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Measurements of the Viscosity of *n*-Heptane + *n*-Undecane Mixtures at Pressures up to 75 MPa

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New absolute measurements of the viscosity of binary mixtures of *n*-heptane and *n*-undecane are presented. The measurements, performed in a vibrating-wire instrument, cover the temperature range 295–335 K and pressures up to 75 MPa. The concentrations studied were 40 and 70%, by weight, of *n*-heptane. The overall uncertainty in the reported viscosity data is estimated to be ±0.5%. A recently extended semiempirical scheme for the prediction of the thermal conductivity of mixtures from the pure components is used to predict successfully both the thermal conductivity and the viscosity of these mixtures, as a function of composition, temperature, and pressure.

KEY WORDS: high pressures; mixtures; *n*-heptane; *n*-undecane; viscosity.

1. INTRODUCTION

In recent years, semiempirical schemes [1–3] based on considerations of the exact hard-sphere theory of transport properties have been applied for the correlation and prediction of the transport properties. For the liquid *n*-alkanes it has been shown [4] that the thermal conductivity, viscosity, and self-diffusion coefficients can, simultaneously, be successfully correlated over a temperature range 100–400 K and pressures up to 600 MPa, with an uncertainty of ±6%. In the case of the transport properties of mixtures, a similar scheme [5, 6] has been applied for the correlation of the thermal conductivity of various binary liquid mixtures at atmospheric pressure, by adopting a simple mixing rule.

In this paper, new absolute measurements of the viscosity of binary mixtures of *n*-heptane and *n*-undecane are presented. At atmospheric

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pressure, the viscosity measurements cover the temperature range 295–335 K, while at 303.15 and 323.15 K the measurements extend up to 75 MPa. Moreover, accurate measurements of the thermal conductivity of these mixtures have recently been reported [7] at atmospheric pressure, over the temperature range 285–350 K. Therefore, these binary mixtures can be used for the examination of the application of the aforementioned scheme to the prediction of the thermal conductivity and viscosity of mixtures.

2. EXPERIMENTAL

The viscosity measurements were performed with the high-pressure vibrating-wire instrument described in detail elsewhere [8]. The viscosity of toluene was measured before and after each liquid to assure the continuing proper operation of the instrument. The absolute uncertainty of the measurements is estimated to be ±0.5%, an estimate confirmed by the measurements of the viscosity of toluene [8]. The samples of *n*-heptane and *n*-undecane were both supplied by BDH Chemicals Ltd., with nominal purities better than 99.5 and 99.0%. The density values used were obtained by Doolittle [9]. The density of the mixture was calculated from the densities of the pure components. The two mixtures studied, 40 and 70%, by weight, of *n*-heptane, were prepared gravimetrically and the uncertainty in their composition was less than 0.005%.

3. RESULTS

Tables I and II present the viscosity measurements of the two binary mixtures of *n*-heptane and *n*-undecane at 303.15 and 323.15 K as a function of pressure. In these tables we provide also the viscosity adjusted to the nominal temperatures of 303.15 and 323.15 K, respectively, by means of a linear correction. Since this correction is very small, however, less than 0.2%, the uncertainty introduced with this assumption is negligible. In Table III, the viscosity measurements at atmospheric pressure as a function of temperature are presented.

The viscosity measurements of both mixtures have been correlated with pressure along each isotherm, for the purpose of interpolation only, by a Tait-like equation, 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. The values of the constants for each isotherm for both mixtures are shown in Table IV. In the same table, the standard deviation of each fit is shown. It can be seen that the maximum standard deviation is ±0.15%. In the same table the constants for our previous measurements [10] of the viscosity of the pure components are also included for comparison purposes. In Fig. 1

Table I. Viscosity of *n*-Heptane + *n*-Undecane Mixture as a Function of Pressure (40%, by Weight, of *n*-Heptane)

Pressure P (MPa)	Temp. T (K)	Density $\rho(T, P)$ $(\text{kg} \cdot \text{m}^{-3})$	Viscosity $\mu(T, P)$ $(\mu\text{Pa} \cdot \text{s})$	Density $\rho(T_{\text{nom}}, P)$ $(\text{kg} \cdot \text{m}^{-3})$	Viscosity $\mu(T_{\text{nom}}, P)$ $(\mu\text{Pa} \cdot \text{s})$
				$T_{\text{nom}} = 303.15$ K	
0.10	303.088	709.0	636.4	708.9	635.9
5.57	303.100	713.4	673.0	713.4	672.6
10.54	303.088	717.3	708.9	717.3	708.4
15.65	303.109	721.2	744.7	721.2	744.3
20.97	303.112	725.1	788.4	725.1	788.1
25.74	303.112	728.6	822.6	728.5	822.3
30.90	303.106	732.1	864.4	732.1	864.0
35.87	303.112	735.5	904.6	735.4	904.2
41.04	303.112	738.8	947.3	738.8	946.9
46.10	303.106	742.0	990.8	742.0	990.4
50.97	303.112	744.9	1034.0	744.9	1033.6
56.03	303.169	747.9	1076.6	747.9	1076.8
60.69	303.222	750.5	1119.8	750.5	1120.7
66.17	303.405	753.3	1164.4	753.5	1167.6
71.94	303.478	756.3	1216.1	756.4	1220.4
				$T_{\text{nom}} = 323.15$ K	
0.10	323.040	693.6	500.9	693.5	500.1
5.27	323.046	698.2	528.5	698.1	527.8
10.44	323.034	702.7	558.9	702.6	558.0
15.50	323.043	707.0	589.0	706.9	588.1
20.67	323.037	711.3	620.6	711.2	619.6
25.64	323.034	715.2	649.9	715.1	648.9
30.80	323.034	719.2	680.9	719.1	679.8
35.67	323.034	722.7	712.2	722.7	711.0
40.73	323.046	726.3	744.4	726.2	743.4
45.90	323.040	729.8	776.9	729.7	775.7
50.87	323.092	733.0	810.1	732.9	809.4
55.83	323.025	736.1	844.9	736.0	843.5
61.10	323.055	739.1	881.5	739.1	880.4
66.47	323.074	742.1	918.0	742.1	917.1

the deviations of the present experimental measurements of the viscosity from those correlated by Eq. (1) are presented. It can be seen that the maximum deviation is less than ±0.2%.

The atmospheric pressure measurements of both mixtures have also been correlated, for the purpose of interpolation only, by an equation of the form

$$\mu = Ae^{B/T} \tag{2}$$

Table II. Viscosity of *n*-Heptane + *n*-Undecane Mixture as a Function of Pressure (70%, by Weight, of *n*-Heptane)

Pressure P (MPa)	Temp. T (K)	Density $\rho(T, P)$ $(\mathrm{kg \cdot m^{-3}})$	Viscosity $\mu(T, P)$ $(\mu\mathrm{Pa \cdot s})$	Density $\rho(T_{\mathrm{nom}}, P)$ $(\mathrm{kg \cdot m^{-3}})$	Viscosity $\mu(T_{\mathrm{nom}}, P)$ $(\mu\mathrm{Pa \cdot s})$
				$T_{\mathrm{nom}} = 303.15$ K	
0.10	302.984	692.0	488.6	691.9	487.8
5.47	303.100	696.5	516.4	696.5	516.1
10.64	303.088	700.8	544.3	700.8	544.0
15.60	303.100	704.8	571.8	704.8	571.5
20.57	303.094	708.7	600.2	708.7	599.9
25.33	303.088	712.3	625.6	712.3	625.2
30.40	303.082	716.1	655.2	716.0	654.8
35.57	303.085	719.7	686.3	719.7	685.9
40.43	303.085	723.1	715.2	723.1	714.7
45.70	303.094	726.6	746.4	726.6	746.0
50.46	303.112	729.7	776.2	729.7	775.9
55.83	303.118	733.1	808.8	733.0	808.6
60.69	303.112	736.0	840.3	736.0	840.0
65.35	303.106	738.7	869.1	738.6	868.7
70.62	303.030	741.6	903.9	741.5	902.9
				$T_{\mathrm{nom}} = 323.15$ K	
0.10	323.202	675.8	393.3	675.9	393.5
5.27	323.202	680.8	416.0	680.8	416.3
10.54	323.190	685.8	439.6	685.8	439.9
15.81	323.168	690.6	463.4	690.6	463.5
20.67	323.156	694.8	486.2	694.9	486.2
25.64	323.223	699.0	508.5	699.0	509.0
30.80	323.220	703.2	531.7	703.2	532.1
35.77	323.217	707.0	555.9	707.1	556.3
41.04	323.211	710.9	581.0	711.0	581.4
46.10	323.205	714.5	605.7	714.5	606.1
51.07	323.223	717.8	630.0	717.8	630.5
56.13	323.223	720.9	654.8	721.0	655.3
62.92	323.211	725.0	688.4	725.0	688.9

Table III. Viscosity of *n*-Heptane + *n*-Undecane Mixture as a Function of Temperature at Atmospheric Pressure (Concentrations as Weight Percentage of *n*-Heptane)

40%			70%		
Temp. T (K)	Density ρ ($\mathrm{kg \cdot m^{-3}}$)	Viscosity μ ($\mu\mathrm{Pa \cdot s}$)	Temp. T (K)	Density ρ ($\mathrm{kg \cdot m^{-3}}$)	Viscosity μ ($\mu\mathrm{Pa \cdot s}$)
297.152	713.4	690.1	300.903	693.6	499.7
303.088	709.0	636.4	302.984	692.0	488.6
312.847	701.5	563.0	312.977	684.1	436.9
323.040	693.6	500.9	317.861	680.2	415.7
332.839	685.8	450.6	323.126	675.9	392.8
			331.942	668.5	360.9

The values of the constants 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 ±0.19%. Also shown for comparison purposes are the constants for our previous measurements of the viscosity of the pure components [10].

4. DISCUSSION

4.1. The Pure Liquids

Whereas the correlations of Eqs. (1) and (2) are suitable for interpolation, they have little or no value for extrapolation and prediction. For such purposes it has been shown [4] that a correlation in terms of the molar

Table IV. Coefficients of Eq. (1) (Concentrations as Weight Percentage of *n*-Heptane)

Temp. (K)	Conc. (%)	μ_0 ($\mu\mathrm{Pa \cdot s}$)	E (−)	D (MPa)	σ (%)
303.15	0	990.53	2.916	256.3	±0.09
	40	635.93	1.982	183.8	±0.15
	70	487.81	1.536	142.9	±0.06
	100	370.70	1.398	133.2	±0.04
323.15	0	747.23	2.055	179.4	±0.07
	40	500.12	1.691	153.8	±0.09
	70	393.52	1.326	119.4	±0.05
	100	304.07	1.264	114.9	±0.08

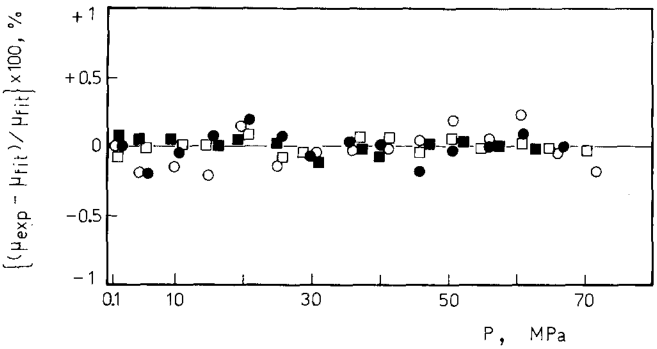

Fig. 1. Deviations of present experimental values of the viscosity of *n*-heptane + *n*-undecane mixtures from Eq. (1). Forty percent, by weight, of *n*-heptane: (○) 303.15 K; (●) 323.15 K. Seventy percent, by weight, of *n*-heptane: (□) 303.15 K; (■) 323.15 K.

volume, V, is much more suitable. The hard-sphere model of the dense fluid state [2] suggests the form of such a correlation since it leads to the result that for a monatomic fluid the quantities, μ^* and λ^*, defined by the equations

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

$$\lambda^* = 1.936 \times 10^7 \left[\frac{M}{RT}\right]^{1/2} \lambda V^{2/3} = F_\lambda(V/V_0) \tag{4}$$

are functions of the reduced molar volume (V/V_0) only, where V_0 is a characteristic molar volume of the fluid which is but weakly dependent. In the above equations M represents the molar mass, R the universal gas constant, and T the absolute temperature.

Earlier studies have shown that if the results of Eqs. (3) and (4) are carried over to polyatomic fluids, the functions F_μ and F_λ are nearly

Table V. Coefficients of Eq. (2) (Concentrations as Weight Percentage of *n*-Heptane)

Conc. (%)	A (μPa · s)	B (K)	σ (%)
0	11.05 ± 0.35	1362.4 ± 9.9	±0.17
40	13.02 ± 0.27	1179.2 ± 6.6	±0.19
70	15.23 ± 0.19	1050.5 ± 4.0	±0.10
100	15.20 ± 0.18	968.3 ± 3.8	±0.03

universal among a large group of liquids, although the functions are not those predicted from the hard-sphere theory [2]. Recently these functions were obtained [4] as the result of a successful attempt of 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 that study, it emerged that it is not the functions μ^* and λ^* which are universal, but a slightly modified version of them, namely,

$$\log \frac{\mu^*}{R_\mu} = 0.877 - 3.79208\, V_r^{-1} + 16.4416\, V_r^{-2} - 24.2509\, V_r^{-3} + 16.354\, V_r^{-4} \tag{5}$$

$$\log \frac{\lambda^*}{R_\lambda} = 1.0655 - 3.538\, V_r^{-1} + 12.121\, V_r^{-2} - 12.469\, V_r^{-3} + 4.562\, V_r^{-4} \tag{6}$$

in which

$$V_r = V/V_0 \tag{7}$$

and where R_μ and R_λ are factors introduced to account for deviations from the behavior of smooth hard spheres. These factors have been correlated [4] as a function of the carbon number C as

$$R_\mu = 0.9858 + 0.0164\, C + 0.001432\, C^2 \tag{8}$$

$$R_\lambda = 0.1989\, C + 1.199 - 2.547\, C^{-1} + 6.404\, C^{-2} - 4.094\, C^{-3} \tag{9}$$

The characteristic molar volume V_0 of the series was also represented in terms of temperature and the carbon number. For *n*-alkanes with carbon numbers in the range C_5–C_{16}, the representation for V_0 (in $m^3 \cdot mol^{-1}$) is

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

where

$$\theta = T/100$$

This scheme, Eqs. (3)–(10), was found to correlate and predict the viscosity and thermal conductivity of *n*-alkanes in the temperature range 100–400 K and at pressures up to 600 MPa, with an uncertainty of ±6%.

4.2. The Mixtures

In a recent paper [5] the following procedure was successfully adopted to correlate the thermal conductivity of mixtures at atmospheric pressure from the pure components. It was postulated that the mixture can be considered as an equivalent liquid with a mole fraction average molecular weight and a characteristic molar volume, V_0^{mix}, given by the following mixing rule:

$$V_0^{\text{mix}} = XV_0^{\text{I}} + (1-X)\,V_0^{\text{II}} - X(1-X)\,k \tag{11}$$

where V_0^{I} and V_0^{II} are the characteristic molar volumes of the pure components, and X is the molar fraction. The quantity k was found to be a constant characteristic of the pure components, independent of temperature and composition, and determined by experimental measurements. Thus, since the characteristic molar volumes of the pure liquids can be determined by the aforementioned scheme, our atmospheric pressure viscosity measurements can be used for the determination of the constant k. Having obtained this constant, then the characteristic molar volume can be calculated and Eqs. (3)–(11) can be used to predict both the viscosity and the thermal conductivity over the whole range of the experimental measurements. The advantage of this scheme is that only one or two measurements at one composition, one temperature, and one of the two properties at atmospheric pressure are sufficient to predict both the viscosity and the thermal conductivity of the mixtures over a very wide range of conditions and compositions.

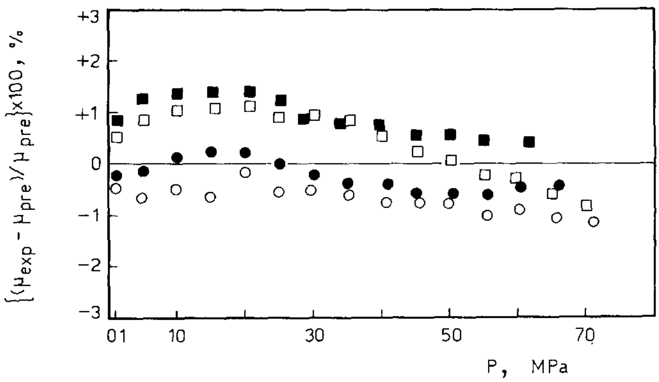

Fig. 2. Deviations of present experimental values of the viscosity of n-heptane + n-undecane mixtures from the scheme of Eqs. (3)–(11). Forty percent, by weight, of n-heptane: (○) 303.15 K; (●) 323.15 K. Seventy percent, by weight, of n-heptane; (□) 303.15 K; (■) 323.15 K.

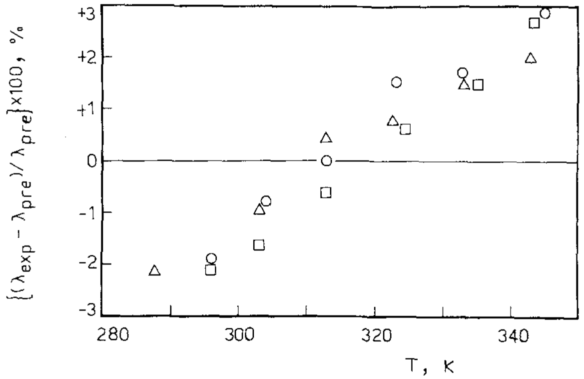

Fig. 3. Deviations of experimental values of the thermal conductivity [7] of *n*-heptane + *n*-undecane mixtures from the scheme of Eqs. (3)–(11). Concentrations as weight percentage of *n*-heptane: (○) 25%; (△) 50%; (□) 75%.

From the present atmospheric pressure viscosity measurements (Table III) and Eqs. (3)–(11), the value of the constant k was found equal to $2.5 \times 10^{-6}\ m^3 \cdot mol^{-1}$. Thus, having obtained the value of this constant, Eqs. (3)–(11) can be used to predict the viscosity and thermal conductivity at any composition and any temperature and pressure. In Fig. 2 the deviations of the present experimental measurements of the viscosity of mixtures from those predicted by the aforementioned scheme are shown. It can be seen that the maximum deviation is less than ±2%. In Fig. 3 the deviations of the atmospheric-pressure experimental measurements, of the mixture thermal conductivity of Wada et al. [7], performed in a transient hot-wire instrument, from those predicted by this scheme are shown. Although there is a definite trend, the maximum deviation is still less than ±3%.

The predictive power of this scheme is thus demonstrated. A measurement of only one of the two properties, at one composition and one temperature at atmospheric pressure, is sufficient to predict both properties at any composition and over a very wide range of temperatures and pressures.

5. CONCLUSIONS

New absolute measurements of the viscosity of binary mixtures of *n*-heptane and *n*-undecane are presented. At atmospheric pressure, the viscosity measurements cover the temperature range 295–335 K, while at 303.15 and 323.15 K the measurements extend up to 75 MPa. The uncertainty of the measurements is estimated to be ±0.5%.

A recently developed semiempirical scheme is applied to the prediction of the viscosity and the thermal conductivity over a wide range of compositions and conditions, based only on the atmospheric pressure measurements of the viscosity of these mixtures. The uncertainty of this scheme was found to be better than ±3%.

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