The Viscosity and Density of *n*-Dodecane and *n*-Octadecane at Pressures up to 200 MPa and Temperatures up to 473 K.

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Abstract

We describe a vibrating-wire instrument for simultaneous measurement of the density and viscosity of liquids under conditions of high pressure. The instrument is capable of operation at temperatures between 298.15 K and 473.15 K at pressures up to 200 MPa. Calibration was performed by means of measurements in vacuum, air and toluene at 298.15 K. For n-dodecane measurements were made along eight isotherms between 298.15 and 473.15 K at pressures up to 200 MPa, while for n-octadecane measurements were measured along 7 isotherms between 323.15 to 473.15 K at pressures up to 90 MPa. The estimated uncertainty of the results is 2 per cent in viscosity and 0.2 per cent in density. Comparisons with literature data are presented.

Key Words

Density, Dodecane, High Pressure, High Temperature, Octadecane, Viscosity

1. Introduction

This work is aimed at reducing gaps in the available viscosity data of hydrocarbons under conditions of high temperature and pressure for the purposes of testing predictive models [1]; we also measure density as this plays a key role in several predictive methods. In this paper, we describe a vibrating wire apparatus for the simultaneous measurement of viscosity and density and report results for *n*-dodecane and *n*-octadecane at pressures up to 200 MPa and in the temperature range of 298 to 473 K.

2. Background

The origins of the vibrating wire technique can be traced back to early research on pendulums and the problem of why the period of oscillation increased with air density. As early as 1830, Bessel recognised that the buoyancy and inertial effects of the air would increase the period of vibration. Stokes [2] recognised that the viscosity of the surrounding air also plays a role and, by applying the Navier-Stokes equations to the pendulum system, arrived at a full analytical solution for the pendulum motion. Stokes then applied the same technique to the problem of an infinitely long cylindrical rod oscillating in an infinite fluid and this formed the hydrodynamic basis for vibrating wire viscometry.

A practical device based on the Navier-Stokes equations was developed in 1963 by Tough and co-workers [3] and the theory was re-visited in 1986 by Retsina and co-workers [4,5] who included the effect of the wire stiffness and obtained a solution appropriate to transient motion. Many practical devices, operating in either steady-state and transient modes, have since been developed [4,5,6,7,8,9].

3. Working Equations

Our implementation of the steady-state vibrating-wire technique is very similar to that described by Audonnet and Pádua [7] in which the wire is driven by a constant sinusoidal current of amplitude I and frequency f the emf $V(f)$ generated across the vibrating wire is measured with a two-phase lock-in amplifier. This measured emf generally comprises two terms; the first, $V_1(f)$, arises from the electrical impedance of the stationary wire, while the second, $V_2(f)$, arises from the motion of the wire. In the analysis, we express V_1 as

$$V_1(f) = a + \mathbf{i}b + \mathbf{i}cf, \tag{1}$$

where a, b and c are real constants, f is the driving frequency and $\mathbf{i} = \sqrt{-1}$. The second contribution is given by [4,5]

$$V_2(f) = \frac{\Lambda f \mathbf{i}}{f_0{}^2 - (1+\beta)f^2 + (\beta' + 2\Delta_0)f^2 \mathbf{i}} . \tag{2}$$

Here, f_0 is the 'buoyancy corrected' fundamental transverse resonance frequency of the wire in vacuum which is related to the true vacuum resonance frequency, $f_{0,\text{vac}}$, by

$$f_0{}^2 = f_{0,\text{vac}}{}^2 - \frac{gV_\text{w}\rho}{16\pi\rho_\text{s}R^2L^2} . \tag{3}$$

Here, g is the gravitational acceleration, V_w is the volume of the weight, ρ is the density of the fluid, ρ_s is the density of the wire, R is the radius of the wire and L is the half

length of the wire. Typically, the true vacuum resonance frequency $f_{0,vac}$ and the internal damping term Δ_0 are determined in calibration measurements and f_0 is calculated for the state of interest from equation (3). The other parameters in equation (3) are an amplitude Λ, and two terms, β and β', that are related to the density ρ and viscosity η of the fluid by the hydrodynamic theory [4,5].

Experimentally, one measures the real and imaginary components of V as a function of frequency f for frequencies in the neighbourhood of f_0 in the fluid of interest. Then the parameters a, b, c, Λ, ρ and η are fitted to $V(f)$ making use of equations (1-3) together with the expression [4,5] relating β and β' to ρ and η. In our work, the lock-in amplifier was operated with offset real and imaginary voltage readings so as to permit measurements to be made on the most sensitive range possible. This offset is absorbed into the parameters a and b.

Theoretical treatments of the vibrating wire have normally considered simple end conditions such as pinned, clamped or free ends [4]. Typically, end-pinned conditions are assumed but experimental vacuum frequencies are found to deviate from the values predicted under that assumption. For example, the vacuum resonance measured by Dix *et al.* [10] is greater by 0.5% than that calculated assuming end-pinned conditions. To reconcile this discrepancy, we write the true vacuum resonance frequency as

$$f_{0,vac} = \frac{1}{4}\kappa\left(\frac{\pi^2 E R^2 \kappa^2}{16\rho_s L^4} + \frac{g M_w}{\pi \rho_s R^2 L^2}\right)^{\frac{1}{2}}, \tag{4}$$

where, E is Young's modulus for the wire, M_w is the mass of the suspended weight, and κ is a parameter the value of which may be adjusted to reflect the end conditions. For end-pinned conditions, κ is exactly unity while, for end clamped conditions, $\kappa \approx 1.05$. In the present work, κ was adjusted to match an experimental measurement of the vacuum resonance frequency at one temperature.

4. Instrument

The vibrating wire viscometer has been designed to operate in the viscosity range 0.3-30 mPa·s and at densities ranging from 600 to 1000 kg·m⁻³. As shown in figure 1, the vibrating wire and magnetic assembly were housed in a commercially-available pressure vessel (HIP model R1-10-30) rated for operation at 200 MPa. The key parameters of the apparatus are listed in table I. The temperature of the fluid was inferred from the reading of a platinum resistance thermometer (PRT) which was mounted in a well in the cap of the pressure vessel. This thermometer was calibrated with an uncertainty of ±0.01 K. The pressure was measured in the external pipework by means of a Paroscientific transducer (model 40K-110) with a full scale reading of 207 MPa and an uncertainty of 0.02 MPa.

1. Feed wires
2. Top clamp
3. Magnets
4. Vibrating wire
5. Bottom clamp and aluminium weight
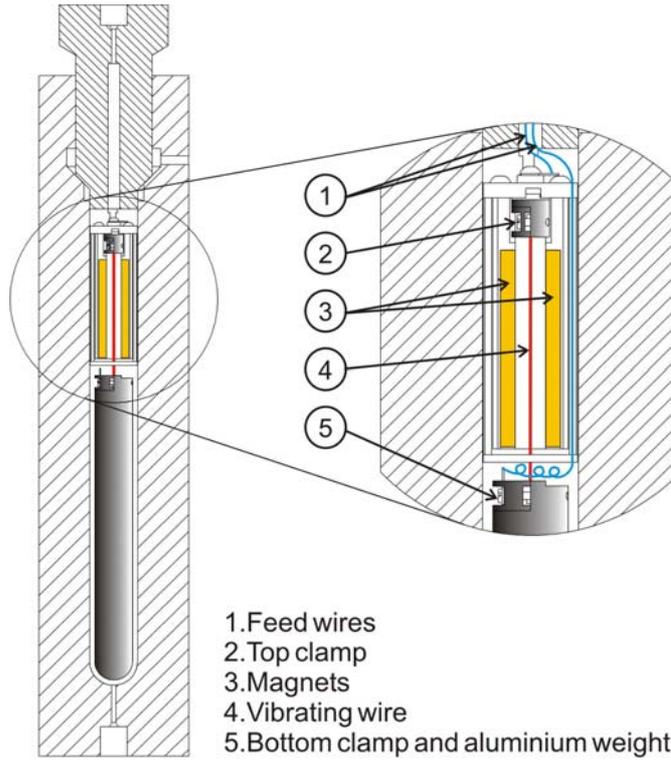
Figure 1. Diagram of the vibrating wire apparatus

Table I. Parameters of the measurement cell

Cell Parameters			Source
Volume		55 cm^3	measured
Tungsten Vibrating Wire			
Half-Length	L	32.5 mm	measured
Radius	R	49.129 μm	calibrated
Density	ρ_s	19300 kg·m^{-3}	from supplier
Young's modulus	E	411 GPa	from supplier
Internal Damping	Δ_0	20×10^{-6}	measured
Thermal expansion	α_s	4.5×10^{-6} K^{-1}	from supplier
End condition perturbation	κ	1.02745	calibrated
Aluminium Mass			
Mass	M_w	134.77 g	measured
Volume	V_w	50.647 cm^3	calibrated
Thermal expansion	α_w	23.6×10^{-6}K^{-1}	Reference [11]
Compressibility	β_w	1.32×10^{-11} Pa^{-1}	Reference [11]

The pressure vessel was enclosed in a massive aluminium block thermostat and insulated from the environment with 40 mm thick Kaowool V.F. ceramic fibreboard. The temperature of the block was controlled in three zones (top 1/5th, middle 3/5[ths] and lower 1/5th) by means of PID controllers (Eurotherm 2210e) operating with PRT sensors and a set of 10 cartridge heaters each rated at 110 W. This arrangement was able to keep the temperature stable and uniform to within ± 0.05 K over a period of days.

5. Calibration

Calibration of the apparatus was performed at 298.15 K by means of measurements in vacuum and in both ambient air and toluene at 0.1 MPa. The toluene was supplied by Riedel-de Haën with a stated mass-fraction purity of 99.9% and was used without further purification. The true vacuum resonance frequency, and hence the value of κ, was obtained from the measurement *in vacuo*. In principle, the internal damping Δ_0 can be obtained from the same measurement but the small-bore pressure tubing used made it difficult to achieve a sufficiently good vacuum in the cell. Accordingly, Δ_0 was obtained from a measurement in ambient air with due allowance for the viscosity and density of air. The radius of the wire radius and the volume of the suspended mass were obtained from the measurement in toluene. The resulting cell parameters are given in table I. It should be noted if one is not careful when measuring the resonance frequency in vacuum or air the wire can be driven to catastrophic non-linear behaviour. Small non-linear behaviour has also been noticed in toluene at 348 K with the apparent viscosity increasing linearly with drive voltage squared as observed by Wilhelm *et al.* [9]. Using a current of 0.9 mA produced a 1% increase in observed viscosity from that at currents below 0.1 mA.

To verify proper operation of the vibrating wire, a complete isotherm was measured after each calibration in toluene. Results obtained with three different wires are compared with literature data in Figures 2 and 3. It is estimated the present result are accurate to within ±0.2% in density and ±2% in viscosity.

Figure 2. Deviation in the density of toluene at 298.15 K from the correlation of Assael *et al.* [12]: ◇ this work May 2002; □ this work August 2002; ○ this work February 2003; ✕ Harris [13]; ✚ Kashiwagi [14].
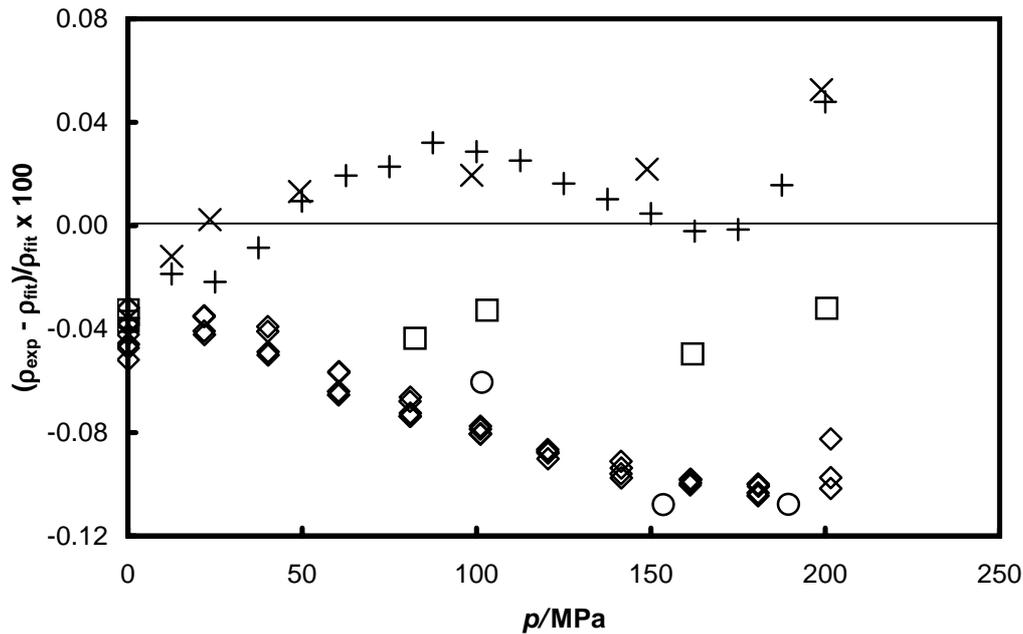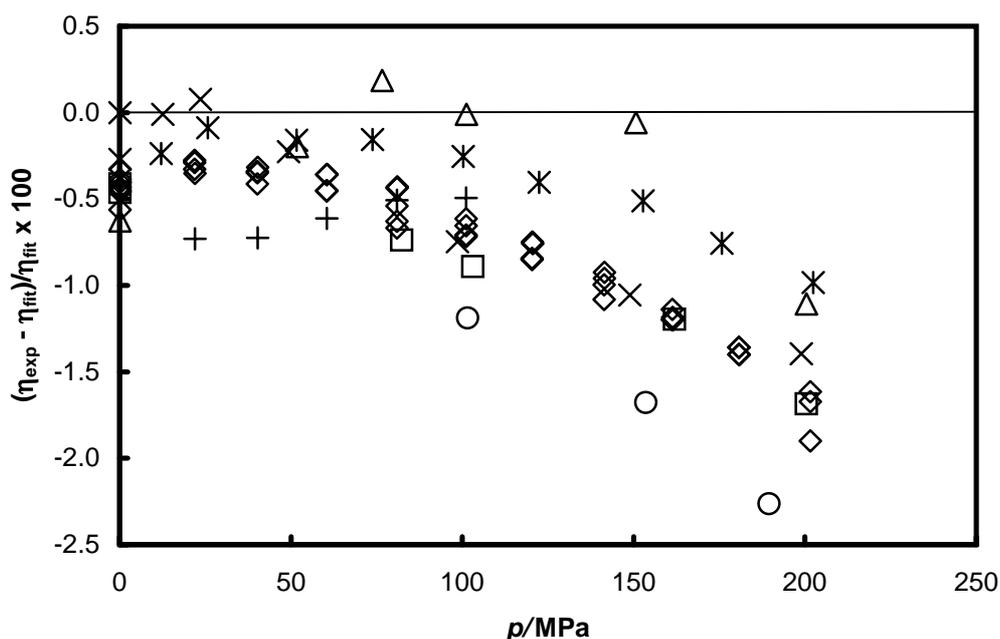
Figure 3. Deviations in the viscosity of toluene at 298.15 K from the correlation of Assael *et al.* [12]: ◇ this work May 2002; ☐ this work August 2002; ○ this work February 2003; △ Dymond [15]; ✕ Harris [13]; ✳ Harris [16]; ＋ Kashiwagi [17].

6. Results

n-dodecane and *n*-octadecane, both of specified mass-fraction purity >99%, were supplied by Aldrich. The viscosity and density of *n*-dodecane were measured along eight isotherms between 298.15 and 473.15 K at pressures up to 200 MPa and the results are presented in table II. The viscosity and density of *n*-octadecane were measured along 7 isotherms between 323.15 to 473.15 K at pressures up to 90 MPa and the results are presented in table III. Higher pressures were not studied due to freezing of *n*-octadecane in the pressure transducer (which was held at approximately 320 K). Small corrections, never more than 0.2% in viscosity and 0.01% in density, have been applied so as to reduce all tabulated results to the stated nominal isotherm temperatures.

Table II. Viscosity and density of *n*-dodecane.

p (MPa)	ρ (kg·m^{-3})	η (mPa·s)	p (MPa)	ρ (kg·m^{-3})	η (mPa·s)	p (MPa)	ρ (kg·m^{-3})	η (mPa·s)
			$T = 298.15$ K					
0.1	746.0	1.344	101.54	799.1	3.750	119.98	806.6	4.378
41.62	771.5	2.139	121.71	806.1	4.497	80.09	790.5	3.102
81.91	790.8	3.154	152.18	817.3	5.728	0.1	746.1	1.343
			$T = 323.15$ K					
0.1	727.4	0.911	121.70	794.5	2.762	161.33	809.1	3.677
42.21	756.8	1.422	160.48	808.9	3.627	81.35	778.1	2.007
81.44	777.3	2.012	191.67	818.8	4.502	0.1	727.5	0.910
			$T = 348.15$ K					
0.1	708.9	0.659	120.49	782.3	1.886	120.15	782.9	1.896
41.45	741.1	1.006	160.27	797.7	2.452	80.66	764.5	1.411
81.85	764.4	1.428	191.19	808.2	2.974	0.1	708.9	0.659
			$T = 373.15$ K					
0.1	689.8	0.503	120.44	770.9	1.406	120.26	771.2	1.405
41.30	726.7	0.777	161.34	787.7	1.809	80.76	751.8	1.073
80.20	750.9	1.069	191.74	798.7	2.149	1.0	690.0	0.503
			$T = 398.15$ K					
0.1	670.8	0.401	121.42	759.9	1.123	0.1	670.9	0.401
40.82	712.1	0.623	159.09	777.2	1.395			
80.51	738.7	0.855	81.06	739.0	0.858			
			$T = 423.15$ K					
0.1	651.1	0.324	121.56	749.4	0.915	0.1	651.1	0.323
40.74	698.1	0.512	163.26	768.2	1.158			
81.22	727.3	0.706	81.03	727.1	0.704			
			$T = 448.15$ K					
1.0	630.3	0.264	120.65	738.7	0.763	0.1	630.4	0.264
407.2	683.9	0.429	162.00	758.3	0.966			
801.4	714.8	0.588	80.81	715.4	0.591			
			$T = 473.15$ K					
1.0	608.9	0.218	121.41	729.0	0.657	0.1	609.0	0.218
404.4	670.2	0.367	160.94	748.6	0.813			
811.0	704.3	0.510	80.16	703.7	0.506			

<div align="center">Table III. Viscosity and density of n-octadecane.</div>

p (MPa)	ρ (kg·m^{-3})	η (mPa·s)	p (MPa)	ρ (kg·m^{-3})	η (mPa·s)	p (MPa)	ρ (kg·m^{-3})	η (mPa·s)
			$T = 323.15$ K					
0.1	762.4	2.460	62.23	799.0	5.033	0.1	763.2	2.466
20.78	776.6	3.196	91.96	812.3	6.728			
40.30	787.7	3.999	40.83	788.7	4.028			
			$T = 348.15$ K					
0.1	744.6	1.595	61.09	783.7	3.092	0.1	744.7	1.597
21.60	760.6	2.065	90.77	797.9	4.035			
42.09	773.4	2.566	40.89	773.1	2.538			
			$T = 373.15$ K					
0.1	726.2	1.123	62.81	771.1	2.167	0.1	726.2	1.123
22.69	745.3	1.467	92.20	786.2	2.766			
43.30	759.5	1.813	40.90	758.1	1.770			
			$T = 398.15$ K					
0.1	709.2	0.834	61.49	757.8	1.584	0.1	709.3	0.834
22.51	730.5	1.088	82.39	769.7	1.874			
42.40	745.6	1.332	40.58	744.4	1.310			
			$T = 423.15$ K					
0.1	691.8	0.646	62.55	746.1	1.241	0.1	691.8	0.646
21.63	715.0	0.841	83.87	758.9	1.469			
42.32	732.2	1.035	40.26	730.7	1.017			
			$T = 448.15$ K					
0.1	674.2	0.516	60.40	732.8	0.980	0.1	674.2	0.516
21.36	700.3	0.676	83.21	747.5	1.170			
41.34	718.5	0.829	39.89	717.3	0.819			
			$T = 473.15$ K					
0.1	656.2	0.420	60.71	721.7	0.816	0.1	656.2	0.420
21.15	685.6	0.558	82.47	736.6	0.965			
41.31	705.8	0.689	40.75	705.5	0.685			

For purposes of interpolation, the density data have been fitted by a Tait-type equation,

$$\rho = \rho_0 \left\{ 1 - C \log_{10}\left(\frac{B+p}{B+p_0}\right) \right\}^{-1}, \tag{5}$$

where $p_0 = 0.1$ MPa, C is a constant and ρ_0 and B are given as follows:

$$\rho_0/(\text{kg·m}^{-3}) = \sum_{i=0}^{2} a_i (T/\text{K})^i, \tag{6}$$

$$B/\text{MPa} = \sum_{i=0}^{2} b_i (T/\text{K})^i \tag{7}$$

The viscosity has been represented by a hard-sphere scheme employed by Assael *et al.* [12] for toluene in which η is given by

$$\eta/(\text{Pa·s}) = \eta^* \left[1.7402 \times 10^9 \ \{V/(\text{m}^3\text{·mol}^{-1})\}^{2/3} \ \{M/(\text{kg·mol}^{-1})\}^{1/2} \{T/\text{K}\}^{1/2} \right]^{-1}, \tag{8}$$

where V is the molar volume, M is the molar mass and η^* is a dimensionless viscosity given by

$$\frac{1}{\eta^*} = \sum_{i=0}^{3} d_i (V/V_0)^{i}. \tag{9}$$

In equation (9), V_0 is a temperature dependent molar core volume given by

$$V_0/(10^{-6}\text{m}^3 \cdot \text{mol}^{-1}) = \sum_{i=0}^{3} e_i (T/\text{K})^{i}. \tag{10}$$

Equations 11 to 10 form self-consistent representations for viscosity and density as functions of temperature and pressure. The values of the parameters determined for *n*-dodecane and *n*-octadecane are given in table IV. For *n*-dodecane, the viscosity is represented with a greatest absolute deviation 1.4% and an average absolute deviation of 0.5% while, for *n*-dodecane, the greatest absolute deviation is 0.8% and the average absolute deviation of 0.2%.

The results for *n*-dodecane are compared with literature data in figures 4 and 5. For density, the agreement with literature date is generally within ±0.2% except for one isotherm at 348 K measured by Dymond and co-workers [18] which deviates by up to -0.3% at high pressure. In the case of the viscosity, the present results agree with those of Dymond [18] and Tanaka [21] at low pressures but show deviations of up to 4% at higher pressures - close to the mutual uncertainty of ±4%.

Table IV. Parameters for *n*-dodecane and *n*-octadecane

Coefficient	*n*-dodecane	*n*-octadecane
$10^{-3}a_0$	0.921984	1.01007
a_1	-0.47516	-0.80587
$10^4 a_2$	-3.922	1.2463
$10^{-3}b_0$	0.3451	0.38809
b_1	-1.1458	-1.2761
$10^3 b_2$	0.9837	1.1143
C	0.2072	0.2021
d_0	0.321621	0.2237588
d_1	-0.4803715	-0.371348
d_2	0.222206	0.188779
$10^2 d_3$	-2.964626	-2.67796
$10^{-2} e_0$	1.9154	2.85892
$10 e_1$	-4.41338	-4.03541
$10^4 e_2$	8.98744	6.10544
$10^7 e_3$	-6.7792	-3.792
M /kg·mol^{-1}	0.17034	0.254504
T_{min} /K	298.15	323.15
T_{max} /K	473.15	473.15
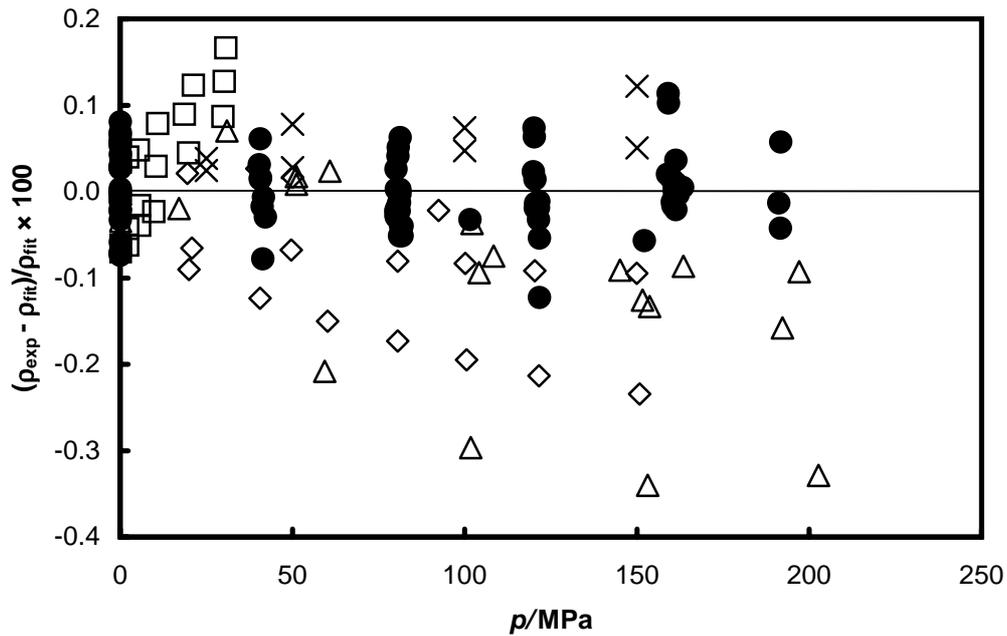
Figure 4. Deviations of the density of *n*-dodecane from equations (5): ● this work ; △ Dymond [18]; ✕ Easteal [19]; ☐ Rousseaux [20]; ◇ Tanaka [21].
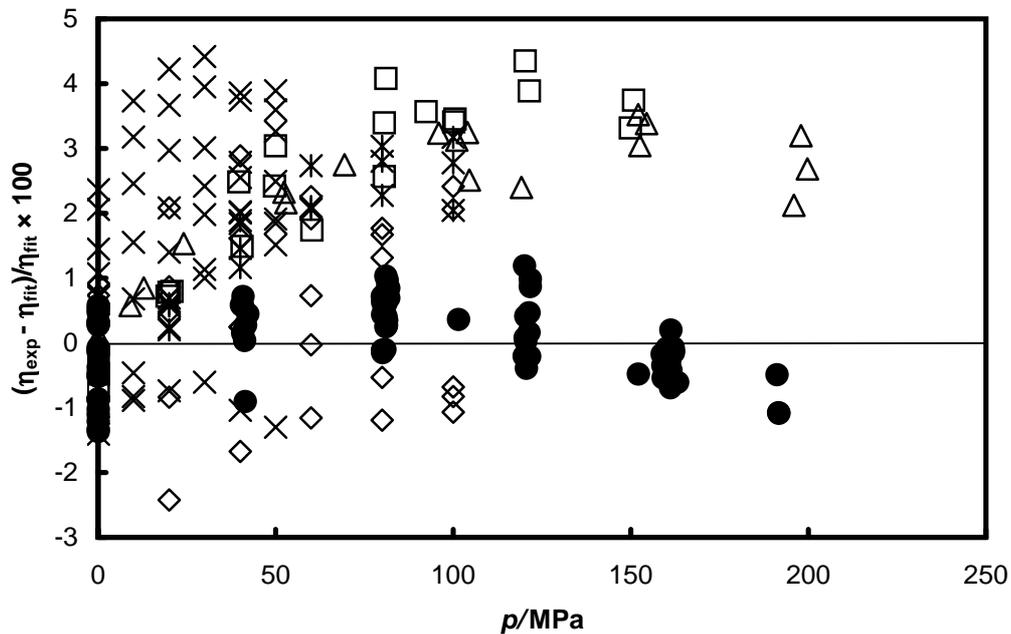
Figure 5. Deviations of the viscosity of *n*-dodecane from equation (8): ● this work ; ◇ Ducoulombier [22]; △ Dymond [18]; ✳ Kashiwagi [17]; ✕ Stephan [23]; ☐ Tanaka[21].

The results for *n*-octadecane are compared with the limited literature data available in figures 6 and 7. The density agrees reasonably well with values determined from sound-speed measurements by Dutour *et al.* [24] although the deviations show a marked temperature dependence with errors ranging from around -0.15% at 323.15 K to around +0.15% at 383.15 K. In the case of viscosity, the results of Ducolombier [22] and

Hogenboom [25] agree with this work at low pressures but show positive deviations of up to 6% at higher pressures. It is interesting to note that, for *n*-dodecane, the results of Ducolombier were in agreement with this work to ±3%.
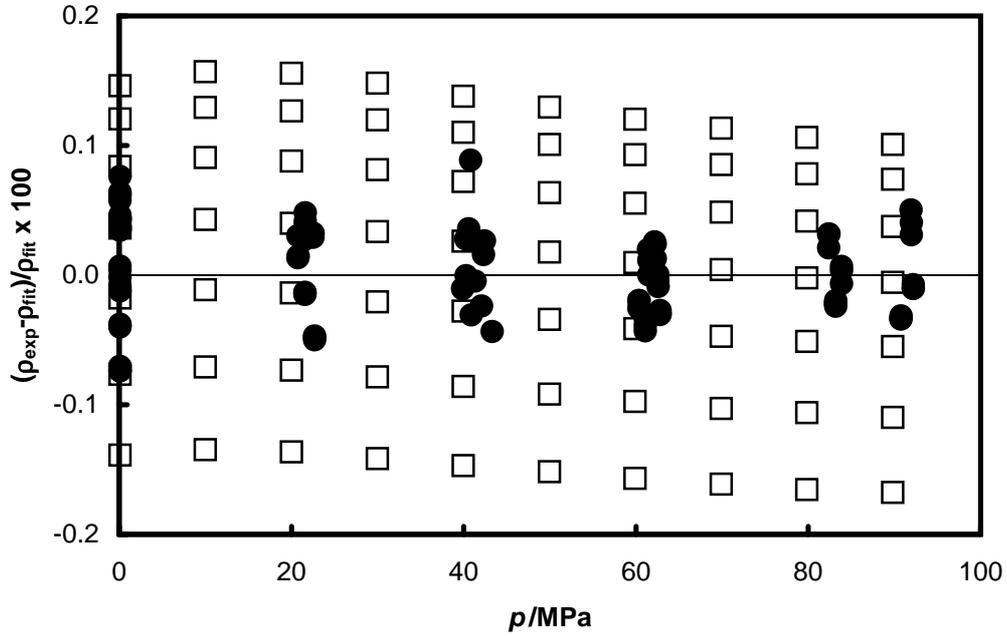
Figure 6. Deviations of the density of *n*-octadecane from equation (5): ● this work ; □ Dutour [24].
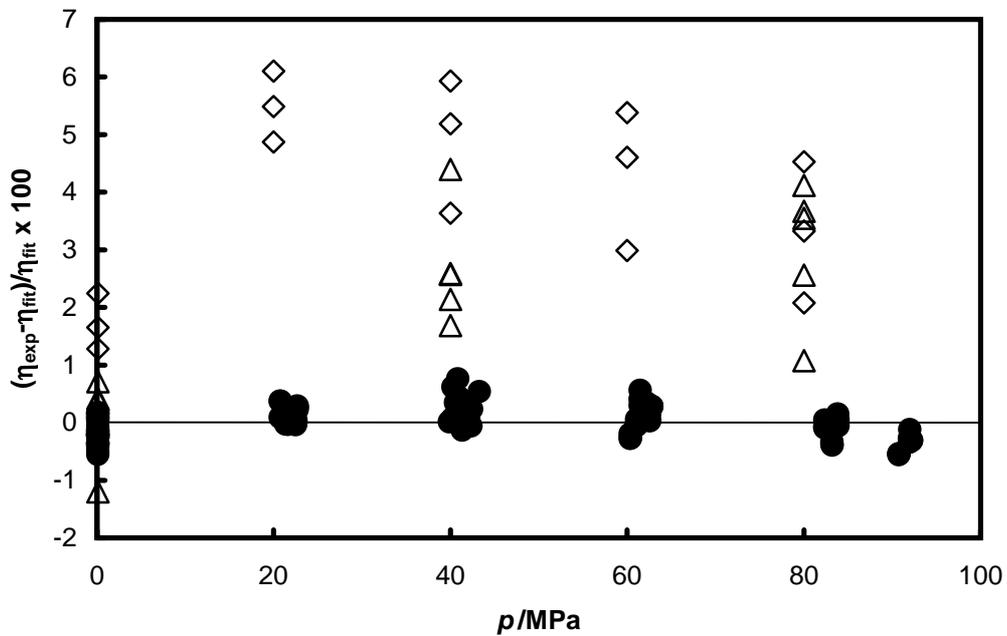
Figure 7. The viscosity of *n*-octadecane from equation (8); ● This work ; ◇ Ducoulombier [22]; △ Hogenboom[25].

7. Conclusions

The results obtained for toluene demonstrate proper working of the new instrument and support an estimated uncertainty of ±2% in viscosity and ±0.2% in density. New results are reported for n-dodecane and n-octadecane. Measurements on other pure liquids and binary mixtures will be reported in the near future.

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