Viscosities of liquid cyclohexane and decane at temperatures between (303 and 598) K and pressures up to 4 MPa measured in a dual-capillary viscometer

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ABSTRACT: The viscosities of cyclohexane and decane are reported at temperatures between (303.15 and 598.15) K and at pressures of (0.1, 1, 2, 3 and 4) MPa. The experiments were carried out with a dual-capillary viscometer that measures the ratio of the viscosities at temperature T and pressure p to that at a reference temperature of 298.15 K and the same pressure. Absolute values of the viscosity were then obtained with an expanded relative uncertainties at 95 % confidence of 3.0 % by combining the measured ratios with literature values of the viscosity at the reference temperature.

KEYWORDS: capillary viscometer, cyclohexane, decane, high temperature, viscosity.

1. INTRODUCTION

The viscosity of hydrocarbons is important in the petroleum industry generally and in fuel applications in particular. Its importance can be seen in the Reynolds number, which is a key determinant in fluid flow and heat transfer phenomena, and also in the Navier-Stokes equations which describe fluid flow in a host of scientific and engineering problems.

The term “endothermic fuel” has been coined to describe the use of liquid hydrocarbon fuels to cool the exterior surfaces of hypersonic vehicles and/or for the regenerative cooling of engine parts. In such applications, the fuel flows through channels in the surfaces to be cooled and absorb heat, in part as a consequence of endothermic cracking reactions, before entering the combustion chambers. In order to model the flow and heat transfer in this situation, it is important to know the viscosity of the fuel as a function of temperature over the operational range, taking into account the progress of cracking reactions. Consequently, the viscosity of complex mixtures is involved but this may be related in modelling to the viscosities of one or more pure substances. Unfortunately, this approach is complicated by the lack of experimental data for representative hydrocarbons at temperatures above about 473 K. Measurements on pure substances at higher temperatures may be compromised by thermal degradation of the sample and by other experimental difficulties. Therefore, in this work, we have developed a dual-capillary viscometer with a short residence time in the high-temperature zone which we hope will permit reliable measurements on several hydrocarbons, ultimately at temperatures up to 773 K. In this paper, we report initial results for two simple liquids, cyclohexane and decane, at temperatures up to almost 600 K and at pressures up to 4 MPa. In future work, we plan to extend the measurements to more representative hydrocarbons and to higher temperatures.

Recently, Tariq et al.¹ critically assessed the available experimental data for the viscosity of cyclohexane and provided a new reference correlation covering a wide range of temperatures (from the triple point to 700 K) and pressures (up to 110 MPa). The authors reported that in 186 papers containing 1427 data points for the viscosity of cyclohexane, the vast majority (165 papers, 504 data points) pertained to atmospheric pressure and near-ambient temperatures.

Very few data were available for cyclohexane at higher temperatures and, amongst the primary data selected for the development of the correlation, only one data set for liquid cyclohexane extended to $T > 441$ K. The available viscosity data for decane have been reviewed and correlated by Huber et al.² and their correlation is implemented in the REFPROP version 9.1 software package.³ At temperatures up to about 400 K, multiple literature sources were in good agreement but at higher temperatures, especially above 450 K, very few data were available. Accordingly, the present work is intended to address the gaps identified in the literature so as to permit improved viscosity correlations to be developed for these two substances.

2. PRINCIPLE

Berg et al.⁴ and May et al.⁵ described the principle of a dual-capillary viscometer for measurements on gases and, in this work, we have adapted the methodology for measurements on liquids. The single-capillary viscometer is based on Poiseuille's law⁶ which describes isothermal, slip-free laminar flow of an incompressible Newtonian fluid in a long straight cylindrical tube. In this situation, the viscosity η is given by the relation

$$\eta = \left(\frac{\Delta p}{Q} \right) \left(\frac{\pi r^4}{8L} \right) = \frac{\Delta p}{QZ}, \quad (1)$$

where Δp is the pressure drop across the capillary, Q is the volumetric flow rate, r and L are the radius and length of the capillary, and Z is the flow impedance of the capillary defined by

$$Z = \frac{8L}{\pi r^4}. \quad (2)$$

A dual-capillary viscometer comprises two capillaries in series (hereafter called the reference capillary and the measurement capillary, respectively), the first maintained at a constant reference temperature T_0 and the second maintained at a test temperature T . In steady-state flow, the test fluid passes through the two capillaries at the same mass flow rate, and the volumetric flow rates in the two capillaries are therefore related by

$$Q(T, p_M) = \left(\frac{\rho(T_0, p_R)}{\rho(T, p_M)} \right) Q(T_0, p_R), \quad (3)$$

where ρ denotes density. In equation (3), we also recognize that there is a pressure drop though the flowing system and define p_R and p_M as the mean absolute pressures in the reference and measurement capillaries, respectively. The dual-capillary viscometer permits measurement of the ratio of the viscosities of the test fluid at temperatures T and T_0 as demonstrated by application of equations (1) and (3) to each capillary leading to the relation:

$$\frac{\eta(T, p_M)}{\eta(T_0, p_R)} = \left(\frac{\Delta p_{M,T}}{\Delta p_{R,T_0}} \right) \left(\frac{\rho(T, p_M)}{\rho(T_0, p_R)} \right) \left(\frac{Z_{R,T_0}}{Z_{M,T}} \right). \quad (4)$$

Here, subscripts M and R refer to the measurement and reference capillaries, respectively. Application of equation (4) to the case in which $T = T_0$ permits evaluation of the impedance ratio from a calibration measurement at that temperature as follows:

$$\frac{Z_{R,T_0}}{Z_{M,T_0}} = \left[\left(\frac{\Delta p_{R,T_0}}{\Delta p_{M,T_0}} \right) \left(\frac{\rho(T_0, p_R)}{\rho(T_0, p_M)} \right) \left(\frac{\eta(T_0, p_M)}{\eta(T_0, p_R)} \right) \right]_{\text{cal}}. \quad (5)$$

In view of equation (2), the impedance ratio for $T \neq T_0$ can then be obtained by consideration of the integrated thermal expansions ΔL and Δr of the length and radius of the capillary leading, for a homogeneous material, to the following relation:

$$\frac{Z_{M,T_0}}{Z_{M,T}} = \left(\frac{L}{L + \Delta L} \right) \left(\frac{r + \Delta r}{r} \right)^4 = \left(1 + \frac{\Delta L}{L} \right)^3 \approx 1 + 3 \frac{\Delta L}{L}. \quad (6)$$

In the present work, capillaries of fused quartz were used for which the mean linear expansion coefficient is about $0.6 \times 10^{-6} \text{ K}^{-1}$.^{7,8} Thus, the thermal expansion term $3\Delta L/L$ was not expected to exceed 0.06 % and, since this was considered negligible, the expression for the viscosity ratio was reduced to:

$$\frac{\eta(T, p_M)}{\eta(T_0, p_R)} = \left(\frac{\Delta p_{M,T}}{\Delta p_{R,T_0}} \right) \left(\frac{\rho(T, p_M)}{\rho(T_0, p_R)} \right) \left[\left(\frac{\Delta p_{R,T_0}}{\Delta p_{M,T_0}} \right) \left(\frac{\rho(T_0, p_R)}{\rho(T_0, p_M)} \right) \left(\frac{\eta(T_0, p_M)}{\eta(T_0, p_R)} \right) \right]_{\text{cal}}. \quad (7)$$

If we arrange for the mean absolute pressure in the reference capillary to be the same during both calibration and measurement, equation (7) simplifies to

$$r_\eta = \frac{\eta(T, p_M)}{\eta(T_0, p_M)} = \left(\frac{\Delta p_{M,T}}{\Delta p_{R,T_0}} \right) \rho(T, p_M) \left[\frac{1}{\rho(T_0, p_M)} \left(\frac{\Delta p_{R,T_0}}{\Delta p_{M,T_0}} \right) \right]_{\text{cal}}, \quad (8)$$

where the terms in square brackets refer to the calibration experiment with $T = T_0$. Equation (8) now gives the viscosity ratio r_η between temperatures T and T_0 at the mean absolute pressure p_M in the measurement capillary during operation at temperature T . In principle, the mean absolute pressure p_M in the measurement capillary during the measurement at temperature T and the calibration at temperature T_0 differ slightly, even though the mean absolute pressures in the reference capillaries are taken to be equal. In practice, the difference is very small, in which case the densities appearing in equation (8) may be evaluated at the same pressure and the viscosity ratio becomes:

$$r_\eta = \frac{\eta(T, p_M)}{\eta(T_0, p_M)} = \left(\frac{\Delta p_{M,T}}{\Delta p_{R,T_0}} \right) \left(\frac{\rho(T, p_M)}{\rho(T_0, p_M)} \right) \left(\frac{\Delta p_{R,T_0}}{\Delta p_{M,T_0}} \right)_{\text{cal}}, \quad (9)$$

where only the last term relates to the calibration run.

When, as in this work, the capillaries are coiled, secondary flow effects can arise leading to additional dissipation and a non-linear dependence of the pressure drop upon flow rate.^{9,10} The magnitude of this effect is governed by the value of the Dean number, De , defined as $De = Re\sqrt{\delta}$, where $Re = 2Q\rho/(\pi r\eta)$ is the Reynolds number, $\delta = r/R$ and R is the radius of curvature of the coil. To correct for the effect of secondary flow, the measured pressure drop should be multiplied by a correction factor $f(De, \delta)$ as discussed by Berg.¹⁰ In the present case, $De \leq 17$ and $\delta = 0.0025$, in which case the following approximation is sufficient:¹⁰

$$f = \left[1 + 16 \left(\frac{De}{De_0} \right)^4 \right]^{-1/16}, \quad (10)$$

where $De_0 = 40.58$.

Experimentally, it is found that differential pressure sensors often exhibit a zero offset which gives rise to an error in the measured ratio of pressure drops which is of increasing magnitude

as the flow rate is reduced. One way of dealing with this problem is to replace the ratio $(\Delta p/Q)$ in equation (1) by the slope $S = (d\Delta p/dQ)$ such that, in a single capillary,

$$\eta = \frac{S}{Z}. \quad (11)$$

When the slope is calculated from experimental $(\Delta p, Q)$ data, for example by linear regression analysis, the effect of any constant offset in the measurement of Δp is eliminated. Accordingly, the final working equation used in this work was as follows:

$$r_\eta = \left(\frac{S_{M,T}}{S_{R,T_0}} \right) \left(\frac{\rho_T}{\rho_{T_0}} \right) \left(\frac{S_{R,T_0}}{S_{M,T_0}} \right)_{\text{cal}}, \quad (12)$$

where ρ_T/ρ_{T_0} is a simplified notation for the ratio of the densities at temperatures T and T_0 at pressure p_M . The slopes in equation (12) are determined from the pressure drop data for the relevant capillary with the volumetric flow rate Q measured at a common temperature and pressure. The experimental pressure drops were multiplied by the secondary-flow correction factor, as determined from equation (10), prior to determining the slopes.

3. EXPERIMENTAL SETUP

The schematic diagram of the experimental apparatus is shown in Figure 1. The dual-capillary viscometer comprised a reference capillary, housed in a water bath maintained at $T_0 = 298.15$ K, and pre-heat and measurement capillaries, both located in an oven maintained at the test temperature T . The water bath had a capacity of 5 L was controlled at the reference temperature to within ± 0.1 K. The high-temperature oven had a rated maximum operating temperature of 773.15 K and a working volume of 30 L. The heavy-duty fan and PID process controller ensured temperature uniformity and stability to within ± 0.5 K or better over the working temperature range. The purpose of the pre-heat capillary was to bring the flowing liquid to the test temperature before it entered the measurement capillary.

The capillaries were of nickel-clad fused silica tubing with an external diameter of 0.79 mm and an internal diameter of 0.25 mm. Zero-dead-volume stainless-steel chromatography fittings with stainless steel ferrules were used for the connections. The reference capillary had a nominal length of 1000 mm, and both the preheat capillary and the measurement capillary were 3000 mm in length. The capillaries were coiled with a radius of curvature of 50 mm.

The test fluid was delivered from a high-pressure syringe pump (ISCO model 100 DM with maximum pressure of 69 MPa) through a filter with a removable 2 μm pore-size frit. The pump was operated in constant flow-rate mode which, according to the specifications, maintained Q constant to within $\pm 0.003Q$. A back pressure regulator (Jasco model BP-2080) at the outlet of the system was used to control the system pressure. An isolating capillary (length 50 mm, internal diameter 0.1 mm) was inserted before the back-pressure regulator to suppress pressure fluctuations upstream associated with flow instability through the regulator.

Tee pieces inserted before and after the reference and measurement capillaries permitted connection to the differential-pressure sensors that were used to measure the pressure drop across each section. These sensors were located at ambient temperature and were connected by means of 0.79 mm o.d. stainless-steel tubing. The differential pressure sensors (Keller, model PRD-33X) provided a digital output of both the differential pressure, with a working range of (0 to 100) kPa, and the absolute upstream pressure, with a working range of (0 to 4) MPa. According to the manufacturer, the uncertainty of the differential pressure was 0.05 kPa, after correction for zero offset, while that of the total pressure was 0.004 MPa.

The temperatures of the water bath and the oven were measured with 4-wire platinum resistance thermometers (TC Direct, model 514-657) manufactured to the IEC60751:2008 standard. A data acquisition system (Agilent model 34970A) fitted with a multiplexer card was used to measure the resistance of the thermometers and transmit the data to the control computer. The thermometers were calibrated by the supplier with reference to ITS-90 at temperatures of (273.15, 473.15, 673.15, and 873.15) K and deviations were found to be within ± 0.1 K at $T \leq 673.15$ K. Considering also the presence of temperature gradients in the oven, the standard

uncertainty of the measurement temperature was taken to be 0.5 K while that of the reference temperature was taken to be 0.1 K.

4. EXPERIMENTAL MEASUREMENTS AND ANALYSIS

Viscosity ratios for cyclohexane and decane are reported in this study and a description of the samples can be found in Table 1. No analysis or purification was attempted.

4.1 Validation Measurement. As the apparatus was newly constructed for this work, some simple initial validation measurements were performed. The pressure drops across the two capillaries were measured with cyclohexane at various volumetric flow rates Q_0 (measured at the pump) with the reference capillary at $T_0 = 298.15$ K, the measurement capillary $T = 373.55$ K, and the pressure just upstream of the measurement capillary at $p = 3.0$ MPa. The results are shown in Figure 2.

The results conform to linear functions of the flow rate Q_0 and were fitted as follows:

$$\Delta p_{R,T_0} / \text{kPa} = 165.30 Q_0 / (\text{mL} \cdot \text{min}^{-1}) - 1.27 \quad (13)$$

$$\Delta p_{M,T} / \text{kPa} = 200.63 Q_0 / (\text{mL} \cdot \text{min}^{-1}) - 0.99 \quad (14)$$

The average absolute relative deviation of the experimental pressure drops from these correlations were 0.13 % and 0.09 % for the reference and measurement capillaries, respectively, indicating a very good linear dependence upon flow rate. We noted in these early measurements larger than expected offsets (the constant terms in equation 13 and 14) despite having adjusted the zero of the differential pressure sensors with both ports open to the atmosphere immediately prior to the measurements. This was attributed to the presence of air in the capillaries connecting the pressure sensors to the flow path. In future measurements, these lines were more carefully purged and smaller offsets were usually observed when the pressure drops were correlated as linear functions of flow rate.

We also compared the viscosities calculated from equations (2), (11), (13) and (14), using the nominal lengths and diameters of the capillaries, with values obtained from the correlation of Tariq et al.;¹ deviations of 2.7 % and 2.6 % were found at the temperatures of 298.15 K and 373.55 K, respectively. These deviations are consistent with the un-calibrated lengths and diameters used to calculate the impedances of the two capillaries; furthermore, those quantities are eliminated from the procedure when viscosities ratios are obtained with equation (12).

The main experimental parameters measured in this study are the pressure drop, temperature and pressure. Figure 3 exemplifies the variability observed in these quantities during measurements under near-steady-state conditions. Here and at each test condition, data were collected for a period at least 20 min under steady-state conditions; the temperature was recorded every 10 s and the pressure drop every 1 s. The data gathered in the final three minutes were averaged to obtain the experimental values associated with the chosen temperature, pressure and flow rate. The standard deviation of the mean temperature was < 0.1 K, while the relative standard deviation of the mean absolute and differential pressures were about 0.3 %.

4.2 Experimental Results. The state points investigated in this study are shown on temperature-pressure diagrams in Figure 4. All the measurements for cyclohexane were in the liquid phase at subcritical pressures, but for decane the critical pressure is lower and many of the measurements were at supercritical pressures. At sub-critical pressures, the measurements extend in temperature up to the saturation temperature of the liquid while, at higher pressures, temperatures up to 598.15 K were studied. The nominal pressures were (0.1, 1, 2, 3 and 4) MPa. At each state point, the pressure drops were measured at three or more different flow rates in the range (0.1 to 0.6) mL/min, depending upon the viscosities at the reference and measurement temperatures. Measurements with both capillaries at the same temperature of 298.15 K were also included to ensure that the impedance ratio was established. The Reynolds number of the test fluid flow was calculated to be in the range of 6 to 340, consistent with laminar flow conditions. The Dean number in the reference capillary never exceeded 2, so that corrections for secondary flow were entirely negligible. Because of the rapid decline of the viscosity with increasing temperature, higher Dean numbers up to a maximum of 17 were found

in the measurement capillary and corrections of up to 2.5 % were applied, although in the majority of cases the correction was less than 1 %. The corrected data were analyzed to obtain the relevant slope ($d\Delta p/dQ$), where Q was the volumetric flow rate at the pump, and the viscosity ratios were then evaluated from equation (12). The experimental viscosity ratios for cyclohexane and decane are given in Tables 2 and 3, together with absolute viscosities obtained using values of $\eta(T_0, p)$ from Tariq et al.¹ for cyclohexane and from Huber et al.^{2,3} for decane.

4.3 Uncertainties Analysis. The dependence of the standard relative uncertainty $u_r(r_\eta)$ of the viscosity ratio r_η upon the experimental slopes was determined by differentiation of equation (12). Including also the uncertainties of the density ratio, the pressure, and the two temperatures T_0 and T , the combined standard relative uncertainty of r_η is

$$u_r^2(r_\eta) = \left[u_r^2(S_{M,T}) + u_r^2(S_{R,T_0}) \right] + \left[u_r^2(S_{M,T_0}) + u_r^2(S_{R,T_0}) \right] + u_r^2(\rho_T/\rho_{T_0}) \\ + \left[r_\eta^{-1}(\partial r_\eta / \partial T)_p u(T) \right]^2 + \left[r_\eta^{-1}(\partial r_\eta / \partial T_0)_p u(T_0) \right]^2 + \left[r_\eta^{-1}(\partial r_\eta / \partial p)_T u(p) \right]^2. \quad (15)$$

Here, $u_r(X)$ is the standard relative uncertainty and $u(X)$ the standard uncertainty of variable X . The first term in square brackets in equation (15) relates to the two slopes determined with the measurement capillary at the experimental temperature T , while the second term in square brackets relates to the two slopes obtained with the measurement capillary at the reference temperature T_0 . The standard relative uncertainties of the slopes measured across the two capillaries under different conditions, as determined by linear regression analysis, varied somewhat but in almost all cases $\sqrt{u_r^2(S_{M,T}) + u_r^2(S_{R,T_0})} \leq 1.5\%$. The term relating to flow through both capillaries at temperature T_0 was smaller: $\sqrt{u_r^2(S_{M,T_0}) + u_r^2(S_{R,T_0})} = 0.5\%$; this was mainly the results of a larger data sample being gathered. The standard uncertainty of the density ratio differs for the two fluids studied. For cyclohexane, based on the equation of state of Penoncello et al.,¹¹ $u_r(\rho_T/\rho_0)$ was taken to be 0.1 % while for decane, based on the equation of state of Lemmon and Span,¹² $u_r(\rho_T/\rho_0)$ was taken to be 0.1 % at $T/K \leq 400$, 0.5 % at $400 < T/K \leq 500$ and 1 % for $T > 500$ K. The temperature uncertainties are $u(T_0) = 0.1$ K and $u(T) = 0.5$ K. As discussed above, the standard uncertainty of p_2 was 0.004 MPa but to account for pressure variations during a measurement, the standard uncertainty ascribed to the pressure

$p_M = (p_2 - 0.5\Delta p_{M,T})$ was taken to be 0.02 MPa. In order to evaluate the effects of the temperature and pressure uncertainties, the derivatives $(\partial r_\eta / \partial T)_p$ and $(\partial r_\eta / \partial p)_T$ in equation (15) were estimated from the correlations of Tariq et al.¹ for cyclohexane and Huber et al.^{2,3} for decane and it was found that the effects of the temperature and pressure uncertainties contributed less than 0.8 % to $u_r(r_\eta)$. The standard relative uncertainties $u_r(r_\eta)$ are shown in Figure 5 for both fluids. The root-mean-square value of $u_r(r_\eta)$ is 1.4 % and at all except one point $u_r(r_\eta)$ is less than 3 %. These individual statistical uncertainties are each based on a small sample, typically three points at different flow rates, and so we finally ascribe a constant standard relative uncertainty of 1.4 % to all points as indicated in Tables 2 and 3. The relative uncertainty of the absolute viscosity is slightly larger than this on account of the uncertainty of $\eta(T_0, p_M)$, which we take to be 0.5 % for both fluids, resulting in a combined standard relative uncertainty of $\eta(T, p_M)$ of 1.5 % and hence an expanded relative uncertainty at 95 % confidence of 3.0 %.

4.4 Correlation of the Viscosity Ratios. At low temperatures, the variation of the viscosity over the pressure range investigated is quite small, as exemplified by the values of $\eta(T_0, p_M)$ in Tables 2 and 3; however, with increasing temperature, the effect of the pressure becomes more pronounced and it is difficult to correlate the data in terms of temperature and pressure as the independent variables. However, the variation of the viscosity is determined largely by density changes as illustrated in Figure 6(a) where we plot the experimental viscosity ratios for both fluids as a function of the density ratios (ρ_T / ρ_0) . This plot demonstrates that $r_\eta(T, p)$ reduces to a function of the single variable (ρ_T / ρ_0) . Specifically, the result for each fluid were found to conform accurately to the following simple two-parameter empirical equation:

$$r_\eta = \exp \left[a \left(\frac{\rho_T}{\rho_{T_0}} \right)^2 + b \left(\frac{\rho_T}{\rho_{T_0}} \right)^{12} - (a + b) \right]. \quad (16)$$

The parameters a and b for each fluid are reported in Table 4 along with the average absolute relative deviation Δ_{AAD} and the maximum absolute relative deviation Δ_{MAD} . Deviations of the experimental viscosity ratios from equation (16) are plotted in Figure 6(b). From these

deviations, we can also conclude that the experimental data are internally consistent to within the estimate experimental uncertainty. Equation (16) is valid between the vapor pressure and $p = 4$ MPa and at temperatures between (298.15 and 523.15) K for cyclohexane or (298.15 and 598.15) K for decane.

5 Discussion

5.1 Viscosity of Cyclohexane. In Figure 7, we compare the new results with data from the literature¹³⁻¹⁹ at pressures up to 10 MPa as deviations from the correlation of Tariq et al.¹ Our results agree well with the majority of the experimental data reported in the literature; however, the data of Rajagapol et al.¹⁷ at temperatures below 400 K and those of Grachev et al.¹⁹ at $T > 450$ K show marked deviations of opposite signs. Our experimental results agree with the new reference correlation of Tariq et al.¹ to within about ± 2.0 % at temperatures up to 423 K but, at temperature above 450 K, the correlation predicts values that are systematically higher than our results by an amount that reaches about 7 % at 523 K. These deviations may be compared with the expanded relative uncertainty of the correlation at 95 % confidence, as reported by Tariq et al., which is 2 % in the liquid phase at $T \leq 440$ K and 5 % at $T > 440$ K. The observed differences between our results and the correlation only exceed the expanded relative uncertainty of the latter at temperatures above 473 K. The deviations observed at high temperatures most probably arise because Tariq et al. relied upon the data of Grachev et al.¹⁹ to constrain the behavior of their correlation in the liquid state at temperatures above 441 K and those data are systematically higher than ours at temperatures above 450 K.

5.2 Viscosity of Decane. Figure 8 compares our new results with data from the literature^{13, 14, 20-29} at pressure up to 10 MPa as deviations from the correlation of Huber et al.^{2,3} At temperatures up to 500 K, our new data agree with the correlation to within about ± 1 %, which is the stated uncertainty of the correlation for the saturated liquid. At higher temperatures, the deviations are somewhat dependent upon pressure and span the interval (-3 to -6) %. The primary experimental viscosity data selected for Huber's correlation (Dymond and Young,¹³

Caudwell,²⁰ Assael et al.,²³ Oliveira and Wakeham,²⁴ Knapstad et al.²⁵) mostly agree with our new results within about 1 %. However, the results of Tohidi et al.,²⁶ Carmichael et al.,²⁸ Estrada-Blatazar et al.,²⁹ all exhibit deviation from our results that are worse than ± 2 %. No previously-published experimental data have been found at temperatures above 523 K for liquid decane.

6 Conclusions

The viscosities of liquid cyclohexane and decane were investigated in a dual-capillary viscometer at temperatures between (303 and 598) K and pressures between (0.1 and 4.0) MPa. The combined expanded relative uncertainty of the results at 95 % confidence was estimated to be 3.0 %. The results confirm the accuracy of existing correlations^{1,2} for the viscosities of these hydrocarbons in the liquid state at temperatures up to about 450 K but indicate significant deviations at higher temperatures. The experimental method was found to work well and should permit future measurements at higher temperatures.

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Table 1. Description of samples

Substance	Source	Mass fraction purity
Cyclohexane	Fluka	0.995
Decane	Aldrich	0.987

Table 2. Experimental viscosity ratios r_η and derived viscosities η of cyclohexane at temperatures T and pressures p_M , with reference temperature $T_0 = 298.15$ K. Also tabulated: density ratios ρ_T/ρ_{T_0} calculated from the equation of state of Penoncello et al.¹¹ and the reference viscosities $\eta(T_0, p_M)$ calculated from the correlation of Tariq et al.^{1 a}

$\frac{T}{\text{K}}$	$\frac{p_M}{\text{MPa}}$	$\frac{\rho_T}{\rho_{T_0}}$	r_η	$\frac{\eta(T_0, p_M)}{\mu\text{Pa} \cdot \text{s}}$	$\frac{\eta(T, p_M)}{\mu\text{Pa} \cdot \text{s}}$
303.1	2.93	0.9940	0.9214	925	852
305.2	0.14	0.9913	0.8940	891	796
305.1	0.96	0.9915	0.8903	900	801
305.2	1.96	0.9914	0.8969	913	819
305.2	3.94	0.9916	0.8953	937	839
313.8	2.92	0.9812	0.7801	925	721
323.7	0.15	0.9683	0.6743	891	601
324.0	1.02	0.9682	0.6835	902	616
323.7	1.99	0.9689	0.6729	913	614
323.7	4.00	0.9695	0.6728	937	631
348.9	0.14	0.9362	0.4853	891	432
348.9	0.99	0.9368	0.4883	901	440
348.9	2.08	0.9374	0.4867	915	445
348.9	3.03	0.9380	0.4869	926	451
348.9	3.93	0.9385	0.4783	938	449
373.7	0.97	0.9042	0.3673	900	331
373.7	2.02	0.9053	0.3675	913	336
373.7	2.93	0.9061	0.3672	925	340
373.7	3.96	0.9071	0.3686	938	346
398.2	0.96	0.8702	0.2864	901	258
398.1	2.00	0.8718	0.2870	914	262
398.2	2.94	0.8731	0.2872	926	266
398.1	4.01	0.8748	0.2883	938	270
422.4	0.96	0.8338	0.2269	901	204
422.5	1.97	0.8361	0.2285	913	209
422.5	2.96	0.8383	0.2302	925	214
422.5	3.96	0.8405	0.2302	936	216
447.5	1.01	0.7923	0.1830	901	165
447.6	2.04	0.7958	0.1804	913	165
447.7	3.01	0.7989	0.1821	925	170
447.7	4.00	0.8020	0.1845	938	174
473.4	1.93	0.7470	0.1436	912	131
473.3	3.00	0.7531	0.1459	926	138
473.4	3.93	0.7575	0.1471	937	139
498.2	3.02	0.6993	0.1141	925	106
497.9	3.05	0.7004	0.1142	926	106
498.1	3.98	0.7078	0.1173	938	110
498.3	4.02	0.7077	0.1173	938	110

523.0	3.05	0.6255	0.0841	927	79.1
523.0	3.97	0.6429	0.0903	937	85.6

^a Standard uncertainties are $u(T) = 0.5$ K; $u(p_M) = 0.02$ MPa; $u_r(r_\eta) = 1.4\%$; $u_r(\eta) = 1.5\%$.

Table 3. Experimental viscosity ratios r_η and derived viscosities η of decane at temperatures T and pressures p_M , with reference temperature $T_0 = 298.15$ K. Also tabulated: density ratios ρ_T/ρ_{T_0} calculated from the equation of state of Lemmon and Span;¹² and reference viscosities $\eta(T_0, p_M)$ calculated from the correlation of Huber et al.^{2,3 a}

$\frac{T}{\text{K}}$	$\frac{p_M}{\text{MPa}}$	$\frac{\rho_T}{\rho_{T_0}}$	r_η	$\frac{\eta(T_0, p_M)}{\mu\text{Pa} \cdot \text{s}}$	$\frac{\eta(T, p_M)}{\mu\text{Pa} \cdot \text{s}}$
303.3	0.15	0.9946	0.9293	848	788
303.2	0.96	0.9947	0.9334	857	800
303.3	2.00	0.9946	0.9315	868	808
303.2	3.01	0.9948	0.9268	878	814
303.1	3.97	0.9948	0.9334	888	828
323.8	0.14	0.9725	0.7137	849	606
323.7	1.12	0.9729	0.7193	857	617
323.7	1.99	0.9729	0.7229	868	628
323.7	3.01	0.9733	0.7126	878	625
323.8	3.96	0.9733	0.7102	888	631
348.9	0.14	0.9454	0.5412	848	459
348.9	1.05	0.9458	0.5423	858	465
348.9	2.09	0.9463	0.5402	869	469
348.9	2.93	0.9467	0.5412	877	475
348.9	3.95	0.9472	0.5418	888	481
373.7	0.13	0.9182	0.4304	847	365
373.7	0.96	0.9188	0.4304	856	368
373.7	2.04	0.9195	0.4297	869	373
373.7	2.89	0.9202	0.4289	876	376
373.7	3.96	0.9210	0.4286	888	381
398.2	0.14	0.8904	0.3470	849	295
398.2	0.99	0.8915	0.3494	857	299
398.2	2.03	0.8926	0.3505	868	304
398.2	2.91	0.8935	0.3519	877	309
398.1	3.94	0.8947	0.3521	887	312
423.5	0.95	0.8621	0.2888	857	247
423.5	1.06	0.8623	0.2865	858	246
423.5	2.11	0.8640	0.2886	868	251
423.4	2.96	0.8652	0.2893	878	254
423.4	3.94	0.8668	0.2903	887	258
447.7	1.06	0.8329	0.2403	857	206
447.7	1.99	0.8350	0.2412	867	209
447.7	2.96	0.8369	0.2420	878	212
447.7	3.99	0.8390	0.2432	888	216
473.4	2.15	0.8031	0.2008	869	174
473.4	2.92	0.8053	0.2019	878	177
473.4	3.99	0.8082	0.2031	888	180
498.3	2.09	0.7692	0.1681	868	146
498.3	3.06	0.7731	0.1701	879	150

498.2	3.89	0.7764	0.1716	887	152
523.1	1.06	0.7253	0.1380	858	118
523.1	1.94	0.7311	0.1401	867	122
523.1	3.00	0.7375	0.1434	878	126
523.0	3.97	0.7428	0.1454	888	129
547.9	1.07	0.6789	0.1116	857	95.7
547.9	1.98	0.6887	0.1154	868	100
547.9	2.94	0.6972	0.1195	878	105
547.9	4.00	0.7056	0.1216	888	108
573.6	1.93	0.6328	0.0917	868	79.6
573.7	2.97	0.6491	0.0974	877	85.5
573.8	4.03	0.6619	0.1024	889	91.0
598.5	2.09	0.5605	0.0712	869	61.9
598.5	2.98	0.5907	0.0793	878	69.6
598.4	4.02	0.6127	0.0838	889	74.5

^a Standard uncertainties are $u(T) = 0.5$ K; $u(p_M) = 0.02$ MPa; $u_r(r_\eta) = 1.4\%$; $u_r(\eta) = 1.5\%$.

Table 4. Parameters a and b in equation (16) for the viscosity ratio, and values of the average absolute relative deviation Δ_{AAD} and the maximum absolute relative deviation Δ_{MAD} for cyclohexane and decane.

Substance	a	b	$\Delta_{AAD}(r_\eta)$	Δ_{MAD}
Cyclohexane	2.9621	0.6689	0.8 %	3.3 %
Decane	2.9855	0.5975	0.8 %	2.1 %

Figure 1. Schematic diagram of the experimental apparatus: p_0 , p_1 , p_2 , absolute pressure sensors; Δp_R , Δp_M , differential pressure sensors; T_0 , T , thermometers.

Figure 2. Experimental pressure drops Δp across the reference capillary at $T_0 = 298.15$ K (●) and across the measurement capillary at $T = 373.55$ K (○) as a function of inlet volumetric flow rate Q_0 of cyclohexane at $p = 3.0$ MPa; —, equations (12) and (13).

Figure 3. Percentage deviations of the experimental pressure drops Δp_R and Δp_M and the absolute pressure p_2 , and deviations of the temperatures T_0 and T , from their respective mean values as a function of time t .

Figure 4. Distribution of data in temperature T and pressure p for (a) cyclohexane and (b) decane: ●, experimental state points; ○, critical point;² —, vapor pressure curve.²

Figure 5. Estimated standard relative uncertainties $u_r(r_\eta)$ of individual viscosity ratio measurements r_η as a function of temperature T : $\circ$, cyclohexane; $\square$, decane; $---$, root-mean-square value of $u_r(r_\eta)$.

Figure 6. (a) Experimental viscosity ratios r_η as a function of density ratio ρ_T/ρ_{T_0} ; (b) relative deviations $\Delta r_\eta/r_\eta = (r_\eta - r_{\eta,\text{calc}})/r_\eta$ between experimental viscosity ratios and values $r_{\eta,\text{calc}}$ calculated from equation (16) with parameters from Table 4: ●, cyclohexane; ○, decane. ---, $\pm 1.5\%$.

Figure 7. Deviations $(\eta_{\text{exp}} - \eta_{\text{corr}})/\eta_{\text{corr}}$ of experimental viscosities of cyclohexane from those predicted by the correlation of Tariq et al.:¹ ○, this study at different pressures (red ≤ 1 MPa, green 2 MPa, blue 3 MPa, purple 4 MPa); □, Dymond and Young;¹³ ◇, Kashiwaji and Makita;¹⁴ △, Pádua et al.;¹⁵ ×, Matsuo and Makita;¹⁶ *, Rajagapol et al.;¹⁷ +, Tanaka et al.;¹⁸ −, Grachev et al.¹⁹

Figure 8. Deviations $(\eta_{\text{exp}} - \eta_{\text{corr}})/\eta_{\text{corr}}$ of experimental viscosities of decane from those predicted by Huber's correlation:^{2,3} ○, this study at different pressures (red ≤ 1 MPa, green = 2 MPa, blue = 3 MPa, purple = 4 MPa); □, Dymond and Young;¹³ ◇, Kashiwaji and Makita;¹⁴ △, Caudwell;²⁰ ×, Naake et al.;²¹ *, Audonnet and Pádua;²² +, Assael et al.;²³ □ (brown), Oliveria and Wakeham;²⁴ ◇ (brown), Knapstad et al.;²⁵ △ (brown), Tohidi et al.;²⁶ × (brown), Lee and Ellington;²⁷ * (brown), Carmichael et al.;²⁸ + (brown), Estrada-Baltazar et al.²⁹

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