was set between 3.0° and 4.0° and measured with a high-precision rotation table with an uncertainty of ±0.005°. Whereas the lower limit is chosen to make instrumental broadening effects negligible, the upper limit of 4.0° is imposed by the excessively weak scattering signal above this angle. The temperature of the cell was measured with two calibrated 100 Ω platinum resistance probes integrated into the main body of the vessel, with a resolution of 0.25 mK, using an ac bridge (Anton Paar, MKT 100). The uncertainty of the absolute temperature measurement was less than ±15 mK. The temperature stability during an experimental run was better than ±1 mK. For each temperature, at least six measurements at different angles of incidence were performed.

In the present work, however, data for the dynamic viscosity η of DIDP were obtained by an exact numerical solution of the dispersion relation, eq 1. For this, data obtained for the dynamics of surface waves, that is, the mean lifetime $\tau_{C,1}$ at a defined wave vector q, were combined with reference data for the interfacial tension σ and density ρ. For the latter, even approximate or less accurate values with an uncertainty of ±10 % allow a successful determination of the dynamic viscosity. Although the use of eq 3 for data evaluation does not allow the determination of the dynamic viscosity with high accuracy, the approximation can be applied to get a good estimate for the uncertainty of our SLS results in an analytical manner by combining in quadrature the errors for the interfacial tension σ, mean lifetime $\tau_{C,1}$, and wave vector q. For the relative uncertainty of the interfacial tension σ, a value of ±0.5 % has been estimated by Caetano et al.[22] Taking into account relative uncertainties of clearly less than (±0.5 and ±0.15) % for the mean lifetime $\tau_{C,1}$ and wave vector q, respectively, the expanded uncertainty ($k = 2$) of our values for the dynamic viscosity η is estimated to be less than ±1.4 %.

Sample Preparation Procedure. For the first SLS measurement series performed in the year 2003, the sample was filled into the measurement cell from the original flask with the help of a syringe, without further treatment. Yet, before this first series was begun, the sample was heated to and kept at a temperature of 373.15 K for several hours, to expedite the disappearance of small air pockets, or bubbles, which originated from the filling procedure and had led to a strong disturbing signal caused by Mie scattering. The actual water content of the sample investigated in this first series within a temperature range between (273.15 and 313.15) K is unknown. However, a maximum water content of 392 ppm could be estimated for this first sample by a Karl Fischer coulometric titration of the sample, left in its original flask until the year 2006. The expanded uncertainty ($k = 2$) of this and all further water content determinations performed within this work is estimated to be less than 20 %.

For the second SLS measurement series, performed in the year 2005, once again the sample was first filled from the original flask into the sample cell via a syringe. Thereafter, an oil-sealed vacuum pump was attached via a cooling trap immersed in liquid nitrogen to the measurement cell, with the purpose of lowering the water content of the sample, which was exposed to a vacuum of 0.5 mbar for about 20 min at room temperature, until boiling phenomena disappeared. The sample was investigated without prior heating within a temperature range between (273.15 and 323.15) K. A water content of 287 ppm was determined by Karl Fischer coulometric titration directly after the SLS measurements.

In the year 2006, a third SLS measurement series was performed, especially motivated by the need to characterize DIDP at a relatively low water content. For this purpose, the sample was treated according to the following preparation procedure prior to filling of the measurement cell. First, about 300 mL of the sample with a water content of 392 ppm was decanted from the original flask into a special glass cylinder equipped with two ports and containing a volume of about 1 L. The filling port was closed with a rubber stopper and the pump port connected to an oil-sealed vacuum pump via a cooling trap, which was immersed in liquid nitrogen. By this, for a period of 3 h, the cylinder, and thus also the sample, was exposed to a vacuum of 0.5 mbar. During this time, the glass cylinder was immersed in a thermostated water bath with a temperature of about 333.15 K. Once again, boiling phenomena could be observed during the first 20 min. After application of the vacuum, the sample was filled directly from the glass cylinder into the measurement cell under ambient conditions. Thereafter, the measurement cell was sealed or closed immediately, and SLS measurements were performed for temperatures between (283.15 and 313.15) K. The sample investigated within this third measurement series had a water content of 151 ppm, which could be determined once again by Karl Fischer coulometric titration directly after the conclusion of the measurements. It is worth mentioning that, at the time of disassembling the cooling trap, residuals with a characteristic smell could be detected in it.

The same characteristic smell could also be detected after a sample had been heated to temperatures up to 433.15 K within a further SLS measurement series, dedicated to the simultaneous determination of viscosity and interfacial tension of high-viscosity fluids by SLS.[12] For these additional measurements, performed right before the second measurement series in the year 2005, the sample was filled dropwise via a syringe filter with a pore size of 200 nm into the measurement cell. Just like for the second series, the cell was evacuated at room temperature before the SLS experiment was begun. This sample was investigated within a temperature range between (323.15 and 433.15) K and proved, nevertheless, to have a water content of less than 550 ppm and thus the highest of all series, as determined once more by Karl Fischer coulometric titration.

Vibrating Tube Method—Density. For over 3 years, we have carried out a number of density measurements based on the vibrating tube method for DIDP at atmospheric pressure. For the density meter (Anton Paar, DMA 5000) used here, long-term drift is eliminated by a reference oscillator built into the measuring cell, and only one adjustment at 293.15 K is sufficient to reach a high accuracy for the whole measuring temperature range. The temperature of the U-tube is controlled within ±1 mK and measured by a high-precision platinum resistance probe with an uncertainty of ±10 mK. For the density meter calibration, standard water and air were used. The calibration procedure was checked by measuring the liquid density of toluene at atmospheric pressure for temperatures between (278.15 and 343.15) K, in intervals of 5 K. Here, the difference between the density values determined by our densimeter and those calculated by the equation of state by Lemmon and Span[23] are smaller than 0.01 %. For toluene the uncertainty in the equation of state by Lemmon and Span[23] for the saturated liquid density approaches 0.01 % around 300 K. However, the expanded uncertainty ($k = 2$) of the present density measurements for DIDP is estimated to be less than ±0.02 %. For this, the calibration error of the apparatus of 0.01 % and the error associated with the following measurement procedure for DIDP have been taken into account. The precision or repeatability of the instrument was better than ±0.001 %.

Although for the evaluation of the dynamic viscosity from the SLS experiment the liquid density is required, it should be noted that even approximate values are sufficient to achieve a high accuracy. Nevertheless, the density measurements presented here also aimed at the study of the effect of sample degradation at higher temperatures, to which the characteristic smell previously described could be attributed.

Pendant Drop Technique—Interfacial Tension. Measurements of the interfacial tension were performed within the scope of the third SLS measurement series before and after the sample treatment described above. A universal surface analyzer (OEG, SURFTENS universal) was used for measuring the interfacial tension of DIDP by the pendant drop method, where the geometrical profile of a pendant drop is compared with the theoretical drop profile obtained from the Laplace equation. At a room temperature of 301.24 K and atmospheric pressure, values of (29.74 and 29.72) mN·m^{-1} were determined for the interfacial tension of the untreated and treated samples, respectively. When an expanded uncertainty ($k = 2$) of ±1 % for the present interfacial tension measurements is taken into account, no difference can be identified in the interfacial tension of these. The present experimental values deviate by about +0.5 % from an appropriate correlation of interfacial tension data given in the literature,[22] where the same DIDP sample has been investigated at atmospheric pressure in dependence on temperature between (288.15 and 308.15) K, in intervals of 5 K, with an estimated overall uncertainty of ±0.5 %.

Results and Discussion

In the following, our results for the density and dynamic viscosity of DIDP will first be compared among themselves, at different experimental conditions. Then, for the results obtained within the third SLS measurement series from the year 2006, a comparison with the literature will take place. It should be noted that only the results from this last series can contribute to the development of DIDP as a future industrial standard in the moderate- to high-viscosity region. Nevertheless, the results obtained for different sample preparation and handling procedures are worth mentioning and should be discussed here, because they contribute not only to a further characterization of DIDP, especially with regard to its thermal and long-term stability, but also to the influence of the water content on the viscosity.

Density of DIDP at Atmospheric Pressure. All data collected during the past 3 years for the density of DIDP at atmospheric pressure are summarized in the upper part of Figure 1. Besides the year in which the density measurement was performed, the individual experimental runs are characterized by different sample preparation or handling procedures. The same DIDP sample was investigated repeatedly in its original state, as purchased from the manufacturer, whereas one run was performed directly after its investigation by SLS, where the sample was subject to a maximum temperature of 433.15 K, and another right after the vacuum preparation procedure described under Experimental Section. The chronological order of different runs within the same year is indicated by the alphabetical order in the figure caption. It should be noted that for each run displayed, the vibrating U-tube instrument was filled with a new sample. The lower part of Figure 1 shows the relative deviations of the density data from a correlation in the form of a polynomial of the third order

$$\rho = \rho_0 + \rho_1 T + \rho_2 T^2 + \rho_3 T^3 \tag{4}$$

where all data collected at LTT Erlangen for over 3 years have been taken into account with the same statistical weight. In eq 4, T is the temperature in K and ρ_0, ρ_1, ρ_2, and ρ_3 are the fit parameters.

As can be seen from the deviation plot of Figure 1, all of the data corresponding to the sample in its original state seem to form one coherent band, even though its water content should have theoretically increased during its 3 year lifetime in our laboratory, due to the partially hydrophilic character of DIDP. Thus, during this period, no deterioration of the original sample is reflected by the density measurement. The sample investigated within the third SLS measurement series shows slightly higher density values in comparison to the sample in its original state. This behavior cannot be explained by the lower water content of 151 ppm of the first, because the density of DIDP is lower than that of water. The most likely reason for the slight increase in density is the extraction of dissolved air resulting from the 0.5 mbar vacuum to which the sample was exposed at a temperature of about 333.15 K. A further, and until now more or less speculative but possible, explanation attributes this behavior to the isomeric mixture composition of DIDP, which might have changed under these conditions as a result of thermochemical rearrangement of isomers or even of thermal degradation. The latter may explain the strange characteristic smell detected after the sample preparation of the third SLS measurement series (see Experimental Section), as well as that perceived in the DIDP sample investigated in the further SLS measurement series reported in ref 12, after heating to temperatures of 433.15 K. For the latter, however, the deviations from all of other density measurements performed for over 3 years lie clearly outside the measurement uncertainty of ±0.02 %.

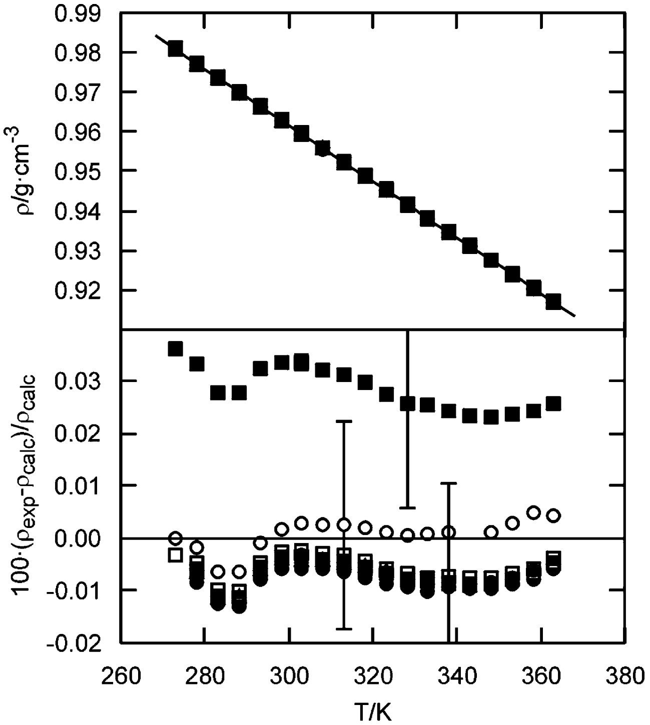

Figure 1. Liquid density of DIDP at atmospheric pressure for a sample from Merck for analysis (>99.5 %) in its original state (△, 2003a; □, 2005a; ⬓, 2005c; ●, 2006b; ◒, 2006c), after investigation by SLS at high temperatures up to 433.15 K (■, 2005b), and after preparation by applying a vacuum of 0.5 mbar at a temperature of 333.15 K (○, 2006a).

Data Comparison for the Density of DIDP at Atmospheric Pressure. Our density values for DIDP obtained within the third SLS measurement series, which is able to contribute to the development of DIDP as an industrial standard in the moderate- to high-viscosity region, are summarized in Table 1 and are compared to measurements of other research groups[8,9,24−26] within IATP for the same material (DIDP from Merck KGaA, nominal purity > 99.5 %) in Figure 2. Here, the correlation of our density data according to eq 4, using the corresponding coefficients given in Table 2, serves as a basis. With the exception of the data of Peleties and Trusler,[25] which measured the density using a pycnometer with an expanded uncertainty of less than ±0.016 %, all other data sets are based on the same

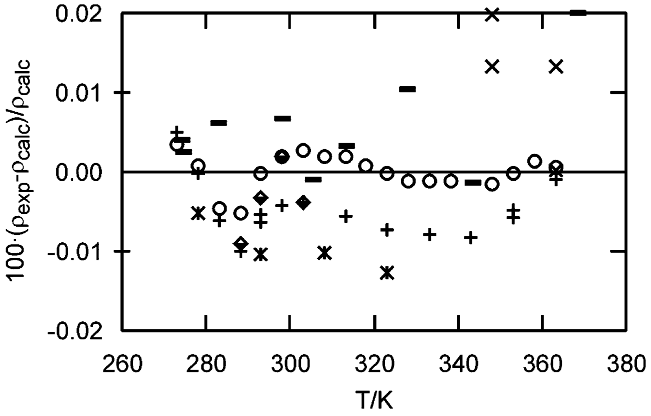

Figure 2. Comparison between the densities given by different authors for a DIDP sample from Merck for analysis (>99.5 %) at atmospheric pressure with that of a sample prepared by applying a vacuum of 0.5 mbar at a temperature of about 333.15 K (—, eq 4 using coefficients from Table 2): ○, Fröba and Leipertz, this work, 2006a; tilted square, bottom solid, Caetano;[8] ∗, Bauer;[24] +, Harris and Bair;[9] ×, Al Motari et al.;[26] ▬, Peleties and Trusler.[25]

Table 1. Density ρ of Diisodecyl Phthalate from $T = (273.15$ to $363.15)$ K at Atmospheric Pressure

T/K	ρ/kg·m^{-3}	T/K	ρ/kg·m^{-3}	T/K	ρ/kg·m^{-3}
273.14	980.74	303.16	959.36	333.16	938.12
278.15	977.13	308.16	955.81	338.16	934.60
283.15	973.51	313.16	952.27	348.15	927.54
288.15	969.94	318.16	948.73	353.15	924.02
293.15	966.43	323.16	945.19	358.15	920.50
298.16	962.90	328.16	941.65	363.15	916.95

Table 2. Coefficients of Equation 4 for the Density of Diisodecyl Phthalate Listed in Table 1

ρ_0/kg·m^{-3}	ρ_1/kg·m^{-3}·K^{-1}	ρ_2/kg·m^{-3}·K^{-2}	ρ_3/kg·m^{-3}·K^{-3}	rms [a]
1211.96	−1.05482	1.04892·10^{-3}	−1.04998·10^{-6}	0.0022

[a] Standard percentage deviation of ρ to the fit.

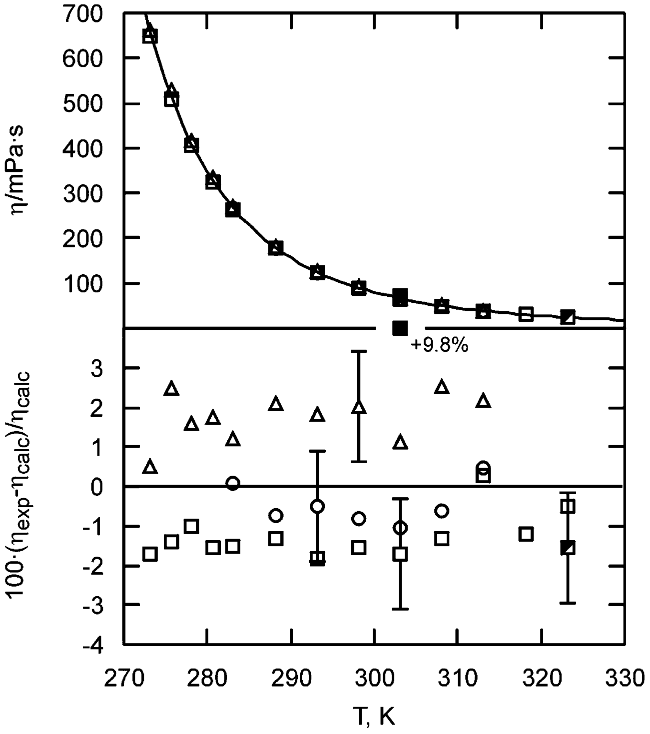

Figure 3. Dynamic viscosity of DIDP at atmospheric pressure for a sample from Merck for analysis (>99.5 %) by SLS under different experimental conditions: △, investigation after sample heating to a temperature of 373.15 K, water content < 392 ppm (2003); ◩ and ■, investigation before and after investigations by SLS at high temperatures up to 433.15 K, respectively, dropwise filling of the measurement cell via a syringe filter with pore size of 200 nm, evacuation of the sample cell at room temperature, water content < 550 ppm (2005); □, investigation after sample preparation in the measuring cell by applying a vacuum of 0.5 mbar at room temperature, water content = 287 ppm (2005); ○, after separate sample preparation by applying a vacuum of 0.5 mbar at a temperature of 333.15 K, water content = 151 ppm (2006).

measuring principle of the vibrating U-tube method. Whereas Harris and Bair,[9] Bauer,[24] and Caetano[8] used an identical vibrating U-tube instrument (Anton Paar, DMA 5000), Al Motari et al.[26] performed density measurements using an external measuring cell (Anton Paar, DMA 602 H). The density measurements reported by Al Motari et al.[26] were obtained with an expanded uncertainty of about ±0.1 % sufficient to introduce a negligible systematic error in the determination of viscosity from a vibrating wire viscometer. The four density values by Bauer[24] in the temperature range between (278.15 and 323.15) K are stated with an expanded uncertainty of less than ±0.02 %. Harris and Bair[9] state an expanded uncertainty of ±0.000 05 g·cm^{-3}, which corresponds to a relative uncertainty for DIDP in the temperature range between (273.15 and 363.15) K of clearly less than ±0.01 %. The overall uncertainty of the density measurements by Caetano[8] is estimated in Caetano et al.[27] not to exceed ±0.1 %. As can be seen from Figure 2, with the exception of the data set by Al Motari et al.[26] and the two data points by Peleties and Trusler[25] at higher temperatures, the maximum deviations between the different data sets are generally not larger than the estimated uncertainty of this work. However, the data by Al Motari et al.[26] and Peleties and Trusler[25] agree with our data within the combined estimated expanded uncertainties of the measurements.

Dynamic Viscosity of DIDP from SLS. The results for the dynamic viscosity of DIDP at atmospheric pressure from SLS are summarized for the three independent SLS measurement series in the upper part of Figure 3. Each data point represents the average value of at least six independent measurements with different angles of incidence Θ_E. In the lower part of Figure 3, the relative deviations of the data are shown with respect to a correlation in the form of a Vogel equation

$$\eta = \eta_0 \exp[B/(T - C)] \qquad (5)$$

where T is the temperature in K and η_0, B, and C are the fit parameters. For the data correlation in Figure 3, the statistical weights of each data point have been assumed to be the same. The exemplarily depicted error bars indicated for each of the SLS measurement series represent the assumed total uncertainty of ±1.4 %, taking into account the uncertainties of the light scattering method and of the interfacial tension data used for data evaluation.

The maximum deviation of the viscosity from the three independent SLS measurement series performed in the temperature range from (273.15 to 323.15) K is about 4 %, which is clearly outside the assumed total uncertainty. An average deviation of about +0.8 % of the third SLS measurement series from the second one may be attributed to the difference in the water content of 136 ppm for the respective samples. Thus, small amounts of water can lower the viscosity of DIDP by about 0.6 % per 100 ppm. This is in agreement with the decrease in viscosity of about 0.5 % per 87 ppm, as was found by Caetano et al.[22] The higher viscosity values obtained within the first SLS measurement series are in contradiction to the higher water content (<392 ppm) of the corresponding sample. This behavior

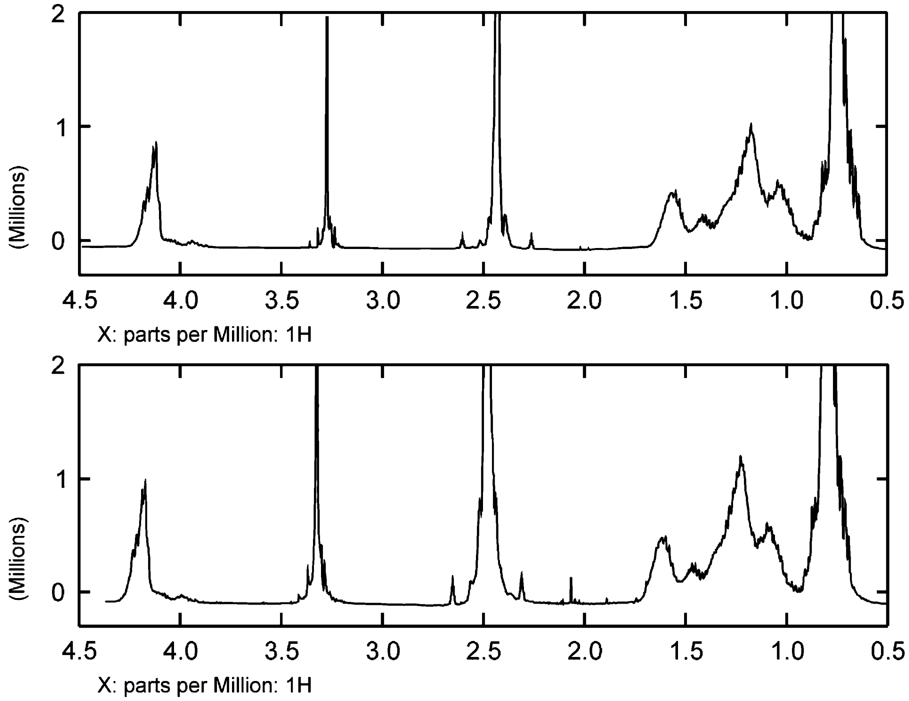

Figure 4. ^{1}H NMR spectra obtained at 400 MHz for DIDP samples before (upper part) and after heating to 433.15 K (lower part). The resonances at about 2.5 ppm and 3.3 ppm are those from the solvent dimethyl-d_6 sulfoxide (DMSO-d_6) and water, respectively. The peaks in the range from about 0.6 ppm to 1.7 ppm and 3.9 ppm to 4.3 ppm result from the aliphatic and adjacent ester protons of DIDP, respectively. An indication of a change in the sample characteristic after sample heating is given by the additional peak at about 2.05 ppm in the lower spectrum.

may be attributed to the sample handling within the first SLS measurement series, whereby before the start of the SLS measurements, the sample was heated to a temperature of 373.15 K.

A more pronounced indication of the interference of the heat pretreatment of the sample on the SLS results for DIDP could be ratified in the additional SLS measurement series, dedicated to the simultaneous determination of interfacial tension and viscosity for DIDP passing the critical damping of surface waves.[12] From this SLS measurement series, two characteristic values at temperatures of (323.15 and 303.15) K are also included in Figure 3, which at the same time represent its first and last data point, respectively. The starting point of this additional series, for which the water content of the sample can be specified to be less than 550 ppm, is about 1 % lower than the corresponding data point of the second SLS measurement series, performed on a sample with a water content of 287 ppm. Thus, this difference may be attributed to the difference in the water content. The higher value of the end point of the additional series, which exhibits a deviation by more than +10 % with respect to the second one, indicates that something happened to the DIDP sample at higher temperatures. Further indications of this behavior include the strange smell detected when the measurement cell was disassembled immediately after this additional series, the comparative measurements of the density (see Figure 1), and the ^{1}H NMR spectra as shown in Figure 4 for a sample in its original state and after heating to 433.15 K. In the lower part of Figure 4, the additional peak in the ^{1}H NMR spectrum at about 2.05 ppm corresponds to about 5.5 % protons with respect to one molecule of DIDP and may thus also indicate a possible reaction or decomposition at higher temperatures.

The quite obscure results by SLS for the viscosity of the DIDP samples processed by a heat pretreatment seems to be coherent by an "apparent" viscosity. The most likely reason for the discrepancies is given by the interfacial tension, which might have changed for the systems after heat pretreatment. The interfacial tension is very sensitive to contamination, so it might have happened that possible degradation products such as alcohols and phthalate acids have lowered it. If, under such conditions, interfacial tension values are used for data evaluation corresponding to a free liquid surface at atmospheric conditions, we obtain an "effective" or "apparent" viscosity, which is much higher than the "true" viscosity.

Table 3. Dynamic Viscosity η of Diisodecyl Phthalate from T = (283.15 to 313.15) K at Atmospheric Pressure[a]

T/K	σ/mN·m^{-1}	ρ/kg·m^{-3}	η/mPa·s
283.15	30.89	973.55	265.6
288.15	30.53	970.00	177.4
293.15	30.17	966.45	123.8
298.15	29.80	962.90	88.44
303.15	29.44	959.35	64.84
308.15	29.08	955.81	48.98
313.15	28.71	952.27	38.01

[a] Directly measured values of the mean decay time $\tau_{C,1}$ at a defined wave vector q of surface fluctuations were combined with literature data for the interfacial tension σ from Caetano et al.[22] and our own density data ρ, eq 4 using coefficients from Table 2, to derive η by an exact numerical solution of the dispersion relation.

Besides revealing an obstacle for developing DIDP as an industrial viscosity standard over an extended temperature range away from room temperature, these results also demonstrate a specific characteristic of the SLS technique itself. For the evaluation of the dynamic viscosity of fluids with high viscosity and/or low interfacial tension, information about the latter is needed. Thus, for an accurate determination of the dynamic viscosity of high-viscosity fluids, one has to ensure that the liquid surface under investigation corresponds to the interfacial tension values used for data evaluation. This, however, could at least be checked at a temperature of 301.24 K for the DIDP sample investigated within the third SLS measurements series (see Experimental Section).

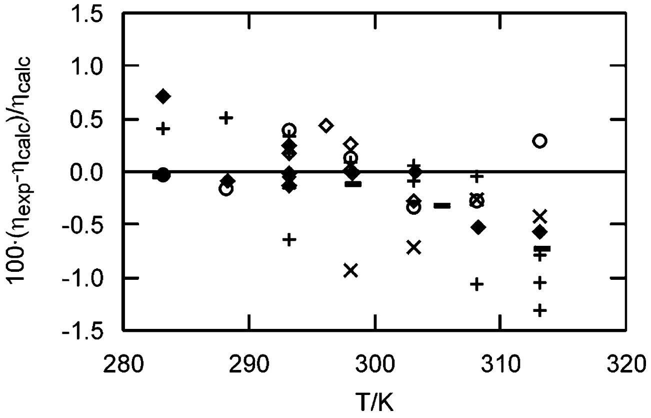

Figure 5. Comparison between the dynamic viscosities of different measurement techniques for a DIDP sample from Merck for analysis (>99.5 %) at atmospheric pressure with that of a sample prepared by applying a vacuum of 0.5 mbar at a temperature of 333.15 K (—, eq 5 using coefficients from Table 4): ○, Fröba and Leipertz, this work, 2006; ◆, Caetano et al.;[27] tilted square, bottom solid, Caetano;[8] ◇, Caetano et al.;[10] ∗, Bauer;[24] +, Harris and Bair;[9] ×, Al Motari et al.;[26] ▬, Peleties and Trusler.[25]

Table 4. Coefficients of Equation 5 for the Viscosity of Diisodecyl Phthalate Listed in Table 3

η_0/mPa·s	*B*/K	*C*/K	rms[a]
598.38	834.595	183.776	0.26

[a] Standard percentage deviation of η to the fit.

Data Comparison for the Dynamic Viscosity of DIDP at Atmospheric Pressure. In the following, the results for the dynamic viscosity of DIDP at atmospheric pressure from the third SLS measurement series are discussed in comparison to the measurements originating from viscometers of different types and operating principles, for the same material (DIDP from Merck KGaA, nominal purity > 99.5 %). Besides our data for the dynamic viscosity, also the interfacial tension and density values from the literature[22] and from our own measurements, respectively, are listed in Table 3, which were used for the data evaluation as described under Experimental Section. The correlation of our data serves as a basis for a comparison in the form of a deviation plot, as shown in Figure 5. For the complete temperature range from (283.15 to 313.15) K studied within the third SLS measurement series, our data can be well represented by a Vogel equation, eq 5, where the corresponding coefficients are given in Table 4. Here, also the standard deviation (root-mean-square, rms) of our data relative to those calculated by eq 5 is reported. It should be noted that the residuals of the experimental data from the fit are not larger than the standard deviations of the individual measurements. Furthermore, because the interfacial tension data from ref 22 used for data evaluation were limited to a temperature range between (288.15 and 308.15) K, the values from SLS and their correlation by eq 5 take the character of extrapolations at higher and lower temperatures, respectively.

Measurements of Bauer[24] performed at 293.15 K with a pair of Ubbelohde viscometers with an expanded uncertainty of ±0.14 % relative to the viscosity of water are included in Figure 5. The measurements by Caetano,[8] Caetano et al.,[10] and Peleties and Trusler[25] were performed by capillary viscometers with expanded uncertainties of ±1.5 %, ±1.5 %, and ±1.5 %, respectively. Harris and Bair[9] performed measurements using a falling-body viscometer, with an estimated expanded uncertainty of ±2 %. Finally, measurements by Al Motari et al.[26] and Caetano et al.[27] are included in Figure 5, where both data sets are based on the vibrating wire method. The estimated overall uncertainty of the results by Caetano et al.[27] does not exceed ±1 % over the whole measurements range and, for the results obtained at temperatures in the vicinity of 293 K, is ±0.8 %. The expanded uncertainty of the measurements by Al Motari et al.[26] is assumed to be ±2 %. It is worth mentioning that all data sets from conventional techniques are based on a calibration of the viscometer with an adequate reference fluid of known viscosity, which in some cases[27] is the primary viscosity reference, that is, water. Of course, the SLS method requires information about the "true" interfacial tension of the fluid "under investigation" for the data evaluation in the case of fluids with high viscosity and/or low interfacial tension, yet no calibration procedure is needed with a fluid of known viscosity. Figure 5 shows excellent agreement between our data from SLS and those given by Bauer,[24] Caetano et al.,[10,27] Caetano,[8] Al Motrai et al.,[26] Peleties and Trusler,[25] and Harris and Bair.[9]

Conclusions

Differences obtained for the "apparent" viscosity between independent SLS measurement series performed for over 3 years at LTT Erlangen for the same DIDP sample in the temperature range from (273.15 to 323.15) K may be attributed to the sample preparation and handling procedure. In this context, it could be demonstrated that small amounts of water lower the viscosity of DIDP by about 0.6 % per 100 ppm. Furthermore, when the sample was pretreated with heat at temperatures of (373.15 and 433.15) K, differences in the "apparent" viscosity of more than +4 % and +10 % resulted, respectively, with respect to the viscosity of the samples treated without heating. The most likely explanation for these discrepancies relies on the interfacial tension, which might have decreased after sample heating due to the formation of degradation products contaminating the liquid surface under investigation. At higher temperatures, in the presence of impurities such as water, alcohols and phthalate acids are possible decomposition products. Of course, at present it is more or less speculative under which conditions DIDP can undergo a reaction. Yet, the fact that the sample undergoes a change after being pretreated with heat is reflected not only by the results of the SLS experiment itself but also by the characteristic smell detected and by the density measurements, as well as by the ^{1}H NMR analysis of the samples before and after heating.

Nevertheless, the present investigations indicate that DIDP is suitable as a working reference fluid at moderate to high viscosity at room temperature, provided that any pretreatment at temperatures above 333.15 K is avoided. Within a specific SLS measurement series, no heat pretreatment was performed and the interfacial tension of the liquid surface under investigation was checked, at least at room temperature, proving to correspond to the values used for the data evaluation of DIDP. This experimental series, which is able to contribute to the development of DIDP as a future industrial standard in the moderate- to high-viscosity region, is in excellent agreement with the data obtained by different conventional techniques. By providing accurate information about the interfacial tension, an uncertainty of less than ±1.4 % can even be achieved by the SLS technique for the viscosity of DIDP, which is comparable to that of conventional methods.

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