The Thermal Conductivity of Xylene Isomers in the Temperature Range 290-360 K

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New absolute measurements of the thermal conductivity of the three xylene isomers are reported. The measurements have been carried out in the temperature range 290-360 K, at atmospheric pressure, in a transient hot-wire instrument. The accuracy of the measurements is estimated to be $+0.5\%$. The measurements presented in this paper have been used in conjuction with our earlier reported measurements of liquid benzene and toluene, at atmospheric pressure, to develop a consistent theoretically based predictive scheme for the thermal conductivity of these five aromatic hydrocarbons. The proposed scheme, containing just one parameter characteristic of each fluid, permits the prediction of the thermal conductivity of the five aromatic hydrocarbons in the temperature range 290-360 K and at pressures up to 350MPa, with an accuracy of $+2.5\%$.

KEY WORDS: *m*-xylene; *o*-xylene; *p*-xylene; thermal conductivity; transient hot-wire technique.

1. INTRODUCTION

In a series of recent papers $[1, 2]$, a transient hot-wire instrument for the measurement of the thermal conductivity was described and results for liquid hexane, heptane, and decane were presented. Based on these results and in conjuction with accurate measurements of other investigators, a consistent theoretically based scheme was succesfully developed for the density dependence of the alkanes. The scheme was also proved reliable in the description of the density dependence of the thermal conductivity of the alcohols [3]. Accurate measurements of the thermal conductivity of toluence and benzene have recently $\lceil 1, 4 \rceil$ also been presented. In an effort

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to extend the applicability of this scheme to the aromatic hydrocarbons, the thermal conductivity of o -xylene, m -xylene, and p -xylene was measured in the temperature range 290-360 K and at atmospheric pressure, with an estimated accuracy of $+0.5\%$. The aforementioned scheme has been consequently applied to our atmospheric pressure measurements of these five aromatic hydrocarbons to predict their thermal conductivity in the temperature range 290-360 K and up to 350 MPa. Comparisons with accurate high-pressure measurements [5-7] show the accuracy of this scheme to be $+2.5\%$ and, thus, demonstrate the power of such a scheme.

2. EXPERIMENTAL

In a previous paper [1], a transient hot-wire instrument for the measurement of the thermal conductivity of liquids was described. The accuracy of the instrument was estimated to be $+0.5\%$. For the present measurements, the instrument has been employed unchanged. The measurements were carried out at atmospheric pressure and the temperature range examined was $290-360$ K. The samples of o -xylene, m -xylene, and p -xylene were all supplied by B.D.H. Chemicals Ltd., and the purity was found to be better than 99 %.

For each measurement, appropriate tests were performed to ensure that the results are free from radiative and convective contributions [2, 8]. As a check of the continuing good operation of the instrument, toluene was measured before and after the measurements of the xylene isomers. The values obtained for toluene were in full agreement with those reported earlier [1].

3. RESULTS

Table I shows the experimental data for the thermal conductivity of the three xylene isomers at atmospheric pressure as a function of temperature. The thermal conductivity values have been represented by a linear function of the absolute temperature T , as

$$
\lambda = a_0 + a_1 T \tag{1}
$$

The coefficients α_i , for each xylene isomer, their variance, and the standard deviation of the fit are shown in Table II. The maximum deviation of the o -xylene, *m*-xylene, and *p*-xylene results is 0.16, 0.19, and 0.25%, respectively, while the corresponding standard deviations are 0.12, 0.12, and 0.20%. Figures 1, 2, and 3 show plots of the deviations of the present measurements from Eq. (1), for each xylene isomer. In the same figures, we

o -Xylene		m -Xylene		p -Xylene	
T (K)	λ $(mW \cdot m^{-1} \cdot K^{-1})$	$\boldsymbol{\mathcal{T}}$ (K)	λ $(mW \cdot m^{-1} \cdot K^{-1})$	\overline{T} (K)	λ $(mW \cdot m^{-1} \cdot K^{-1})$
295.41	130.7	294.53	131.2	295.63	128.9
299.15	129.6	301.26	129.2	299.62	127.2
305.39	128.4	304.48	128.8	305.54	125.9
311.01	126.8	308.69	127.5	308.42	124.9
316.59	125.3	313.55	126.4	314.98	123.1
323.72	123.8	318.85	125.0	320.81	121.6
328.58	122.6	326.61	122.9	327.27	120.1
336.77	120.8	332.22	121.5	331.58	118.7
339.43	119.9	338.15	120.0	339.06	117.2
346.13	118.2	350.54	116.4	346.87	114.7
351.78	117.1	358.71	114.5	356.93	111.8
356.41	115.6				

Table I. The Thermal Conductivity of o-Xylene, m-Xylene, and p-Xylene as a Function of Temperature at Atmospheric Pressure

have included measurements of other investigators. The only other set of accurate measurements that were performed in a similar transient hot-wire instrument, with a claimed accuracy of $+0.3\%$, is the high-pressure measurements of Taxis et al. [7]. The measurements of Taxis et al. [7], extrapolated to atmospheric pressure, show a deviation from our present measurements of under 1%, which is in agreement with the mutually claimed accuracies. The only other transient type of measurements are those of Mallan et al. [9], which show a deviation of 3%, and those of Kerimov et al. [11], which show a deviation of -1% . Both instruments, however, did not employ the full theory for transient measurements and were operated on a relative basis. The measurements of Rastorguev and Pugash [10], Akhundov and Gasanova [12, 13], Poltz and Jugel [14],

Table II. Coefficients of the Least-Squares Straight-Line Fit of the Thermal Conductivity as a Function of the Temperature

	α_0 $(mW \cdot m^{-1} \cdot K^{-1})$	α_{1} $(\mu W \cdot m^{-1} \cdot K^{-2})$	σ (%)
o -Xylene	$202.49 + 0.6$	$-243 + 1.9$	0.12
m -Xylene	207.91 ± 0.7	-260 ± 2.0	0.12
p -Xylene	$208.43 + 1.0$	-270 ± 3.7	0.20

Fig, 1, Deviations of the experimental thermal conductivity values of o-xylene from Eq. (1). (\bullet) Present work; (\bullet) Ref. 7; (\uparrow) Ref. 10; $(\overline{\leftrightarrow})$ Ref. 11; $(\overline{\leftrightarrow})$ Ref. 12; $(\overline{\leftrightarrow})$ Ref. 15; $(\overline{\leftrightarrow})$ Ref. 16; (\equiv) Ref. 18; (E) Ref. 19; (\bigodot) Ref. 20; (E) Ref. 21; (E) Ref. 23.

Fig. 2. Deviations of the experimental thermal conductivity values of *m*-xylene from Eq. (1). (\bullet) Present work; (\bullet) Ref. 7; (\uparrow) Ref. 10; ($\overline{+)}$ Ref. 11; ($\overline{+}$) Ref. 12; (\Box) Ref. 14; (\Box) Ref. 18; ($\overline{=}$) Ref. 19; (III) Ref. 22; (III) Ref. 25.

Fig. 3. Deviations of the experimental thermal conductivity values of p-xylene from Eq. (1). (\bullet) Present work; (\bullet) Ref. 7; (\blacksquare) Ref. 9; (\Box) Ref. 10; (\Box) Ref. 11; (\Box) Ref. 13; (\Box) Ref. 17; (\Box) Ref. 18; $({\blacksquare})$ Ref. 19; $({\blacksquare})$ Ref. 23.

Tufeu et al. [15], Gudzinowicz et al. [16], Mukhamedzyanov et al. [17], Briggs [18], Linder [19], Filippov [20], Vargaftik [21, 22], and Riedel [23] were all performed in various types of steady-state instruments. Only investigators whose measurements depart less than 10% from Eq. (1) are presented. The discordancy of the literature values can be seen.

4. DISCUSSION

In the case of normal alkanes [24], it has been proved possible to develop a reliable scheme for the representation of the thermal conductivity based upon the results of a rigid-sphere model of a fluid. The essence of the representation is that the experimental group

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

is, for a particular fluid, a function only of the molar volume V to an effective core volume V_0 , which is itself but weakly temperature dependent. In Eq. (2), M is the molar mass and R is the universal gas constant.

In the case of alkanes it has been found that λ^* is universal among alkanes from ethane to tridecane [24]. A similar representation was found to be valid for the alcohols from methanol to hexanol [25]. It is therefore

	β_0 $(10^{-6} \text{ m}^3 \cdot \text{mol}^{-1})$	β_1 $(10^{-9} \text{ m}^3 \cdot \text{mol}^{-1})$
Benzene	48.59	-6.74
Toluene	63.57	-15.74
o -Xylene	76.48	-17.77
m -Xylene	78.96	-20.00
p -Xylene	79.39	-22.42

Table III. Coefficients of the Least-Squares Straight-Line Fit of the Effective Core Volume as a Function of the Temperature

worthwhile to examine whether a similar representation of the data of aromatic hydrocarbons can be achieved. For this scheme we have used our earlier data for benzene [4] and toluene [1] and the present data of o -xylene, *m*-xylene, and p -xylene. All these measurements were performed at atmospheric pressure and covered a temperature range of 290-360 K.

For the predictive scheme and guided by the results of earlier work [24, 25], we have represented λ^* by the equation,

$$
\ln \lambda^* = 4.8991 - 2.2595 \ln(V/V_0) \tag{3}
$$

where the two constants were based on the theoretical calculation of the effective core volume of hexane $\lceil 24 \rceil$ and were subsequently found to be universal among the alkanes and the alcohols. Using our experimental data of each aromatic hydrocarbon, the effective core volume was calculated at each temperature and was fitted to a least-squares straight line as a function of the absolute temperature T , for each fluid, as

$$
V_0 = \beta_0 + \beta_1 T \tag{4}
$$

The coefficients β_i are shown in Table III, while in Table IV typical values

 V_{0} $(10^{-6} \,\mathrm{m}^3 \cdot \mathrm{mol}^{-1})$ Temperature (K) Benzene Toluene o -Xylene m -Xylene p -Xylene 300 46.57 58.85 71.15 72.96 72.66 330 46.37 58,38 70.62 72.36 71.99 360 46.16 57.90 70.08 71.76 71.32

Table IV. Typical Values of the Effective Core Volume for the Aromatic Hydrocarbons for Various Temperatures

Fig. 4. Deviations of the experimental thermal conductivity values of benzene from the predictive scheme, Eqs. (2) – (4) . 1: $(①)$ Present **work. 2:** (\Box) 310 **K**, (\bigoplus) 320 **K**, (\Box) 344 **K**, (\odot) 360 **K** [5].

Fig. 5. Deviations of the experimental thermal conductivity values of toluene from the predictive scheme, Eqs. (2)-(4). 1: (@) Present work. 2: (\Box) 308 K, (\oplus) 320 K, (\Box) 330 K, (\bigcirc) 345 K, (\oplus) **360 K [6].**

of the effective core volume are shown. The maximum deviation of the thermal conductivity of the five aromatic hydrocarbons calculated with this scheme was found to be 0.3% . In order to test the power of this scheme, we have subsequently used Eqs. (3) and (4) and the values for the effective core volumes calculated from our atmospheric pressure measurements, to predict the high-pressure measurements of Li et al. I-5] for benzene, Nieto de Castro et al. $\lceil 6 \rceil$ for toluene, and Taxis et al. $\lceil 7 \rceil$ for the xylene isomers. All these were performed in a similar transient hot-wire instrument and enjoy an accuracy of $+0.4\%$. The measurements of benzene [5] covered a pressure range of $4-350 \text{ MPa}$, and the measurements of toluene [6] a pressure range 2-210 MPa. The measurements of the three xylene isomers [7] extented to 420 MPa but density values were available only to 50 MPa. Figures 4, 5, and 6 show the deviations of these high-pressure experimenal data from those predicted with the scheme of Eqs. (3) and (4). It can be seen that the maximum deviation is 2.5 %. This result provides ample confirmation of the universality of Eq. (3) among the five aromatic hydrocarbons examined and permits ready and reliable interpolation and extrapolation to a very wide range of conditions.

Fig. 6. Deviations of the experimental thermal conductivity values of the three xylene isomers from the predictive scheme, Eqs. (2)-(4). o-Xylene--1: (\bullet) Present work. 2: (O) 308 K, (\leftrightarrow) 318 K, (\leftrightarrow) 337 K, $(\mathbf{0})$ 360 K [7]. m-Xylene--1: $(\mathbf{1})$ Present work. 2: (\square) 308 K, (\pm) 318 K, (\pm) 337 K, (\pm) 360 K $[7]$. p-Xylene--1: (A) Present work. 2: (\triangle) 308 K, (\triangle) 318 K, (\triangle) 337 K, (\triangle) 360 K [7].

5, CONCLUSIONS

The thermal conductivity of o -xylene, m -xylene, and p -xylene has been measured at atmospheric pressure as a function of temperature with an absolute accuracy of $+0.5\%$. These values have been used in conjuction with our earlier measurements of benzene and toluene to developed a predictive theoretically based scheme able to predict the thermal conductivity at high pressures with an accuracy of $+ 2.5 \%$.

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