

Density and Viscosity Measurements of 2,2,4-Trimethylpentane (Isooctane) from 198 K to 348 K and up to 100 MPa

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New density and viscosity results for 2,2,4-trimethylpentane at temperatures from 198 K to 348 K and pressures up to 100 MPa are reported. The measurements of both properties were performed simultaneously using a vibrating-wire instrument operated in the forced mode of oscillation. The present set of measurements extends those found in the literature to the high-pressure and low-temperature region. Correlations for both the density and the viscosity are presented, and comparisons are established with various sets of results from the literature. The estimated uncertainties of the results are $\pm 0.05\%$ for the density and $\pm 2.5\%$ for the viscosity.

Introduction

In previous publications (Pádua *et al.*, 1996a,b) the authors have investigated the simultaneous measurement of the density and the viscosity of fluids using a vibrating-wire instrument. Measurements were reported on a number of liquids at pressures up to 100 MPa, at temperatures from 200 K to 350 K, and the accuracy of the method was assessed.

The motivations for the present study of the density and viscosity of 2,2,4-trimethylpentane (isooctane) were twofold. Firstly, the study is a further test of the technique, since 2,2,4-trimethylpentane is a reference fluid recommended by IUPAC for density measurements at atmospheric pressure (Girard, 1987). It has been proposed as a reference fluid for other properties, namely viscosity, thermal conductivity, and refractive index (Malhotra and Woolf, 1990), and also as a consequence of its technological importance, a large amount of data can be found in the literature covering the temperature range of the present results. Some results of compressed liquid densities (Dymond *et al.*, 1985b; Holzapfel *et al.*, 1986; Malhotra and Woolf, 1990; Papaioannou *et al.*, 1991) and viscosities (Dymond *et al.*, 1985a) are available at temperatures above ambient, enabling comparisons of the present results along their entire pressure range.

Secondly, the authors intend to complement the data available in the literature for the two properties in question, mainly in the compressed liquid at subambient temperatures where, as far as the authors are aware, there is a total lack of data.

The instrument used in the present work has been built essentially as a hydrostatic weighing densimeter, in which the density of the fluid sample is related to the buoyancy force exerted on an immersed sinker. A vibrating-wire sensor is placed inside the measuring cell to provide a means of determining the apparent weight of the sinker and, because the wire vibrates in the presence of the fluid, its characteristics of oscillation depend also upon the viscosity of the sample. The viscosity is obtained as a

secondary result of the density measurements, as the present instrument has not been optimized specifically toward a high precision in the viscosity (Pádua *et al.*, 1996b).

A rigorous, physically sound mathematical model of the measuring cell (Retsina *et al.*, 1986; Dix *et al.*, 1991; Pádua *et al.*, 1994, 1996b) permits the calculation of both properties from a single measurement of the resonance curve of the wire. No calibrations are necessary except for one single reference experiment to determine two parameters of the cell: the radius of the wire and the volume of the sinker. This reference experiment can take place at ambient temperature and atmospheric pressure. The mathematical model, and the conformity of the practical instrument to it, have been validated (Pádua *et al.*, 1996a,b), and the accuracy and precision of the technique have been established.

From the point of view of studying the technique, the results reported here explore a wider range of viscosities than has been done so far, since the viscosity of 2,2,4-trimethylpentane changes 30-fold in the present range of thermodynamic conditions.

Method

Vibrating-body sensors have been used often for the measurement of viscosities of fluids. In particular, vibrating wires (van der Gulik, 1991) have some advantages since they possess a simple shape, are amenable to rigorous theoretical treatment, and can be readily obtained in a number of conducting materials (most importantly metals) with virtually any diameter. The device generally employed to set the wire in oscillation and, at the same time, to detect the amplitude of motion is an electromagnetic coupling. A permanent magnetic field is created around the wire and a current is fed through it to provide a force that drives the wire in a direction perpendicular to its longitudinal axis. The velocity amplitude of the wire can be determined from the electromotive force arising at its terminals owing to its motion inside the magnetic field.

The viscosity is measured via the hydrodynamic effects of the fluid on the wire motion, especially the damping of

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the oscillations. In a viscometry technique based essentially on the same theoretical model as the present densimetry method (Retsina *et al.*, 1987), the transient mode of vibration is used and the viscosity is obtained from the decrement of the free oscillations after an initial pulse (Oliveira, 1991; Assael *et al.*, 1992b). The density of the fluid plays a part in the hydrodynamic effects too, and a knowledge of this property is necessary before the working equations can be solved with respect to the viscosity. Using this fact, a simultaneous determination of both properties has been attempted with a vibrating-disk viscometer (Krall *et al.*, 1987), but the uncertainties in the density were of the same order as those in the viscosity, $\pm 0.5\%$.

The limitations of the above methods in the determination of densities arise from the fact that the hydrodynamic effects are insufficiently sensitive to the density of the fluid.

Using a completely different approach, vibrating bodies have been used in densimetry, namely vibrating tubes that are filled with the sample under study (Albert and Wood, 1984; Majer *et al.*, 1991). These sensors are generally operated in forced mode of oscillation and their resonant frequency is related to the density of the liquid. The detection method based on the electromagnetic coupling is also present in these methods. These techniques offer a high precision but, owing to the complicated shape of the oscillator and to the deformations caused by temperature and pressure, a complete model is not available and empirical working equations must be used. Measurements are performed in a purely relative manner, requiring calibration with reference fluids over the entire range of thermodynamic conditions. The absence of reliable calibrants at extreme conditions places limitations on their accuracy. Typically, high-pressure vibrating-tube densimeters have maximum working pressures of 40 MPa.

Highly accurate densimetry methods make use of Archimedes' principle (Haynes *et al.*, 1976; Hales and Gundry, 1983; Wagner *et al.*, 1995). The effect of temperature and pressure on a simple-shaped, solid sinker can be accurately determined so that, once the cell parameters are known, no further calibrations are required. In order to measure the buoyancy force acting on the sinker, hydrostatic weighing densimeters employ a magnetic suspension device to transmit the apparent weight to an exterior balance. The region of very high pressures has been unattainable by these methods owing to difficulties in operating a magnetic suspension through the thick metallic walls of the pressure vessels.

The present method of vibrating-wire densimetry can be viewed as being a hydrostatic weighing method in which a vibrating-wire sensor is used to measure the buoyancy force. The sinker is suspended vertically from a thin, metallic wire, whose axial tension will depend upon the apparent weight of the sinker. The tension of the wire can be related to its resonant frequency of transverse oscillations, which can be very accurately determined under a forced mode of vibration. The difference between the resonant frequencies observed in a fluid and under vacuum permits the measurement of the density. Since the sensor is placed inside the pressure vessel, the measuring cell is compact and the technique is not limited to low pressures. The simple shape of the vibrating element has allowed the formulation of an accurate model, and so the method does not have to rely on extensive calibration procedures. It benefits, therefore, from the high accuracy characteristic of hydrostatic techniques.

It is important to note that, in the present method, the determination of the density does not rely to first order upon the hydrodynamic effects of the fluid surrounding the

vibrating wire, although these must be considered in the model. Typically (for our instrument with a fluid of density of 1000 kg m^{-3} and a viscosity of 1 mPa s), the buoyancy effect is responsible for 84% of the shift in resonant frequency in relation to that observed under vacuum, the remaining 16% arising from the hydrodynamic contribution. This enhanced sensitivity to the density, obtained through the hydrostatic weighing character of the present method, is the key factor that distinguishes it from the vibrating-wire viscometers.

The hydrodynamic effect is nonetheless present and provides a means of measuring the viscosity simultaneously with the density, although not so precisely. In the forced mode of vibration, the viscosity can be related to the width of the resonance curve (Retsina *et al.*, 1986; Pádua *et al.*, 1996b).

The technique has been presented and discussed in detail elsewhere (Dix *et al.*, 1991; Pádua *et al.* 1994, 1996b). In these publications, the original model of Retsina *et al.* (1986), which concerns the mechanics of vibration of the wire and the hydrodynamic effects of the fluid, has been extended to include the buoyancy effect.

Experimental Section

The apparatus and experimental setup were described elsewhere (Pádua *et al.*, 1994, 1996b) and the equipment was used without any change for the present measurements. The procedure used to determine two parameters of the measuring sensor (the volume of the sinker and the radius of the wire) was presented in detail and validated in a previous publication (Pádua *et al.*, 1996b). The reference fluid was 2,2,4-trimethylpentane at 298.15 K and 0.10 MPa, and the parameters of the cell were confirmed with cyclohexane. The densities of the reference samples had been measured independently, with uncertainties of the order of 0.01%, using a pycnometer calibrated with distilled water and distilled mercury. Assuming the values for the cell parameters determined with 2,2,4-trimethylpentane, the density of cyclohexane could be reproduced with an error of 0.02%, which is in the limit of precision of the present instrument. We conclude that no significant improvements would arise if water had been directly used as a reference fluid. The same values of the cell parameters determined by Pádua *et al.* (1996b) were assumed for the present measurements.

For operation at conditions away from the reference experiment, which took place at 298.15 K and 0.10 MPa, the dimensions of the tungsten wire and of the aluminum sinker were corrected using the thermal-expansion and compressibility coefficients of these materials (Pádua, 1994).

The measurements presented here were performed in two different samples of 2,2,4-trimethylpentane on different occasions with 1 year between them. The first set consists of three isotherms from 298 K to 348 K, and the second set consists of five isotherms from 198 K to 298 K. All of the measurements were carried out up to 100 MPa. The maximum working pressure is imposed by the pressure vessel used in the experimental assembly, and not by limitations of the densimeter sensor. The first sample is that for which we have previously reported results for the density (Pádua *et al.*, 1994) at temperatures above ambient. Since the first report of the measurements we have been able to improve the interpretation of the raw experimental data by means of a more detailed model of the process of detection of the wire motion (Pádua, 1994; Pádua *et al.*, 1996b). For that reason we present here the density results for this sample analyzed in this new way. The density

results reported now depart by less than 0.1% from those given earlier but have an improved accuracy because of the theoretical improvement. We are also able, by virtue of this improved theory, to present viscosity data for that sample, which was impossible hitherto. The results obtained with the second sample at atmospheric pressure were used in the series of measurements intended to validate the correct operation of the instrument described elsewhere (Pádua *et al.*, 1996b). This set of results is reported here in its entirety.

Both samples of 2,2,4-trimethylpentane have been obtained from Merck, p.a. grade with nominal purity higher than 99.5% and water content below 0.01%. They were prepared in exactly the same way: after being stored over 4 Å molecular sieves to remove water and other low molecular weight impurities, the samples were glass-distilled under nitrogen using calcium hydride as desiccant and finally degassed by helium spraying. The densimeter cell was filled under vacuum through a filter, to avoid admission of solid particles. The initial and final purities were monitored by gas chromatography, and the final samples were pure in excess of 99.7%. The impurities are likely to be other branched alkanes of very similar properties, possibly including *n*-heptane, which has a boiling point very close to that of 2,2,4-trimethylpentane. An independent measurement of the density of both samples was performed at 298.15 K and 0.102 MPa using a glass pycnometer with ca. 60 cm³ of capacity, whose volume had been calibrated with distilled water and distilled mercury (Pádua, 1994). The values obtained were 687.84 ± 0.05 kg m⁻³ and 687.85 ± 0.05 kg m⁻³, respectively. The value recommended by IUPAC for a sample 99.75% pure is 687.85 kg m⁻³ (Girard, 1987). Other literature values for samples of similar purity, all measured using commercial vibrating-tube densimeters, are 687.82 ± 0.30 kg m⁻³ for 2,2,4-trimethylpentane of purity >99% (Dymond *et al.*, 1985a), 687.83 ± 0.02 kg m⁻³ for a purity of 99.8% (Malhotra and Woolf, 1990), and 688.1 ± 0.005 kg m⁻³ for a purity of 99.5% (Papaioannou *et al.*, 1991). The viscosities in the same conditions were measured using a glass capillary viscometer calibrated with distilled water, resulting in a value of 0.472 ± 0.003 mPa s for both samples, which compares to the literature values of 0.4718 ± 0.0024 mPa s (Dymond *et al.*, 1985a), 0.478 ± 0.001 mPa s (Aminabhavi *et al.*, 1994), 0.476 ± 0.001 mPa s (Bauer and Meerlander, 1984), and 0.479 ± 0.002 mPa s (Mussche and Verhoeve, 1975).

Two different temperature control systems were used: for the set of measurements above ambient temperature, a large (120 L) oil bath; for the low-temperature range a special cryostatic bath controlled by a circulating cryostat. The temperature stability during measurements is better than ±0.002 K, and the uncertainty of the readings is ±0.01 K. Calibrations of the platinum resistance thermometer were done against a triple point of water cell and against a secondary-standard platinum thermometer recently calibrated at multiple fixed points of the ITS-90 scale by the National Physics Laboratory, U.K. The measurements of pressure above ambient have an uncertainty within ±0.03 MPa up to 35.0 MPa (a capacitance pressure transducer was used in this range), and within ±0.07 MPa up to 100 MPa (a Heise bourdon-tube gauge was used in this range). Calibrations of the manometers were done against a Ruska 2450 dead-weight balance.

Results and Discussion

The results of the density and viscosity of 2,2,4-trimethylpentane along eight isotherms from 197.93 to 348.16 K

Table 1. Experimental Density and Viscosity of 2,2,4-Trimethylpentane

p/MPa	$\rho/\text{kg m}^{-3}$	$\eta/\text{mPa s}$	p/MPa	$\rho/\text{kg m}^{-3}$	$\eta/\text{mPa s}$
$T = 197.93 \text{ K}$					
0.10	770.91	3.19	60.10	800.15	6.90
10.13	776.12	3.72	70.10	804.52	7.77
20.13	781.17	4.26			
30.10	786.52	4.75			
40.10	791.34	5.43			
50.10	795.82	6.16			
$T = 222.91 \text{ K}$					
0.10	749.32	1.58	60.10	780.86	3.33
10.10	755.20	1.84	70.10	785.54	3.71
20.10	761.03	2.10	80.10	788.88	4.16
30.12	766.87	2.36	90.10	792.69	4.55
40.10	771.31	2.66	100.05	796.96	4.96
50.10	775.91	2.98			
$T = 248.35 \text{ K}$					
0.10	727.33	0.939	60.10	762.21	1.80
10.13	734.35	1.06	70.10	766.68	1.99
20.10	740.85	1.19	80.15	771.05	2.19
30.10	746.69	1.33	90.10	775.30	2.39
40.12	752.26	1.48	100.10	779.00	2.61
50.10	757.43	1.64			
$T = 273.15 \text{ K}$					
0.10	707.72	0.650	60.10	747.24	1.22
10.10	715.91	0.733	70.00	752.11	1.33
20.13	723.35	0.821	80.10	756.74	1.45
30.12	730.04	0.914	90.10	761.30	1.59
40.10	736.14	1.01	99.90	765.55	1.72
50.10	741.90	1.11			
$T = 298.15 \text{ K}$					
0.10	687.82	0.473	60.10	732.70	0.886
10.10	697.43	0.539	70.00	738.20	0.971
20.10	705.95	0.602	80.00	743.41	1.05
30.10	713.54	0.669	90.10	748.25	1.14
40.05	720.57	0.736	100.10	753.07	1.23
50.05	726.83	0.812			
$T = 298.15 \text{ K}$					
0.10	687.87	0.474	60.15	732.95	0.881
10.10	697.40	0.535	70.10	738.39	0.961
20.25	706.31	0.598	80.10	743.45	1.04
30.00	713.55	0.667	90.15	748.68	1.14
40.15	720.83	0.733	100.10	753.41	1.24
50.15	726.97	0.806			
$T = 323.16 \text{ K}$					
0.10	666.80	0.365	60.10	718.70	0.679
10.25	678.51	0.414	70.10	724.81	0.735
20.15	688.50	0.463	80.10	730.06	0.803
30.20	697.16	0.514	90.15	735.31	0.869
40.10	705.03	0.568	100.10	740.70	0.933
50.25	712.08	0.623			
$T = 348.16 \text{ K}$					
0.10	644.75	0.289	60.10	703.00	0.558
10.10	658.54	0.330	70.10	709.69	0.604
20.10	669.83	0.372	80.15	716.04	0.662
30.20	679.92	0.414	90.10	721.94	0.710
40.25	688.85	0.457	100.10	727.38	0.767
50.15	696.24	0.512			

are listed in Table 1. For each temperature, the density, ρ , and viscosity, η , are presented as a function of pressure, p . In each isotherm, about half of the data were obtained while increasing the pressure, and the remaining along decreasing pressures. No sign of hysteresis could be found within the precision of the measurements. The measurements at 298.15 K were performed once with each different sample to provide a measure of the repeatability of the instrument. The deviations between values in these isotherms are at most 0.03%, as can be seen in Figure 1. The results above 70 MPa at the lowest isotherm are omitted since, with the present vibrating wire, the high viscosity of the fluid gives rise to very wide resonance peaks, and the level of resolution characteristic of the

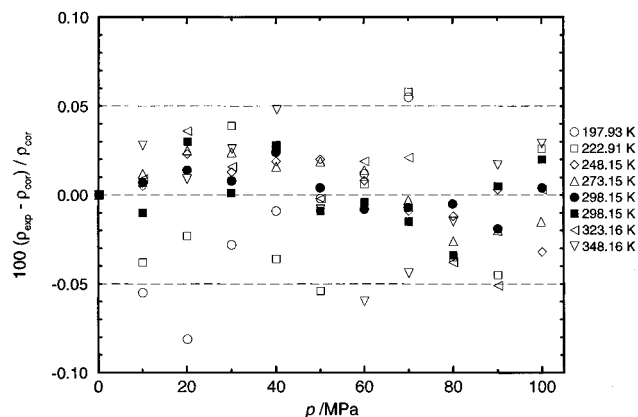


Figure 1. Density of 2,2,4-trimethylpentane at high pressures: deviations of the present results from the Tait equation. The filled symbols allow comparisons of the two isotherms at 298.15 K, obtained with the different samples.

Table 2. Coefficients of Eqs 1 and 5

T/K	B/MPa	$10^6 V_0/\text{m}^3 \text{mol}^{-1}$
197.93	115.1	95.94
222.91	101.4	94.57
248.35	86.59	93.13
273.15	71.70	92.10
298.15	58.37	91.14
298.15	58.15	91.08
323.16	46.34	90.27
348.16	37.11	89.86

remaining values could not be attained in these conditions. A thicker vibrating wire would improve the precision of measurements at higher viscosities.

The estimated uncertainties of the results in Table 1 are based upon that of earlier studies (Pádua *et al.*, 1996a,b). The density results have an estimated uncertainty of $\pm 0.05\%$. The viscosity is obtained with an estimated uncertainty of $\pm 2.5\%$. Such uncertainties in the viscosity are not the best that could be achieved with a purpose-built viscometer, but the results reported here at high pressures, below room temperature are the only ones known to the authors.

A Tait-type equation (Dymond and Malhotra, 1988) was employed to correlate the density results as a function of pressure,

$$\frac{\rho - \rho_0}{\rho} = C \log_{10} \frac{B + p}{B + p_0} \quad (1)$$

where $p_0 = 0.10 \text{ MPa}$ and $\rho_0 = \rho(T, p_0)$. The symbols B and C represent two adjustable parameters. C is generally constant for a given substance or even for classes of substances, and B is temperature dependent. Values for the parameters are listed in Table 2, and $C = 0.200$. The correlation of eq 1 and Table 2 represents the present results with a standard deviation of $\pm 0.026\%$. A deviation plot is shown in Figure 1.

For the purpose of interpolation, the densities at 0.10 MPa were represented as a function of temperature by a polynomial equation of the form

$$\rho_0(T) = \sum_{i=0}^n d_i (T/298.15)^i \quad (2)$$

whose optimized coefficients are listed in Table 3. Deviations of the experimental densities from this equation are within $\pm 0.05\%$.

Table 3. Coefficients of Eqs 2 and 3

i	b_i/MPa	$d_i/\text{kg m}^{-3}$
0	84.673	1075.92
1	360.00	-728.82
2	-644.71	535.38
3	258.25	-194.78

In the Tait equation, the behavior of each isotherm along the pressure is modeled by the parameter B , which generally exhibits a smooth behavior with temperature. We represented this temperature dependence by an equation of the form

$$B(T) = \sum_{i=0}^n b_i (T/298.15)^i \quad (3)$$

the coefficients of which are listed in Table 3. The $(p\rho T)$ surface defined by the Tait equation, with temperature-dependent ρ_0 and B as given by eqs 2 and 3, represents the present results with a standard deviation of $\pm 0.04\%$.

The present density results at atmospheric pressure, along the entire temperature range, were compared with four different sets of literature values in a previous publication (Pádua *et al.*, 1996b). The deviations of the present values to the densities recommended by IUPAC (Girard, 1987) from 293.15 K to 323.15 K are smaller than $\pm 0.03\%$, while the deviations to the densities of Dymond *et al.* (1985b), from 278.15 K to 338.15 K, and of Malhotra and Woolf (1990), from 298.15 K to 348.15 K, are within $\pm 0.05\%$. The present values agree with those reported by Vargaftik (1975), from 203.15 K to 353.15 K, with errors below $\pm 0.10\%$ except for the value reported by that author at the lowest temperature, which shows a deviation of -0.15% from eq 2.

For the compressed liquid, comparisons were carried out with five sets of results found in the literature, all at temperatures above 273.15 K. Dymond *et al.* (1985b) measured volume ratios using a bellows volumometer, along a series of isotherms up to about 500 MPa, of which three isotherms lie in the temperature range of the present results. The initial densities of these isotherms, at atmospheric pressure, were measured using a vibrating-tube densimeter. The reported estimated accuracy of the densities at high pressure is $\pm 0.1\%$ (Dymond *et al.*, 1985b), although the same authors quoted a value of $\pm 0.2\%$ in a different publication (Dymond *et al.*, 1985a). Four values in each isotherm fall within the pressure range of the present measurements. The deviations of these experimental points from the present correlation using the Tait equation are plotted in Figure 2. The maximum deviation observed is of 0.12% at 298.19 K at 99.1 MPa, which is commensurate with the combined uncertainties. The points of Dymond *et al.* (1985b) at 323.15 K and 348.01 K are in excellent agreement with the present correlation, showing deviations of $\pm 0.03\%$ at most.

Malhotra and Woolf (1990) reported correlations of experimental volume ratios of 2,2,4-trimethylpentane, obtained using a bellows volumometer, along seven isotherms from 278.15 K to 338.15 K and up to 280 MPa. Densities at atmospheric pressure were measured using a vibrating-tube densimeter. The estimated accuracy of the volume ratios is of $\pm 0.1\%$ (Malhotra and Woolf, 1990). Density values obtained using the Tait equation with parameters given by eqs 5a and 5b of Malhotra and Woolf (1990), which represents their volume ratios with an error within $\pm 0.14\%$, are compared with the present correlation in Figure 2. There is a clear trend of the deviations with temperature, which is absent from the comparison with the

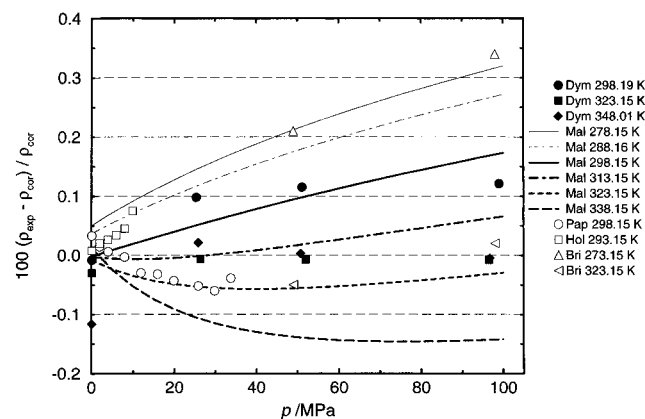


Figure 2. Density of 2,2,4-trimethylpentane at high pressures: deviations from the Tait equation of the results of Dymond *et al.* (1985b), Malhotra and Woolf (1990), Papaioannou *et al.* (1991), Holzapfel *et al.* (1986), and Bridgman (1932).

results of Dymond *et al.* (1985b). Nevertheless, the densities calculated at temperatures 298.15 K, 313.15 K, 323.15 K, and 338.15 K agree with the present results within $\pm 0.15\%$. Only the two lower isotherms, at 278.15 K and 288.15 K, exhibit larger positive deviations at high pressure, reaching $+0.3\%$.

We can find no reason that would justify a loss of accuracy of the present measurements in these conditions. For example, if an error of 10% had been present in the pressure corrections of the volume of the aluminum sinker at 100 MPa, the resulting density error would be 0.01%. Along the remaining isotherms, a total agreement with the literature is observed, as was the case for other fluids previously studied (Pádua *et al.*, 1996a,b). The coefficients of thermal expansion employed for the temperature corrections of the volume of the sinker are accurate within 5% (Davis, 1993), leading to a worst-case error of 0.03% in the calculated fluid densities (at 197.93 K). At the lowest temperature measured by Malhotra and Woolf (1990), 278.15 K, the error in the fluid density due to inaccuracy of the temperature corrections would be less than 0.01%. The accuracy of the corrections for the effects of temperature on the elements of the measuring sensor is substantiated by measurements performed using the same instrument from 198 K to 350 K, in three different fluids (Pádua *et al.* 1996a,b).

A set of ten density values measured using a vibrating-tube densimeter, along one isotherm at 298.15 K and up to 33.81 MPa, was published by Papaioannou *et al.* (1991). The uncertainty claimed for these density measurements is of the order of $\pm 0.015\%$ ($1 \times 10^{-4} \text{ g cm}^{-3}$) in their entire pressure range. The sample used was obtained from the same supplier of the samples employed for this work. The deviations of these results from the present correlation are plotted in Figure 2. They range from $+0.03\%$ at atmospheric pressure to -0.06% at 33.81 MPa. This set is in very good agreement with the present results, showing deviations of opposite sign of the deviations of the data of Dymond *et al.* (1985b) and Malhotra and Woolf (1990) at the same temperature.

Another six densities at 293.15 K have been reported by Holzapfel *et al.* (1986), at pressures up to 10.0 MPa, with uncertainties of $\pm 0.003\%$. A plot of the deviations of this set is also included in Figure 2. The maximum deviation observed is of $\pm 0.08\%$ at 10.0 MPa.

Finally, Bridgman (1932) measured volume ratios of 2,2,4-trimethylpentane up to 980 MPa. Two isotherms, at 273.15 K and 323.15 K, are suitable for comparison. The accuracy of these results should be better than $\pm 0.5\%$

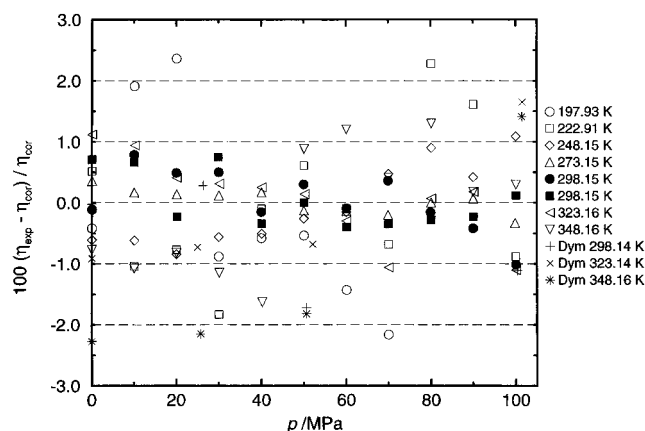


Figure 3. Viscosity of 2,2,4-trimethylpentane at high pressures: deviations from the correlation using eq 4 of the present results and of the results of Dymond *et al.* (1985a).

Table 4. Coefficients of Eqs 5–7

i	c_i	$10^6 v_i / \text{m}^3 \text{ mol}^{-1}$	e_i
0	2.0914	114.34	21.210
1	-0.3633	-36.395	-40.402
2	1.9306	13.166	32.569
3	-0.3158		-9.4401

(Malhotra and Woolf, 1990). We assumed the present values of density at atmospheric pressure as starting points for the isotherms of Bridgman (1932). Comparison with these results is included in the deviation plot of Figure 2. At 273.15 K deviations in the densities reach $+0.34\%$ at 98.07 MPa, but at 323.15 K deviations are below $\pm 0.05\%$.

The viscosity of 2,2,4-trimethylpentane was correlated using a scheme based on the hard-sphere theory of transport in dense fluids. This scheme has been successfully applied to the series of *n*-alkanes (Assael *et al.*, 1992a) and to several other liquids. A reduced, dimensionless viscosity, η^* , is defined by

$$\eta^* = 6.035 \times 10^8 (MRT)^{-1/2} V^{2/3} \eta \quad (4)$$

where M is the molar mass, R the gas constant, T the temperature, and V the molar volume. The reduced viscosity should be a function of the ratio of the molar volume to a close-packed volume, V_0 , only. This characteristic hard-sphere volume generally decreases with increasing temperature, which can be interpreted as an account for the finite steepness of the real intermolecular potential.

A value of $V_0(323.16 \text{ K}) = 90.27 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ was initially assumed (Fareleira *et al.*, 1990), and a characteristic volume for each isotherm was found by superimposing the isotherms on a single curve with the form

$$\ln \eta^* = \sum_{i=0}^n c_i \left(\frac{V_0}{V - V_0} \right)^i \quad (5)$$

The values for the characteristic volumes are presented in Table 2. The coefficients c_i were determined by least squares fitting to the entire set of points and are listed in Table 4. The determination of the characteristic volumes by superposition of the isotherms and the optimization of the parameters of eq 5 were done simultaneously. This correlation represents the present viscosity results with a standard deviation of $\pm 0.8\%$. A deviation plot is shown in Figure 3.

The characteristic volumes exhibit a smooth temperature dependence, which we found to be nonlinear, mainly toward

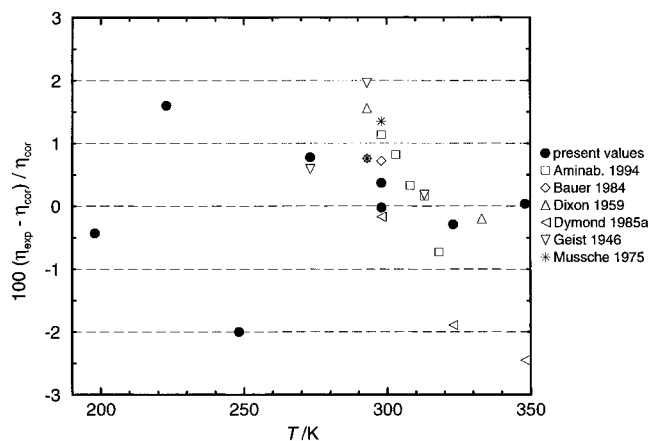


Figure 4. Viscosity of 2,2,4-trimethylpentane at 0.1 MPa: deviations from the correlation using eq 7 of the present results and of the results of Aminabhavi *et al.* (1994), Bauer and Meerlander (1984), Dixon (1959), Dymond *et al.* (1985a), Geist and Cannon (1946), and Mussche and Verhoeve (1975).

the highest temperature. Interpolation of V_0 with temperature can be performed using

$$V_0(T) = \sum_{i=0}^n v_i (T/298.15)^i \quad (6)$$

whose optimized coefficients are listed in Table 4. This equation represents the present characteristic volumes with errors below $\pm 0.1\%$. The smooth behavior of $V_0(T)$ and the correct superimposition of all the isotherms on a single curve tests the internal consistency of the present results. It is noteworthy that the viscosity of 2,2,4-trimethylpentane changes 30-fold in the range of conditions covered by the present study.

For the compressed liquid, one set of viscosity measurements was found in the literature, covering the present pressure range (Dymond *et al.*, 1985a). These results were obtained using a high-pressure falling-body viscometer and the reported accuracy is of $\pm 2\%$. Twelve points, along three isotherms at 298.14 K, 323.14 K, and 348.16 K can be directly compared with the present values. Deviations of the experimental measurements of Dymond *et al.* (1985a) from the present correlation are shown in Figure 3. The maximum deviations observed are roughly within $\pm 2\%$, with no noticeable trends with pressure.

Comparisons over a wider temperature range could only be performed using the results at atmospheric pressure. For that purpose, the present viscosities at 0.10 MPa were represented by a polynomial of the form

$$\ln \eta_0^*(T) = \sum_{i=0}^n e_i (T/298.15)^i \quad (7)$$

whose coefficients are given in Table 4. This equation represents the present results within $\pm 2\%$. A deviation plot is presented in Figure 4, which includes comparisons with literature data from six different sources at temperatures between 273.15 K and 348.15 K. The uncertainties of the literature values are $\pm 0.3\%$ (Aminabhavi *et al.*, 1994; Bauer and Meerlander, 1984; Dixon, 1959), $\pm 0.5\%$ (Dymond *et al.*, 1985a; Geist and Cannon, 1946), and $\pm 1\%$ (Mussche and Verhoeve, 1975). All of the deviations are commensurate with the combined uncertainties. No viscosity results were found in the literature at temperatures below 273.15 K. The above comparisons, and the internal

consistency of the results, corroborate the estimate of the uncertainty of the present viscosities as $\pm 2.5\%$.

Conclusions

Simultaneous measurements of density and viscosity using one single vibrating-wire sensor yield accuracies that compare favorably with pure densimetry and viscometry methods over equivalent ranges of thermodynamic conditions.

The upper limit of the viscosities attainable using the present experimental arrangement, without compromising the resolution in the density, is of the order of 8 mPa s. Use of a thicker vibrating wire would allow precise measurements in fluids of higher viscosity.

The results presented here for 2,2,4-trimethylpentane were shown to be in good agreement with data from the literature, in the regions of temperature and pressure where comparisons were possible. The present results of compressed liquid densities and viscosities below 273.15 K complement those available in the literature.

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