International Journal of Thermophysics, Vol. 22, No. 3, 2001

Thermal Conductivity of Toluene + Cyclopentane Mixtures: Measurements and Prediction

M. J. Assael[1, 2] **and N. K. Dalaouti**[1]

Received October 23, 2000

New measurements of the thermal conductivity of toluene, cyclopentane, and a binary mixture of 60 wt% toluene are presented. The measurements cover the temperature range from 235 to 345 K and from the saturation line up to 20 MPa pressure. The measurements were performed with a transient hot-wire instrument. The uncertainty of the measurements is estimated to be ±0.5%. The present results are employed to examine the predictive power of a theoretically based scheme for the calculation of the transport properties of mixtures.

KEY WORDS: cyclopentane; mixture; thermal conductivity; toluene; transient hot-wire technique.

1. INTRODUCTION

This paper presents new measurements of the thermal conductivity of toluene, cyclopentane, and a binary mixture of them. The viscosity measurements of these liquids were presented in a previous work [1] and have been used to examine the predictive power of two schemes for the prediction of the transport properties of fluids.

Toluene has been proposed as a viscosity reference liquid over a wide range of temperatures and pressures by the Subcommittee of Transport Properties of the International Union of Pure and Applied Chemistry [2]. In the case of thermal conductivity, a standard reference equation along the saturation line, which covers the temperature range 190 to 550 K, has recently been proposed [3]. Cyclopentane is also under consideration as a viscosity and thermal conductivity reference liquid.

---

[1] Chemical Engineering Department, Aristotle University, 54006 Thessaloniki, Greece.

[2] To whom correspondence should be addressed. E-mail: assael@transp.eng.auth.gr

0195-928X/01/0500-0659$19.50/0

The present measurements of the thermal conductivity of the toluene + cyclopentane system were used to examine the predictive power of the Vesovic–Wakeham scheme [4–6] for the prediction of the transport properties of mixtures. This theoretically based scheme, used for the prediction of the transport properties of fluid mixtures from those of the pure components, was applied by Vesovic and Wakeham for high-pressure gases. In a recent paper, Assael et al. [7] modified this scheme and applied it to the prediction of the viscosity of *n*-hexane + toluene and *n*-hexane + cyclohexane liquid mixtures, as well as to the prediction of the viscosity of toluene + cyclopentane mixtures [1].

The large deviations in the predicted values were attributed to the incorrect determination of the pseudo-radial distribution function of the pure components. It is thus of interest to calculate these from thermal conductivity measurements.

2. EXPERIMENTAL

2.1. Instrument

The transient hot-wire instrument employed for the present high-pressure measurements of toluene, cyclopentane, and a 60 wt% toluene + 40 wt% cyclopentane mixture has been employed in the past for the measurement of the thermal conductivity of refrigerants. Thus, it has already been described [8], so only a brief summary is presented here. The technique involves the measurement of the temperature rise of a thin wire, by means of its resistance increase, over a period of 1 s after the initiation of electrical heating in it while surrounded by the liquid under test. The present instrument consists of two 25-μm-diameter tantalum wires. All electrical connections to the wires were made of tantalum wire, with a diameter of 0.5 mm, which extended outside the pressure vessel. PTFE sleaving ensured electrical insulation between the wires and the supports. The wires were mounted in a stainless-steel cell, while a constant tension and vertical alignment of the wires were achieved by a tantalum weight attached at the bottom of each wire. The cell consists of two cylindrical compartments, formed by machining two cylindrical holes centered on the split diameter of a rod and parallel to its axis. One half carried the four wire end supports and was attached to the top plate of the pressure vessel.

The temperature rise of the wires was measured by recording their resistance increase, incorporating the two wires in the arms of a Wheatstone-type computer-controlled bridge, as described elsewhere [8].

2.2. Apparatus

The transient hot-wire cell was placed in the pressure vessel, which was made of stainless steel, with a maximum working pressure of 50 MPa. The whole apparatus was employed for the measurement of the thermal conductivity of refrigerants [8]. Sealing the pressure vessel was accomplished by stainless-steel springs coated with graphite-carbon filled PTFE o-rings made by Bal Seal Engineering Europe BV. The pressure vessel was placed in a 20-liter thermostatic bath. The temperature of the bath was controlled by circulating a heat-transfer fluid, whose temperature was controlled by a Julabo F81-MV external circulator. Above room temperature, ethylene glycol was employed as a heat-transfer fluid both in the bath and in the external circulator, while at lower temperatures propanol was used in the bath and ethanol in the circulator. In this way, the temperature in the bath was very stable and the temperature gradients were kept to a tolerable level (<100 mK). The temperature was recorded by three platinum-resistance thermometers embedded along the pressure-vessel wall. The thermometers were calibrated vs a Class 1 NPL-certified, Tinsley platinum resistance thermometer, to an uncertainty of better than ± 20 mK. All temperatures refer to ITS-90. Finally, the pressure inside the pressure vessel was measured by a Druck PTX520 pressure transmitter, with an uncertainty of 0.1 MPa. The uncertainty of the measurements is estimated to be $\pm 0.5\%$, while their precision is much better.

The thermal conductivity of the pure fluids and their mixture was first measured over the whole temperature range at atmospheric pressure. Then the thermal conductivity was measured as a function of pressure, for several isotherms (every 20 K) that cover the entire temperature range. The liquid was initially pressurized at the maximum pressure for each isotherm, and the pressure was reduced to 1 bar.

3. WORKING EQUATION

According to the theory of the transient hot-wire technique, the thermal conductivity of the medium surrounding the wire can be derived by the following equation [9, 10]:

$$\Delta T_{\mathrm{id}} = \Delta T_{\mathrm{w}} + \sum_i \delta T_i = \frac{q}{4\pi\lambda(T_{\mathrm{r}}, \rho_{\mathrm{r}})} \ln\left[\frac{4at}{r_a^2 C}\right] \tag{1}$$

where T_{r} is the reference temperature and ρ_{r} is the density of the medium. In this equation, q is the heat input per unit length of the wires, r_a is the radius of the wire, and C is a numerical constant. The symbol a represents the thermal diffusivity of the fluid, while t is the elapsed time. The various correction terms δT_i have been identified [10] and are all rendered less than 0.5% of the ideal temperature rise ΔT_{id}, by the design of the wire and the operation of the instrument. As follows from Eq. (1), an essential feature of the correct operation of the instrument is that the measured data ΔT_{w} should be a linear function of $\ln t$. In Eq. (1), it is assumed that all heat is transferred by conduction only. The presence of any other means of heat transfer, such as radiation, would have been to add curvature to this linear representation [8]. In all our measurements, no curvature or systematic trend was noticed, and thus, no radiation correction was necessary.

4. RESULTS

The toluene employed was 99.9% pure as supplied by BDH (ARISTAR grade). Cyclopentane was supplied by Fluka, with a nominal purity better than 99.5%. The samples were dried over molecular sieves and were introduced in the vessel under vacuum.

The density of the pure components and the mixture was calculated in the same way it was calculated in the viscosity measurements [1]. The density of toluene was calculated by a Tait-type correlation, proposed recently by the Subcommittee of Transport Properties of the International Union of Pure and applied Chemistry, after a critical examination of all measurements [2], with a standard deviation of ±0.05%. For cyclopentane, an equation of state reported by Baonza et al. [11], with an accuracy of ±0.06%, was used. The density of the mixture was calculated from the densities of the pure components assuming no change of volume upon mixing. The mixture studied was 60%, by weight, toluene, and was prepared gravimetrically with an uncertainty in the composition of less than 0.005%.

The thermal conductivity measurements of toluene, cyclopentane, and a binary mixture at atmospheric pressure are presented in Table I. The measurements at elevated pressures are presented in Tables II, III, and IV for toluene, cyclopentane, and this mixture, respectively. It should be noted that, although the viscosity of toluene was much higher than that of cyclopentane, with differences of 80% at low temperatures [1], the thermal conductivity values of these liquids are comparable. The difference in the thermal conductivity of toluene and cyclopentane never becomes larger than about 3%. However, for a proper theoretical treatment for both viscosity and thermal conductivity, it is very important to have these measurements.

As already mentioned, the Subcommittee of Transport Properties of the International Union of Pure and Applied Chemistry has proposed toluene

Table I. Measurements of the Thermal Conductivity of Toluene + Cyclopentane Mixtures at Atmospheric Pressure

T (K)	ρ ($\mathrm{kg \cdot m^{-3}}$)	λ ($\mathrm{mW \cdot m^{-1} \cdot K^{-1}}$)
	100%, by weight, toluene	
234.105	920.5	147.7
242.952	912.7	145.5
253.279	903.5	143.0
263.409	894.4	140.2
273.496	885.3	137.4
283.338	876.2	134.4
296.726	863.8	131.0
306.275	854.9	128.4
316.568	845.2	125.5
325.872	836.3	122.7
336.041	826.5	120.3
345.715	817.2	117.3
	60%, by weight, toluene	
234.806	868.5	148.5
242.309	861.6	146.4
252.070	852.6	143.2
262.058	843.3	140.1
273.754	832.2	136.7
283.494	822.9	133.7
293.924	812.9	129.9
309.615	797.5	125.6
	100%, by weight, cyclopentane	
234.702	800.7	151.9
242.794	793.5	148.5
251.877	785.2	144.5
262.521	775.3	140.6
273.104	765.2	136.1
283.790	754.8	132.2
293.246	745.4	129.0
303.338	735.3	125.7
308.288	734.3	123.8

as a standard reference liquid for thermal conductivity [3]. A standard reference equation along the saturation line that covers the temperature range 190 to 550 K has been proposed. The uncertainty of this equation is ±1%. Although there is a distinct difference in slopes, the present measurements of the thermal conductivity of toluene at atmospheric pressure agree with the standard equation well within its uncertainty.

Table II. Measurements of the Thermal Conductivity of Toluene as a Function of Pressure

T (K)	P (MPa)	ρ ($kg \cdot m^{-3}$)	λ ($mW \cdot m^{-1} \cdot K^{-1}$)
234.098	0.10	921.8	147.4
234.097	1.10	922.3	147.7
234.496	3.57	923.3	148.3
234.461	5.75	924.5	148.4
234.078	7.20	925.6	149.4
253.114	0.10	904.2	142.3
253.216	2.20	905.3	142.8
253.312	4.50	906.6	143.7
253.286	6.40	907.8	144.7
253.212	9.20	909.4	145.5
253.300	11.96	910.9	145.7
273.511	0.10	885.4	137.0
273.479	3.50	887.7	138.2
273.548	6.05	889.3	139.3
273.626	9.40	891.4	139.6
273.710	11.70	892.8	140.1
273.674	15.28	895.0	141.5
296.516	0.10	864.1	130.7
296.318	2.68	866.3	131.7
296.422	5.76	868.5	132.7
296.243	7.71	870.1	133.8
296.426	10.28	871.8	134.0
296.371	12.47	873.4	135.0
296.467	14.49	874.7	135.5
316.345	0.10	845.6	125.5
315.961	3.10	848.6	126.5
316.060	6.25	851.1	127.8
316.101	9.12	853.4	128.6
316.155	12.45	856.0	130.0
316.153	14.95	857.9	131.0
316.400	18.42	860.4	132.2
335.677	0.10	827.3	120.3
336.009	3.23	830.0	121.5
335.931	6.34	833.0	122.5
336.032	9.10	835.4	123.9
335.978	12.33	838.3	124.8
335.959	15.02	840.7	125.9
336.342	17.82	842.7	126.6

Table III. Measurements of the Thermal Conductivity of Cyclopentane as a Function of Pressure

T (K)	P (MPa)	ρ ($\text{kg} \cdot \text{m}^{-3}$)	λ ($\text{mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$)
236.065	0.10	799.5	151.1
236.072	2.58	801.0	152.2
236.138	5.19	802.5	153.7
235.943	8.17	804.4	154.1
235.666	11.12	806.4	154.8
235.735	13.90	807.9	156.2
253.151	0.10	784.0	143.8
253.285	2.40	785.5	144.7
253.073	5.27	787.6	146.0
253.250	7.20	788.7	146.4
253.102	10.13	790.7	147.9
252.984	13.16	792.8	148.6
252.780	16.18	794.8	149.8
273.988	0.10	764.3	136.0
273.994	2.62	766.3	136.9
274.091	5.03	768.1	137.8
273.979	7.05	769.8	138.4
273.912	10.40	772.3	139.7
273.915	13.53	774.6	141.4
273.938	15.80	776.2	142.4
293.659	0.10	745.0	128.4
293.615	2.60	747.4	129.3
293.782	5.85	750.1	130.7
293.788	9.25	753.1	132.1
293.783	12.30	755.6	133.5
293.347	15.60	758.7	134.6
308.286	0.10	730.2	123.0
308.219	2.24	732.5	124.3
308.336	5.11	735.3	125.9
308.330	7.81	737.9	127.0
308.366	10.26	740.2	128.4
308.392	13.40	743.0	129.4

The measurements of the thermal conductivity of cyclopentane and of the toluene + cyclopentane mixture at atmospheric pressure were fit by the following equation:

$$\frac{\lambda}{\lambda(298.15\ \text{K})} = \sum_{k=0}^{2} a_k T_{\text{r}}^{k} \qquad (2)$$

Table IV. Measurements of the Thermal Conductivity of the 60 wt% Toluene + 40 wt% Cyclopentane Mixture as a Function of Pressure

T (K)	P (MPa)	ρ $(\mathrm{kg \cdot m^{-3}})$	λ $(\mathrm{mW \cdot m^{-1} \cdot K^{-1}})$
236.020	0.10	867.4	148.0
235.987	2.59	868.9	148.9
235.954	5.11	870.4	149.7
235.940	7.66	871.9	150.6
235.886	10.07	873.3	151.3
235.675	12.92	875.1	152.1
235.493	15.22	876.5	152.5
252.981	0.10	851.7	143.0
253.222	2.85	853.3	144.2
253.260	5.27	854.9	144.7
253.267	7.65	856.4	145.9
253.294	10.75	858.3	146.5
253.079	13.60	860.2	147.4
273.889	0.10	832.1	136.8
273.970	2.50	833.8	137.3
273.957	5.02	835.7	138.0
273.878	7.62	837.6	138.8
273.938	10.22	839.4	139.6
293.863	0.10	812.9	130.1
293.782	2.53	815.1	130.9
293.802	4.85	817.0	132.1
293.793	7.15	818.9	133.2
293.947	9.30	820.5	133.7
293.961	13.35	823.6	135.0
308.508	0.10	798.6	126.4
308.392	2.00	800.5	126.9
308.443	4.65	802.9	127.1
308.447	7.75	805.7	128.4
308.521	9.90	807.5	130.0

For cyclopentane, $T_r = T/T_c$, where T_c is the critical temperature, while for the mixture, $T_r = T/298.15$ K. The coefficientas a_k, the value of the thermal conductivity at 298.15 K, and the critical temperatures are shown in Table V. The maximum deviation of the experimental values from the values calculated by Eq. (2) is less than 0.5%.

Table V. Coefficients of Eqs. (2), (3), (23), (24), and (26) and Critical Parameters

a_0	—	0.8997	0.0079
a_1	—	−2.5228	−0.7290
a_2	—	2.1651	1.7211
T_c (K)	591.75	511.7	—
λ (298.15 K) $(\mathrm{mW \cdot m^{-1} \cdot K^{-1}})$	130.8	126.8	129.0
h_0	0.2264	0.8864	−2.0548
h_1	1.7841	−0.8769	0.0057
h_2	−1.1011	1.2374	0.1532
h_3	−0.8941	−0.8924	2.8953
h_4	0.3179	0.3521	—
ρ_c $(\mathrm{kg \cdot m^{-3}})$	290.2	269.75	—
ρ_0 $(\mathrm{kg \cdot m^{-3}})$	—	—	808.77
σ_{ij} (nm)	0.5852	0.5404	0.5617
ε_{ij}/k_B (K)	485.6	396.6	426.5
θ_0 (—)	1.5164	1.545	—
θ_1 (—)	0.4651	—	—
v_1 $(10^{-6}\,\mathrm{m^3 \cdot mol^{-1}})$	152.536	254.835	—
v_2 $(10^{-6}\,\mathrm{m^3 \cdot mol^{-1}})$	−525.768	−1502.70	—
v_3 $(10^{-6}\,\mathrm{m^3 \cdot mol^{-1}})$	1341.767	4422.421	—
v_4 $(10^{-6}\,\mathrm{m^3 \cdot mol^{-1}})$	−1585.622	−5805.67	—
v_5 $(10^{-6}\,\mathrm{m^3 \cdot mol^{-1}})$	704.246	2839.825	—
f_0 $(\mathrm{J \cdot mol^{-1} \cdot K^{-1}})$	-2.435×10	-5.362×10	—
f_1 $(\mathrm{J \cdot mol^{-1} \cdot K^{-2}})$	5.125×10^{-1}	5.426×10^{-1}	—
f_2 $(\mathrm{J \cdot mol^{-1} \cdot K^{-3}})$	-2.765×10^{-4}	-3.031×10^{-4}	—
f_3 $(\mathrm{J \cdot mol^{-1} \cdot K^{-4}})$	4.911×10^{-8}	6.485×10^{-8}	—

The measurements of the thermal conductivity of the pure liquids and the mixture as a function of pressure were fit, for interpolation purposes, by an equation of the form

$$\frac{\lambda}{\lambda(298.15\ \mathrm{K})} = \sum_{k=0}^{2} h_k T_r^k + \sum_{k=3}^{4} h_k \rho_r^k \tag{3}$$

The coefficients h_k are given in Table V. Again, for the pure liquids $T_r = T/T_c$ and $\rho_r = \rho/\rho_c$, where T_c and ρ_c are the critical temperature and density, respectively, while for the mixture $\rho_r = \rho/\rho_0$ and ρ_0 corresponds to the density at 298.15 K and at atmospheric pressure. Values for T_c, ρ_c, and ρ_0 are given in Table V.

The deviations of the thermal conductivity measurements of the pure liquids and their binary mixture from the above equation are shown in Figs. 1–3. As can be seen, the maximum deviation is less than 0.5%.

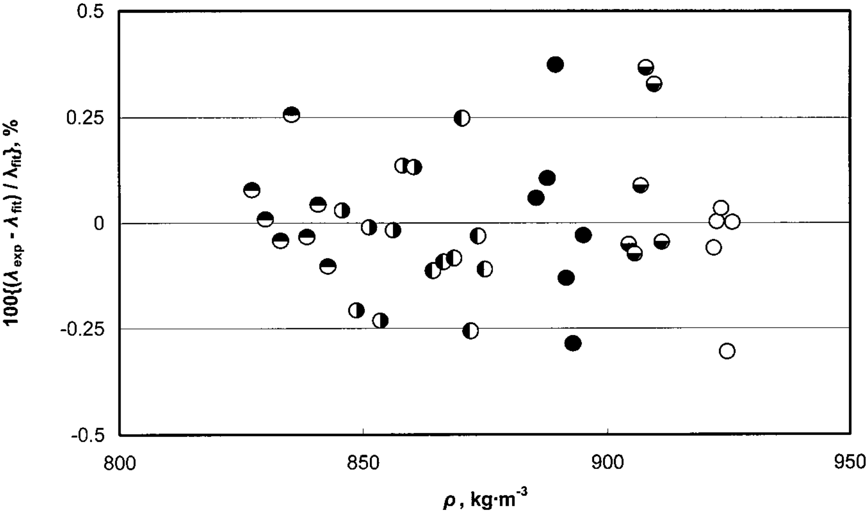

Fig. 1. Deviations of the thermal conductivity measurements of toluene from the values calculated from Eq. (3): (○) 234 K; (◒) 253 K; (●) 273 K; (◐) 296 K; (◑) 316 K; (◓) 336 K.

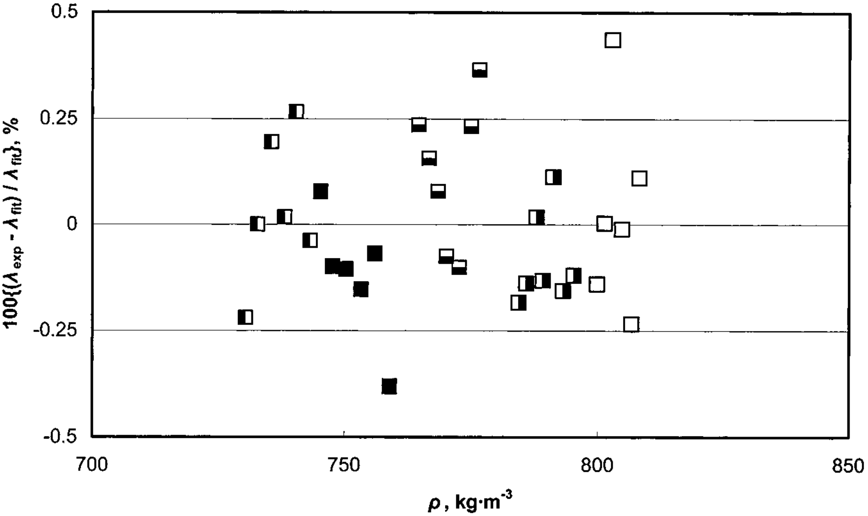

Fig. 2. Deviations of the thermal conductivity measurements of cyclopentane from the values calculated from Eq. (3): (□) 235 K; (◨) 253 K; (⬓) 273 K; (■) 293 K; (◧) 308 K.

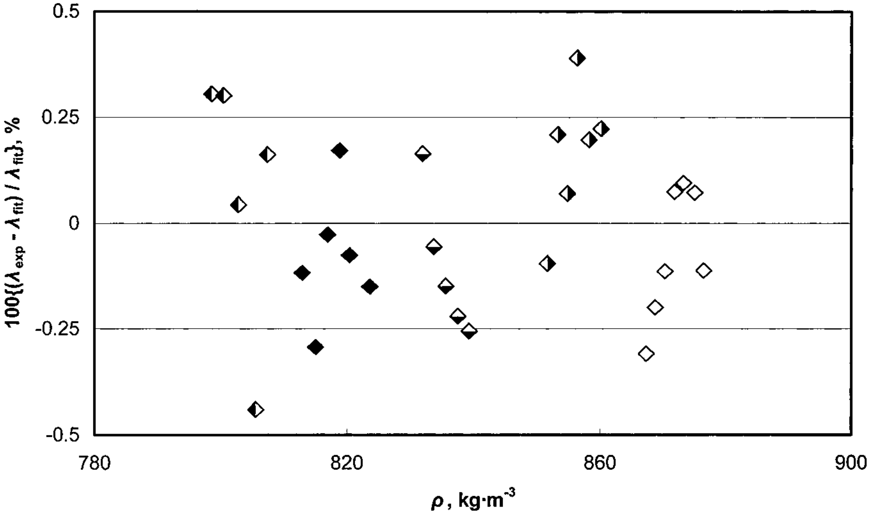

Fig. 3. Deviations of the thermal conductivity measurements of the mixture from the values calculated from Eq. (3): (◇) 235 K; (⬗) 253 K; (⬙) 273 K; (◆) 293 K; (⬖) 308 K.

In Fig. 4, deviations of the high-pressure thermal conductivity measurements of toluene of other investigators from the values calculated from Eq. (3) are shown. All these measurements were also performed in transient hot-wire instruments. The measurements of Kitazawa and Nagashima [12] have an uncertainty of ±1.6%, while the measurements of Kashiwagi et al. [13] have a quoted uncertainty of ±1%. These measurements are in very good agreement with the present ones. Nieto de Castro et al. [14] measured to within an uncertainty of ±0.3%. The agreement between those values and the present ones is within the mutual uncertainty of the two instruments. The measurements of Taxis et al. [15], with an uncertainty of ±0.3%, are also in very good agreement with the present values. The measurements of Yamada et al. [16] have an uncertainty of ±0.5%. The deviation from the present values is just over the mutual uncertainty of the two instruments. Finally, the older measurements of the thermal conductivity of toluene at high pressures that were performed in our laboratory [8], with an uncertainty of ±0.5%, are in very good agreement with the present results.

As far as the thermal conductivity of cyclopentane is concerned, only one investigator [17] has reported measurements, at atmospheric pressure. These measurements were performed in a steady-state parallel-plate instrument, with an uncertainty of ±1%, and deviate from the present results by about 3%, which is slightly over the mutual uncertainty of the two instruments.

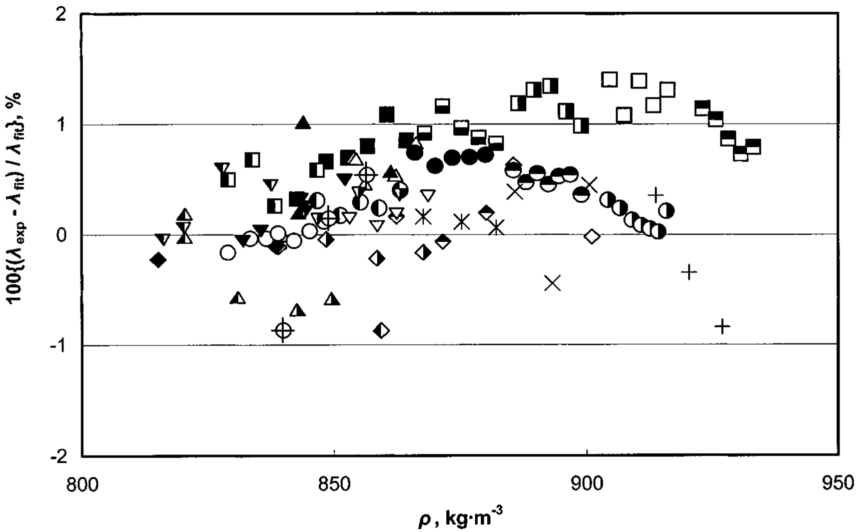

Fig. 4. Deviations of the thermal conductivity of toluene of other investigators, from the values calculated from Eq. (3). Kitazawa and Nagashima [12]: (+) 243 K; (×) 273 K; (∗) 293 K; (⊕) 323 K. Kashiwagi et al. [13]: (◇) 273 K; (⬘) 298 K; (⬗) 313 K; (⬖) 323 K; (◆) 348 K. Nieto de Castro et al. [14]: (△) 308 K; (▲) 320 K; (◭) 330 K; (◮) 345 K. Taxis et al. [15]: (▽) 308 K; (⧩) 307 K; (▼) 330 K; (⧨) 347 K. Yamada et al. [16]: (⬒) 233 K; (□) 253 K; (◨) 273 K; (⬓) 293 K; (■) 313 K; (◧) 333 K. Assael et al. [8]: (◑) 253 K; (◓) 273 K; (●) 293 K; (◐) 313 K; (○) 333 K.

No other study has reported results for the thermal conductivity of a toluene + cyclopentane mixture.

5. THEORETICAL ANALYSIS

The Vesovic–Wakeham scheme for the prediction of the transport properties of fluids has been used for the prediction of the viscosity of toluene + cyclopentane mixtures [1]. The scheme, however, did not give satisfactory results. The predicted values were higher than the experimental measurements, with a difference that increased from 14% at high temperatures, to about 60% at lower temperatures, where the pure-component viscosity ratio was high.

These differences were attributed to incorrect determination of the pseudo-radial distribution function, connected with the sharp increase in the viscosity with density. Hence, since this is one of the very few theoretically based schemes available, it is of great importance to examine the possibility of calculating the pseudo-radial distribution function from the thermal conductivity values.

According to this scheme [4], the thermal conductivity λ of a dense fluid mixture can be written in the form

$$\lambda = \lambda(\mathrm{mon}) + \lambda(\mathrm{int}) \tag{4}$$

In this equation, $\lambda(\mathrm{mon})$ denotes the contribution of translational energy transport to the thermal conductivity and $\lambda(\mathrm{int})$ denotes the contribution of internal energy transport. The term $\lambda(\mathrm{mon})$ is expressed by

$$\lambda(\mathrm{mon}) = -\begin{vmatrix} L_{11} & \cdots & L_{1N} & Y_1 \\ \vdots & & \vdots & \vdots \\ L_{N1} & \cdots & L_{NN} & Y_N \\ Y_1 & \cdots & Y_N & 0 \end{vmatrix} \Bigg/ \begin{vmatrix} L_{11} & \cdots & L_{1N} \\ \vdots & & \vdots \\ L_{N1} & \cdots & L_{NN} \end{vmatrix} + \kappa_{\mathrm{mix}} \tag{5}$$

where

$$Y_i = x_i \left[1 + \sum_{j=1}^{N} \frac{2m_i m_j}{(m_i + m_j)^2} x_j \gamma_{ij} \bar{\chi}_{ij} \rho_{\mathrm{m}} \right] \tag{6}$$

$$L_{ii} = \frac{x_i^2 \bar{\chi}_{ii}}{\lambda_i^0(\mathrm{mon})} + \sum_{j=1,\, j \neq i}^{N} \frac{x_i x_j \bar{\chi}_{ij}}{2\lambda_{ij}^0(\mathrm{mon})\, A_{ij}^*(m_i + m_j)^2} \times \left(\frac{15}{2} m_i^2 + \frac{25}{4} m_j^2 - 3m_j^2 B_{ij}^* + 4m_i m_j A_{ij}^* \right) \tag{7}$$

$$L_{ij(j \neq i)} = -\frac{x_i x_j \bar{\chi}_{ij}}{2\lambda_{ij}^0(\mathrm{mon})\, A_{ij}^*} \frac{m_i m_j}{(m_i + m_j)^2} \left(\frac{55}{4} - 3B_{ij}^* - 4A_{ij}^* \right) \tag{8}$$

$$\kappa_{\mathrm{mix}} = \left(\frac{16}{5\pi} \right) \frac{10}{9} \rho_{\mathrm{m}}^2 \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{x_i x_j m_i m_j}{(m_i + m_j)^2} \bar{\chi}_{ij} \gamma_{ij}^2 \lambda_{ij}^0(\mathrm{mon}) \tag{9}$$

$$\lambda(\mathrm{int}) = \sum_{i=1}^{N} \left[\frac{\lambda_i^0 - \lambda_i^0(\mathrm{mon})}{\bar{\chi}_{ii}} \right] \left[1 + \sum_{j=1,\, j \neq i} \frac{x_j \lambda_i^0(\mathrm{mon})\, \bar{\chi}_{ij} A_{ii}^*}{x_i \lambda_{ij}^0(\mathrm{mon})\, \bar{\chi}_{ii} A_{ij}^*} \right]^{-1} \tag{10}$$

In these equations, ρ_{m} is the molar density of the mixture, x_i and x_j are the mole fractions of species i and j, and m_i and m_j are their molecular masses (kg). Furthermore, λ_i^0 represents the thermal conductivity of species i at zero density and $\lambda_i^0(\mathrm{mon})$ is the translational contribution to the thermal conductivity of the same component. The quantity $\lambda_{ij}^0(\mathrm{mon})$ is the interaction thermal conductivity for species i and j. These two terms, $\lambda_i^0(\mathrm{mon})$ and $\lambda_{ij}^0(\mathrm{mon})$, can be obtained from the equation

$$\lambda_{ij}^0(\mathrm{mon}) = \frac{15k_{\mathrm{B}}(m_i + m_j)\, \eta_{ij}^0}{8m_i m_j} \tag{11}$$

The dilute-gas limit interaction viscosity of species i and j, η_{ij}^0, can be obtained from [18]

$$\eta_{ij}^0 = \frac{5}{16}\left[\frac{2m_i m_j}{(m_i + m_j)}\frac{k_B T}{\pi}\right]^{1/2}\frac{1}{\sigma_{ij}^2 \Omega_{ij}^*(T_{ij}^*)} \tag{12}$$

where

$$\ln \Omega_{ij}^*(T_{ij}^*) = \sum_{k=0}^{4} b_k [\ln(T_{ij}^*)]^k \qquad \text{and} \qquad T_{ij}^* = T/(\varepsilon_{ij}/k_B) \tag{13}$$

In the equations above, k_B is the Boltzmann constant in $J \cdot K^{-1}$, σ_{ij} and ε_{ij}/k_B represent the length and energy scaling parameters, in m and K, respectively, and the coefficients b_k are given in Table V. Equations (12) and (13) can also be employed for the calculation of the dilute-gas viscosity, η_i^0, of pure component i.

In Eqs. (7), (8), and (10), the symbols A_{ij}^* and B_{ij}^* represent weak functions of the intermolecular potential for the i–j interaction, which can be calculated from [18]

$$\ln A_{ij}^*(T_{ij}^*) = \sum_{k=0}^{4} c_k [\ln(T_{ij}^*)]^k \tag{14}$$

and

$$\ln B_{ij}^*(T_{ij}^*) = \sum_{k=0}^{3} d_k [\ln(T_{ij}^*)]^k \tag{15}$$

where the coefficients c_k and d_k are given in Table VI. The length and energy parameters σ_{ij} and ε_{ij}/k_B were calculated from the critical constants [7] and are listed in Table V.

Table VI. Coefficients b_k, $a_{\lambda k}$, c_k, and d_k

k	b_k	c_k	d_k	$a_{\lambda k}$
0	0.46649	0.1281	0.1789	1.0655
1	−0.57015	−0.1108	−0.1233	−3.538
2	0.19164	0.0962	0.0558	12.120
3	−0.3708	−0.0271	−0.0074	−12.469
4	0.00241	0.0024	—	4.562

The pure-fluid pseudo-radial distribution function was expressed in terms of the experimental thermal conductivity, λ_i, at the same molar density and temperature as [4]

$$\bar{\chi}_i(\rho_{\mathrm{m}}, T) = \frac{\beta}{2} \frac{(\lambda_i - \rho_{\mathrm{m}} \gamma_{ii} \lambda_i^0(\mathrm{mon}))}{\rho_{\mathrm{m}}^2 \gamma_{ii}^2 \lambda_i^0(\mathrm{mon})} + \beta \left[\left(\frac{(\lambda_i - \rho_{\mathrm{m}} \gamma_{ii} \lambda_i^0(\mathrm{mon}))}{2\rho_{\mathrm{m}}^2 \gamma_{ii}^2 \lambda_i^0(\mathrm{mon})} \right)^2 - \frac{\lambda_i^0}{\beta \rho_{\mathrm{m}}^2 \gamma_{ii}^2 \lambda_i^0(\mathrm{mon})} \right]^{1/2} \tag{16}$$

where $1/\beta = 0.5329$, while the pseudo-radial distribution function $\bar{\chi}_{ij}$, for molecules i and j in the presence of all other species in the mixture, is [4]

$$\bar{\chi}_{ij}(\rho_{\mathrm{m}}, T) = 1 + \frac{2}{5} \sum_{k=1}^{N} x_k(\bar{\chi}_k - 1) + \frac{[6/5(\bar{\chi}_i - 1)^{1/3} (\bar{\chi}_j - 1)^{1/3} \sum_{k=1}^{N} x_k(\bar{\chi}_k - 1)^{2/3}}{(\bar{\chi}_i - 1)^{1/3} + (\bar{\chi}_j - 1)^{1/3}} \tag{17}$$

Finally, the parameter γ_{ij} represents the shortening of the mean free path for interactions of species i and j in a dense gas and, according to the Enskog theory, is [19]

$$\gamma_{ii} = \tfrac{12}{15} N_{\mathrm{A}} \pi \sigma_{ii}^3 \tag{18}$$

As in the case of viscosity [1], it is related to the characteristic close-packed volume $V_{0,i}$, given by

$$V_{0,i} = N_{\mathrm{A}} \sigma_{ii}^3 / \sqrt{2} \tag{19}$$

and thus

$$\gamma_{ii} = 1.2 \times 2.961\, V_{0,i} \tag{20}$$

It should be pointed out that this scheme requires the thermal conductivity of the two pure components at the same temperature and molar density as that of the mixture. In the case of the thermal conductivity of toluene, this resulted in values at very high pressures, while in the case of the thermal conductivity of cyclopentane, this resulted in values at very low densities. To calculate these at the same molar density, the Dymond–Assael method was employed [20]. According to this method the reduced thermal conductivity, λ^*, is defined by

$$\lambda^* = 1.936 \times 10^7 \left(\frac{M}{RT} \right)^{1/2} \frac{\lambda V^{2/3}}{R_\lambda} \tag{21}$$

where V is the molar volume $(\mathrm{mol}\cdot\mathrm{m}^{-3})$, M is the molar mass, R is the universal gas constant, and R_λ is a roughness factor introduced to account for nonspherical-shape effects.

The reduced thermal conductivity is a function only of the volume ratio, V/V_0, where V_0 is a characteristic volume, which corresponds in a hard-sphere system to the volume of close-packing. The universal curve is expressed by the equation

$$\log \lambda^* = \sum_{k=0}^{4} a_{\lambda k}(V_0/V)^k \tag{22}$$

The values of the coefficients $a_{\lambda k}$ are given in Table VI.

The equation that gives the characteristic volume V_0 of the pure components is the same as used for the viscosity of toluene + cyclopentane mixtures. These values were optimized with the experimental data for the thermal conductivity of the pure components, and the optimum value of R_λ is

$$R_\lambda = \sum_{0}^{1} \theta_k T_{\mathrm{r}}^k \tag{23}$$

while the characteristic volume is

$$V_0 = \sum_{k=1}^{5} v_k (T/T^c)^k \tag{24}$$

with the coefficients v_k and θ_k given in Table V.

Finally, the value of the thermal conductivity of the pure components at zero density λ_i^0 is required. This was calculated from the viscosity of pure components at zero density η_i^0 by the modified Eucken formula [21]

$$\frac{\lambda_i^0 m_i}{\eta_i^0 C_{Vi}} = 1.32 + 1.77(R/C_{Vi}) \tag{25}$$

where C_{Vi} is the molar heat capacity at a constant volume of species i. This can be derived from the perfect-gas isobaric heat capacity of the pure component, $C_{Vi} = C_{Pi} - R$, which is a function of temperature,

$$C_{Pi} = \sum_{k=0}^{3} f_k T^k \tag{26}$$

The coefficients f_k for toluene and cyclopentane are given in Table V.

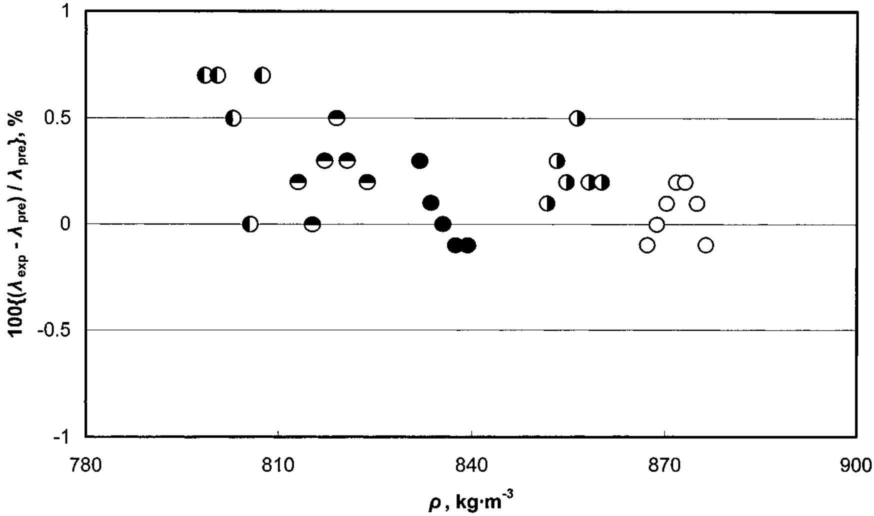

Fig. 5. Deviations of the thermal conductivity of toluene + cyclopentane mixture from the values predicted by the Vesovic–Wakeham scheme: (○) 235 K; (◑) 253 K; (●) 273 K; (◓) 293 K; (◐) 308 K.

The results of this scheme for the prediction of the thermal conductivity of the toluene + cyclopentane mixture are very good. As shown in Fig. 5, the maximum deviation between the experimental and the predicted values is 0.7%. This, of course, was expected, since the pure component values do not deviate by more than 3%.

It is very interesting, however, to note that the values for the pseudo-radial distribution function $\bar{\chi}_i(\rho_m, T)$ of toluene and cyclopentane calculated from viscosity and thermal conductivity data are very different. As shown in Fig. 6, viscosity data gave very large values of $\bar{\chi}_i(\rho_m, T)$, which vary from about 300 to 40 for toluene and from about 35 to 15 for cyclopentane, in the temperature range from 235 to 308 K. The values of pseudo-radial distribution function derived from thermal conductivity data for the same temperature range are much smaller and vary from about 28 to 20 for toluene and from 18 to 13 for cyclopentane. If we use the values of $\bar{\chi}_i(\rho_m, T)$ calculated from thermal conductivity data for the viscosity analysis, the predicted viscosity values for the toluene + cyclopentane mixture become significally smaller than the experimental results and deviate up to 200% at the lowest temperature.

In Fig. 7, the values of the pseudo-radial distribution function for toluene and cyclopentane calculated from viscosity and thermal conductivity data are shown as a function of the ratio (V/V_0) of each component.

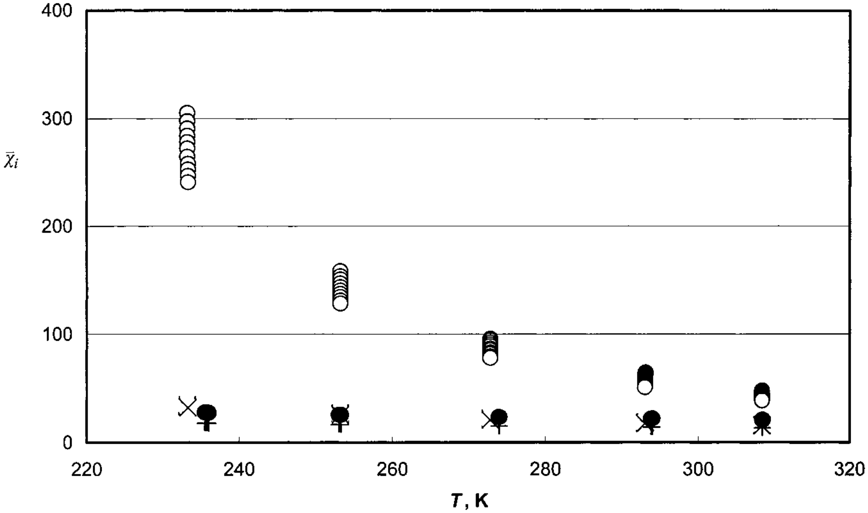

Fig. 6. Values of the pseudo-radial distribution function of toluene and cyclopentane, calculated from viscosity and thermal conductivity data, as a function of the temperature: (○) $\bar{\chi}_i(\rho_m, T)$ of toluene, from viscosity data; (×) $\bar{\chi}_i(\rho_m, T)$ of cyclopentane, from viscosity data; (●) $\bar{\chi}_i(\rho_m, T)$ of toluene, from thermal conductivity data; (+) $\bar{\chi}_i(\rho_m, T)$ of cyclopentane, from thermal conductivity data.

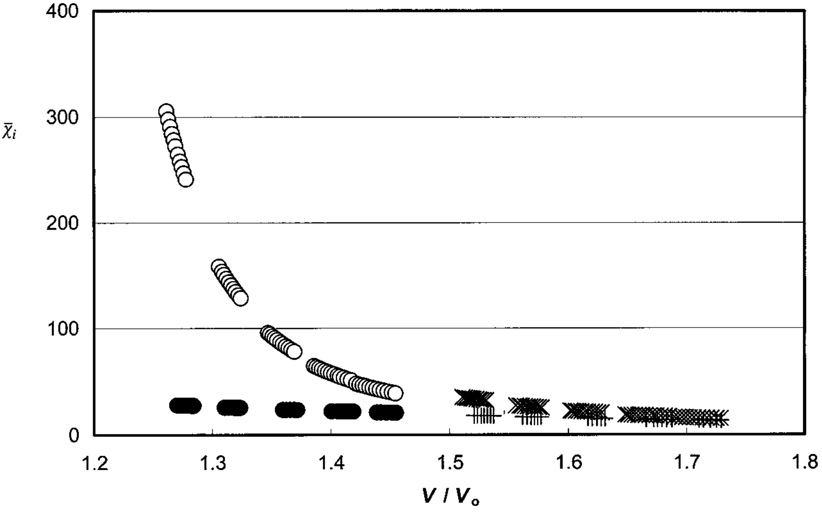

Fig. 7. Values of the pseudo-radial distribution function of toluene and cyclopentane, calculated from viscosity and thermal conductivity data, as a function of the (V/V_0) ratio: (○) $\bar{\chi}_i(\rho_m, T)$ of toluene, from viscosity data; (×) $\bar{\chi}_i(\rho_m, T)$ of cyclopentane, from viscosity data; (●) $\bar{\chi}_i(\rho_m, T)$ of toluene, from thermal conductivity data; (+) $\bar{\chi}_i(\rho_m, T)$ of cyclopentane, from thermal conductivity data.

It can be seen clearly that the values agree well only for high values of this ratio. Indeed, in that area where agreement is good, the scheme predicts very well both viscosity and thermal conductivity.

It can therefore be concluded that the scheme can be applied successfully only when the molar volume is much higher than the close-packed volume and thus the hard-sphere approximations are valid.

5. CONCLUSIONS

The new measurements of the thermal conductivity of toluene + cyclopentane mixtures presented here allowed the investigation of the limits of application of the Vesovic–Wakeham scheme. It was thus concluded that the scheme can be employed to predict successfully the viscosity and thermal conductivity of mixtures, provided it is applied in the range where the molar volume is much higher than the close-packed volume.

REFERENCES

1. M. J. Assael, N. K. Dalaouti, and J. H. Dymond, *Int. J. Thermophys.* **21**:621 (2000).
2. M. J. Assael, H. M. T. Avelino, N. K. Dalaouti, J. M. N. A. Fareleira, and K. R. Harris, *Int. J. Thermophys.* **22**:789 (2001).
3. M. L. V. Ramires, C. A. Nieto de Castro, R. A. Perkins, Y. Nagasaka, A. Nagashima, M. J. Assael, and W. A. Wakeham, *J. Phys. Chem. Ref. Data* **29**:2 (2000).
4. V. Vesovic and W. A. Wakeham, *High Temp. High Press.* **23**:179 (1991).
5. V. Vesovic and W. A. Wakeham, *Int. J. Thermophys.* **10**:125 (1989).
6. V. Vesovic and W. A. Wakeham, *Chem. Eng. Sci.* **44**:2181 (1989).
7. M. J. Assael, N. K. Dalaouti, E. Perperi, J. H. Dymond, and W. A. Wakeham, *Int. J. Thermophys.* **21**:357 (2000).
8. M. J. Assael, E. Karagiannidis, and W. A. Wakeham, *Int. J. Thermophys.* **13**:735 (1992).
9. W. A. Wakeham, A. Nagashima, and J. V. Sengers (eds.), *Experimental Thermodynamics, Vol II. Measurement of the Transport Properties of Fluids* (Blackwell Scientific, London, 1991).
10. J. J. Healy, J. J. de Groot, and J. Kestin, *Physica* **82C**:392 (1976).
11. V. G. Baonza, M. A. Caceres, and J. D. Nunez, *Ber. Bunsenges. Phys. Chem.* **96**:1859 (1992).
12. N. Kitazawa and A. Nagashima, *Bull. JSME* **24**:374 (1981).
13. H. Kashiwagi, T. Hashimoto, Y. Tanaka, H. Kubota, and T. Makita, *Int. J. Thermophys.* **3**:201 (1982).
14. C. A. Nieto de Castro, R. D. Trengove, and W. A. Wakeham, *Rev. Port. Quim.* **28**:17 (1985).
15. B. Taxis, M. Zalaf, and W. A. Wakeham, *Int. J. Thermophys.* **9**:21 (1988).
16. T. Yamada, T. Yaguchi, Y. Nagasaka, and A. Nagashima, *High Temp. High Press.* **25**:513 (1993).
17. B. C. Sakiadis and J. Coates, *AIChE J.* **9**:121 (1957).
18. G. C. Maitland, E. B. Smith, M. Rigby, and W. A. Wakeham, *Intermolecular Forces* (Clarendon Press, Oxford, 1981), pp. 564–567.

19. S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases*, 2nd ed. (Cambridge University Press, London, 1952), Chap. 16.
20. M. J. Assael and J. H. Dymond, in *Transport Properties of Fluids: Their Correlation, Prediction and Estimation*, J. Millat, J. H. Dymond, and C. A. Nieto de Castro, eds. (Cambridge University Press, New York, 1996), pp. 226–250.
21. R. C. Reid, J. M. Prausnitz, and B. E. Poling, *The Properties of Gases and Liquids*, 4th ed. (McGraw–Hill, New York, 1988), pp. 493–495.