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Measurements of the Viscosity of *n*-Heptane, *n*-Nonane, and *n*-Undecane at Pressures up to 70 MPa

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New absolute measurements of the viscosity of *n*-heptane, *n*-nonane, and *n*-undecane are presented. The measurements were performed with a vibrating-wire instrument at temperatures of 303.15 and 323.15 K and pressures up to 70 MPa. The overall uncertainty in the reported viscosity data is estimated to be ±0.5%. A recently developed semiempirical scheme for the correlation and prediction of the thermal conductivity, viscosity, and self-diffusion coefficients of *n*-alkanes is applied to the prediction of the viscosity of *n*-heptane, *n*-nonane, and *n*-undecane. The comparison of these predicted values with the present high-pressure measurements demonstrates the predictive power of this scheme.

KEY WORDS: high pressure; *n*-heptane; *n*-nonane; *n*-undecane; viscosity.

1. INTRODUCTION

In the last decade, new, absolute, accurate measurements of the transport properties of *n*-alkanes over a wide range of temperatures and pressures have been performed. Thus, the thermal conductivity of *n*-alkanes up to hexadecane has been accurately measured [1–8], with many measurements extending up to about 600 MPa pressure [9–14]. The few existing measurements of the self-diffusion coefficient [15–18] have been performed at pressures up to 150 MPa. In the case of the measurement of the viscosity of *n*-alkanes, most of the measurements extend to high pressures [19–26], with the exception of *n*-heptane, *n*-nonane, *n*-undecane, and *n*-tridecane.

Based on the aforementioned measurements of the transport properties of *n*-alkanes, a semiempirical scheme was recently developed [27], for

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the correlation and prediction of these properties. This scheme was shown to be able to predict the thermal conductivity, the viscosity and the self-diffusion coefficient of *n*-alkanes with an uncertainty of ±6% over the temperature range 100 to 400 K and pressures up to 600 MPa.

In this paper, new absolute measurements of the viscosity of *n*-heptane, *n*-nonane, and *n*-undecane are reported. The temperatures studied were 303.15 and 323.15 K at pressures up to 70 MPa. The overall uncertainty of the reported values is estimated to be better than ±0.5%.

2. EXPERIMENTAL

The viscosity measurements were performed with the high-pressure vibrating-wire instrument described in detail elsewhere [28]. The measurements have been carried out along two isotherms, 303.15 and 323.15 K, at pressures up to 70 MPa. The samples of *n*-heptane, *n*-nonane, and *n*-undecane were all supplied by BDH Chemicals Ltd., with nominal purities better than 99.5, 99.0, and 99.0%, respectively. The density values used were obtained by Doolitle [29].

To assure the continuing good operation of our instrument, the viscosity of toluene was measured before and after every liquid in the fashion described elsewhere [29, 30]. The overall uncertainty of the viscosity measurements is estimated to be better than ±0.5%.

3. RESULTS

Tables I to III list the experimental data for the viscosity of *n*-heptane, *n*-nonane, and *n*-undecane along the two isotherms at 303.15 and 323.15 K. Table IV presents measurements of the viscosity of these liquids at atmospheric pressure as a function of temperature.

For comparison purposes, we have used a Tait-like equation to correlate each isotherm of the present measurements as

$$\ln\left[\frac{\mu}{\mu_0}\right] = E\ln\left[\frac{D+P}{D+0.1}\right] \tag{1}$$

where μ_0 represents the experimental viscosity at atmospheric pressure, and P denotes the pressure. The values of the constants for each isotherm for the three liquids are shown in Table V. In the same table the standard deviation of each fit is shown. It can be seen that the maximum standard deviation is ±0.14%.

In Fig. 1, the deviations of the present experimental measurements of the viscosity of *n*-heptane from those correlated by Eq. (1) are presented.

Table I. Viscosity of *n*-Heptane at 303.15 and 323.15 K, as a Function of Pressure

303.15 K			323.15 K		
Pressure (MPa)	Density (kg·m^{-3})	Viscosity (μPa·s)	Pressure (MPa)	Density (kg·m^{-3})	Viscosity (μPa·s)
0.10	675.6	370.7	0.10	659.1	304.1
5.42	680.4	390.9	5.67	664.8	322.6
10.69	685.0	411.9	10.54	669.7	339.5
15.66	689.2	432.7	15.60	674.6	357.1
20.52	693.2	452.6	20.72	679.3	375.0
25.74	697.3	474.2	25.69	683.7	392.0
30.70	701.2	494.9	30.60	687.9	409.0
35.67	704.9	516.1	35.26	691.7	425.3
40.83	708.7	538.2	38.00	693.8	436.3
45.39	711.9	558.0	43.57	698.0	456.0
50.97	715.7	582.3	52.69	704.2	489.4
55.83	718.9	604.3	60.90	709.3	520.1
61.00	722.1	627.8	63.94	711.1	531.3
65.96	725.1	649.6			
69.41	727.1	665.7			

Table II. Viscosity of *n*-Nonane at 303.15 and 323.15 K, as a Function of Pressure

303.15 K			323.15 K		
Pressure (MPa)	Density (kg·m^{-3})	Viscosity (μPa·s)	Pressure (MPa)	Density (kg·m^{-3})	Viscosity (μPa·s)
0.10	710.2	617.0	0.10	694.7	486.9
5.29	714.3	650.5	5.47	699.5	515.1
10.23	718.1	684.3	10.44	703.8	542.1
14.90	721.6	718.4	15.60	708.1	571.9
19.96	725.3	755.5	20.47	712.0	601.8
25.33	729.1	796.1	25.64	716.0	630.2
30.50	732.6	835.3	28.07	717.9	646.0
35.77	736.1	876.5	45.85	730.3	756.2
40.63	739.3	916.0	50.97	733.6	788.5
45.29	742.2	956.6	55.43	736.3	817.6
49.75	744.9	997.3	60.90	739.5	854.1
55.12	748.0	1045.3	65.71	742.3	886.1
58.87	750.1	1076.8	69.00	744.1	908.5
64.65	753.2	1128.7			

Table III. Viscosity of *n*-Undecane at 303.15 and 323.15 K, as a Function of Pressure

303.15 K			323.15 K		
Pressure (MPa)	Density ($kg \cdot m^{-3}$)	Viscosity ($\mu Pa \cdot s$)	Pressure (MPa)	Density ($kg \cdot m^{-3}$)	Viscosity ($\mu Pa \cdot s$)
0.10	733.0	990.5	0.10	718.5	747.2
5.32	736.9	1048.5	5.57	722.8	793.1
10.64	740.7	1112.6	10.54	726.6	838.3
15.60	744.2	1175.6	15.60	730.4	884.7
20.57	747.5	1239.9	20.57	734.1	933.6
25.64	750.8	1306.1	25.64	737.7	983.0
30.90	754.2	1377.2	30.70	741.3	1032.8
35.87	757.2	1450.8	35.87	744.8	1085.8
40.83	760.1	1523.6	40.88	748.1	1138.1
45.90	763.0	1600.7	45.90	751.3	1190.9
50.97	765.8	1679.0	50.97	754.4	1248.7
55.93	768.4	1756.9	55.93	757.3	1302.8
60.90	771.0	1842.8	62.42	761.0	1378.4

The maximum deviation of the present measurements is less than ±0.15%. In the same figure measurements of other investigators are also included. The only other absolute measurements are those performed by Knapstad et al. [19] at atmospheric pressure in an oscillating-cylinder viscometer with an uncertainty of ±0.5%. The deviations of these measurements from

Table IV. Viscosity of *n*-Heptane, *n*-Nonane, and *n*-Undecane as a Function of Temperature at Atmospheric Pressure

	Temperature (K)	Density ($kg \cdot m^{-3}$)	Viscosity ($\mu Pa \cdot s$)
n-Heptane	298.15	679.5	391.2
	303.15	675.5	370.7
	313.15	667.5	335.2
	323.15	659.1	304.1
n-Nonane	303.15	710.2	617.0
	313.15	702.5	546.2
	323.15	694.7	486.9
n-Undecane	303.15	733.0	990.5
	313.15	725.8	855.5
	323.15	718.5	747.2
	333.15	711.1	661.1

Table V. Coefficients of Eq. (1)

Liquid	Temperature (K)	μ_0 (μPa · s)	E	D (MPa)	σ (%)
n-Heptane	303.15	370.70	1.398	133.2	±0.04
	323.15	304.07	1.264	114.9	±0.08
n-Nonane	303.15	617.03	2.564	242.2	±0.14
	323.15	486.89	1.641	148.9	±0.11
n-Undecane	303.15	990.53	2.916	256.3	±0.09
	323.15	747.23	2.055	179.4	±0.07

those correlated by Eq. (1) is less than ±0.3%, which is well within the mutual uncertainty of the two instruments. The results of other measurements included in Fig. 1 were all performed on a relative basis, and the instruments were callibrated with water. The fitted high-pressure measurements of Kashiwagi and Makita [31], performed in a torsionally vibrating crystal instrument with an uncertainty of ±2%, show a maximum deviation of 0.7% from the present measurements. At atmospheric

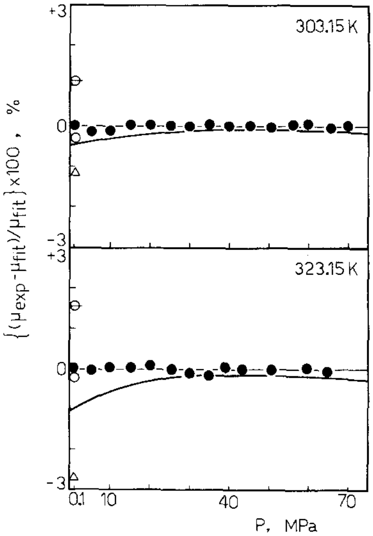

Fig. 1. Deviations of the experimental measurements of the viscosity of *n*-heptane from Eq. (1). (●) Present work; (○) Ref. 19; (——) Ref. 31; (△) Ref. 32; (⊖) Ref. 33.

pressure, the measurements of Wakefield and Marsh [32], performed in an Ostwald-type viscometer with a quoted uncertainty of ±0.5%, show a maximum deviation of ±2.7% from the those correlated by Eq. (1). The measurements of Golubev [33], performed also at atmospheric pressure, in a capillary viscometer with an uncertainty of ±1%, show a maximum deviation of ±1.6% from the present measurements.

In Fig. 2, the deviations of the present measurements of the viscosity of *n*-nonane from those correlated by Eq. (1) are presented. The maximum deviation is ±0.2%. To our knowledge, no other high-pressure measurements of the viscosity of *n*-nonane exist. In the same figure two other sets of relative measurements at atmospheric pressure are also included. The measurement of Wakefield and Marsh [32], performed in an Ostwald-type viscometer with a quoted uncertainty of ±0.5%, show a maximum deviation of 1.5% from those correlated by Eq. (1). The measurements of Bingham and Fornwalt [34], performed in a capillary viscometer calibrated with water with a quoted uncertainty of ±0.3%, show a maximum deviation of ±0.4%, which is well within the mutual uncertainty of the two instruments.

The deviations of the present measurements of the viscosity of *n*-undecane from those correlated by Eq. (1) are shown in Fig. 3. The maximum deviation is less than ±0.15%. To our knowledge, no other high-pressure measurements of the viscosity of *n*-undecane exist. In the

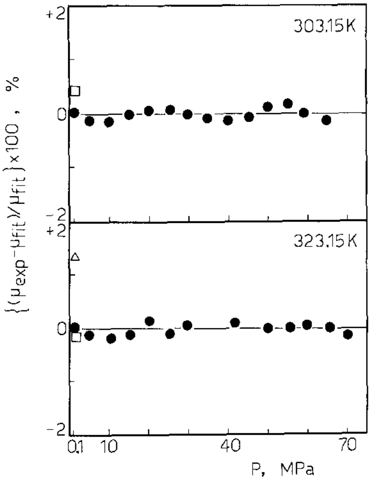

Fig. 2. Deviations of the experimental measurements of the viscosity of *n*-nonane from Eq. (1). (●) Present work; (△) Ref. 32; (□) Ref. 34.

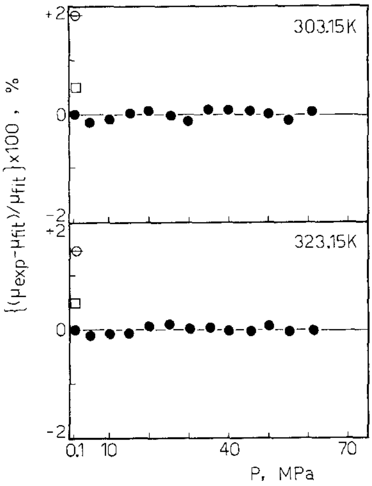

Fig. 3. Deviations of the experimental measurements of the viscosity of *n*-undecane from Eq. (1). (●) Present work; (⊖) Ref. 33; (□) Ref. 34.

same figure the relative measurements of Golubev [33] and Bingham and Fornwalt [34] are also included. The maximum deviation of the measurements of Golubev [33] is 1.7% from those correlated by Eq. (1), while the measurements of Bingham and Fornwalt [34] show a maximum deviation of 0.5%, which is well within the mutual uncertainty of the two instruments.

4. THE DENSITY DEPENDENCE

Whereas the correlation of the pressure dependence of the viscosity by means of Eq. (1) is suitable for interpolation, it has little or no value for extrapolation and prediction. For such purposes it has been shown [27, 35, 36] that a correlation in terms of the molar volume or density is much more suitable. The hard-sphere model of the dense fluid [35] suggests the form of such a correlation since it leads to the result that for a monatomic fluid the quantity, μ^*, defined by the equation

$$\mu^* = 6.035\ 10^8 \left[\frac{1}{MRT}\right]^{1/2} \mu V^{2/3} = F_\mu(V/V_0) \tag{2}$$

is a function of the reduced molar volume (V/V_0) only, where V_0 is a characteristic molar volume of the fluid which is but weakly temperature dependent.

Earlier studies have shown that if the result of Eq. (2) is carried over to polyatomic fluids, the function F_μ is nearly universal among a large group of n-alkanes, although the function is not the one predicted by the hard-sphere theory [36]. In the case of the thermal conductivity, it has been shown that the equivalent function, F_λ, is universal among a larger group of liquids including other hydrocarbons, alcohols, and diols, and this has been made the basis of a powerful prediction scheme for the thermal conductivity of such fluids [35].

For the n-alkanes the most recent and refined form for the function F_μ is that given by Assael et al. [27] as a result of a successful attempt to obtain a simultaneous representation of the thermal conductivity, viscosity, and self-diffusion coefficients of liquid n-alkanes over the temperature range 100–400 K and pressures up to 600 MPa. In this study, it emerges that it is not the function μ^* which is universal, but a slightly modified version of it, namely,

$$\log \frac{\mu^*}{R_\mu} = 0.877 - 3.79208\, V_\mathrm{r}^{-1} + 16.4416\, V_\mathrm{r}^{-2} - 24.2509\, V_\mathrm{r}^{-3} + 16.354\, V_\mathrm{r}^{-4} \tag{3}$$

in which

$$V_\mathrm{r} = V/V_0 \tag{4}$$

and where R_μ is a factor introduced to account for deviations from the behavior of smooth hard-spheres. The factor R_μ has been correlated as a function of the carbon number, C, by the expression

$$R_\mu = 0.9858 + 0.0164\, C + 0.001432\, C^2 \tag{5}$$

Following this scheme, the characteristic molar volume, V_0, has been evaluated using a series of accurate measurements of the transport properties of n-alkanes. It was, thus, successfully represented as a series in terms of the absolute temperature and the carbon number. For the n-alkanes, pentane to hexadecane, their representation is

$$10^6\, V_0 = 106.677 - 13.655\,\theta + 1.6266\,\theta^2 + (C-6)(18.028 - 1.2\,\theta)(0.944 + 0.0035\, C) \tag{6}$$

where

$$\theta = T/100$$

It follows that Eqs. (2)–(6) form a consistent set for the prediction of the viscosity of n-alkanes for the temperature range 100 to 400 K and pressures up to 600 MPa, with an uncertainty of better than ±6% [27].

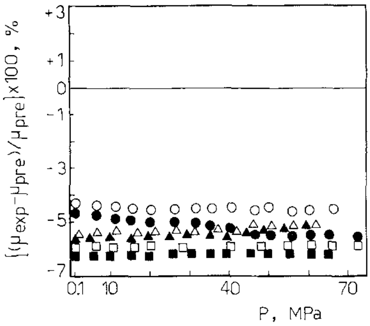

Fig. 4. Deviations of the experimental measurements of the viscosity of *n*-heptane, *n*-nonane, and *n*-undecane from the values predicted by Eqs. (2)–(6). 303.15 K: (●) *n*-heptane; (■) *n*-nonane; (▲) *n*-undecane. 323.15 K: (○) *n*-heptane; (□) *n*-nonane; (△) *n*-undecane.

In the derivation of the described scheme, viscosity data for *n*-heptane, *n*-nonane, and *n*-undecane were not used, as they were not available at that time. In Fig. 4, the deviations of the present measurements of the viscosity of *n*-heptane, *n*-nonane, and *n*-undecane from the values predicted by the aforementioned scheme are shown. Although it seems that the predicted values are systematically higher, they are still within 6% of the experimental values. Thus the predictive power of this scheme is demonstrated. At this point it should be noted that the 6% uncertainty of this scheme [27] was a consequence of a simultaneous correlation of the three transport properties of the *n*-alkanes (over a range of 100 to 400 K and pressures up to 600 MPa), as a function only of the carbon atoms, the temperature, and the molar volume.

5. CONCLUSIONS

New, absolute high-pressure measurements of the viscosity of *n*-heptane, *n*-nonane, and *n*-undecane were reported with an estimated uncertainty of ±0.5%. A universal procedure for the prediction of the viscosity of liquid *n*-alkanes was shown to predict the present data with an accuracy acceptable for many purposes.

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