Thermal Conductivity and Thermal Diffusivity of Xylene Isomers in the Temperature Range 308–360 K at Pressures up to 0.38 GPa

B. Taxis,¹ M. Zalaf,¹ and W. A. Wakeham¹

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New, absolute measurements of the thermal conductivity of the three xylene isomers within the temperature range 308–360 K for pressures up to 0.38 GPa are reported. In addition, for two of the isomers, *m*-xylene and *p*-xylene, it has been possible to measure the thermal diffusivity simultaneously within the same range of conditions. The accuracy of the thermal conductivity data reported is one of ± 0.3 %, whereas for the thermal diffusivity the estimated accuracy is ± 6 %. It is found that the density dependence of the thermal conductivity for all of the xylenes can be well represented by one equation based on a rigid-sphere model in the same way that has proved successful for normal alkanes. The thermal diffusivity data have been employed to derive heat capacities for the xylenes over a range of pressures.

KEY WORDS: heat capacity; high pressure; *m*-xylene; *o*-xylene; *p*-xylene; thermal conductivity; thermal diffusivity.

1. INTRODUCTION

This paper reports a continuation of the investigation of the thermal conductivity of simple organic liquids over a range of pressures by means of the transient hot-wire technique [1-3]. Results are presented for the three isomers of xylene: *o*-xylene, *m*-xylene, and *p*-xylene. The motivation for this study of aromatic systems is, in part, to establish a reliable interpolation and prediction scheme for their thermal conductivity similar to that which has proved successful for alkanes [4]. In addition, the study is conducted to investigate the variation of the thermal conductivity among isomers of aromatic compounds parallel to that conducted for alkanes [5, 6].

¹ Department of Chemical Engineering and Chemical Technology, Imperial College, London SW7 2BY, United Kingdom.

With the aid of a reappraisal of the theory of the transient hot-wire technique [7] and small changes in the experimental procedures [8], it has also been possible to determine the thermal diffusivity of *m*-xylene and *p*-xylene over a range of pressures. Whereas the accuracy of the determinations is modest $(\pm 6\%)$ [7], it is possible to derive from them values of the heat capacity of the two liquids that have not previously been reported over a range of pressures.

2. EXPERIMENTAL

The thermal conductivity and thermal diffusivity measurements have been performed in the transient hot-wire instrument described elsewhere [9], using the modified computer-controlled system described in Ref. 10. For the present measurements, the thermal conductivity cells remained unchanged apart from the replacement of the platinum sensing elements [9]. However, small changes were made to the manner in which the computer-controlled bridge was operated, in order to secure the highest precision in the measurement of the thermal diffusivity.

The changes were guided by a review of the theory of the transient hot-wire technique as applied to thermal diffusivity measurements [7]. That review indicated that the largest single source of error in the thermal diffusivity measurements arose from the determination of the absolute resistance of the platinum wires at the equilibrium temperature of a measurement prior to a run. Consequently, extreme care was taken in the performance of that measurement in the manner described in detail elsewhere [8]. The precision of the thermal conductivity measurements is left unaltered by this change of procedure, but that of the thermal diffusivity determinations is improved by a factor of two.

The accuracy of the absolute thermal diffusivity measurements, but not the thermal conductivity measurements, is further limited by the uncertainty in the determination of the radius of the 7- μ m platinum sensing elements [7, 8]. Consequently, we have evaluated the thermal diffusivity of *m*-xylene and *p*-xylene by the relative method described in Ref. 7. For this purpose we have employed as a reference value the thermal diffusivity κ_{ref} , of toluene at a temperature of 328.5 K and atmospheric pressure [7]

$$\kappa_{\rm ref} = 8.01 \times 10^{-8} \,{\rm m}^2 \cdot {\rm s}^{-1} \tag{1}$$

The adoption of toluene as the reference fluid means that fresh measurements of the thermal conductivity and thermal diffusivity under the reference conditions have been necessary. The opportunity has been taken to repeat the measurements of the thermal conductivity of toluene over a

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wider range of conditions, to check the continued proper operation of our instrument by comparison with our earlier results [2]. It should be emphasized that whereas the thermal diffusivity is evaluated on a relative basis, the measurements of the thermal conductivity of all the liquids studied remain absolute.

The samples of *m*-xylene, *o*-xylene, *p*-xylene, and toluene were all supplied by Aldrich Chemical Co., Gillingham, U.K., and, after distillation and degasification, had a confirmed purity in excess of 99.9%. The measurements on toluene were carried out along four isotherms, 308, 317.6, 330, and 347 K, at pressures up to 50 MPa. For the xylenes, isotherms at 308, 318, 337.6, and 360 K were studied up to a maximum pressure of 380 MPa or the solidification pressure.

For each measurement, appropriate tests were performed to ensure that the results are free from radiative and convective contributions as described earlier [2, 9]. For the application of small corrections in the data reduction we have employed the density data given by Kashiwagi et al. [11] for toluene and by Mamedov et al. [12] for the xylenes. For the xylenes, the highest pressure for which the density has been measured is 50 MPa. Consequently, solely for the purpose of making these corrections, it has been necessary to extrapolate the equation of state fitted to these data for the higher pressures. The effect of this extrapolation on the reported thermal conductivity data is negligible.

3. RESULTS

The thermal conductivity data, corrected to nominal temperatures as described earlier [9], are listed in Tables I to IV. The correction of the thermal conductivity to the nominal temperature never amounted to more than $\pm 0.3\%$ so that the additional uncertainty in the reported data is negligible. It is estimated that the overall error in the tabulated thermal conductivity is one of $\pm 0.3\%$. The corresponding density is also quoted whenever it lies within the range of direct measurements [12]. No extrapolated density data have been quoted. In addition, the thermal diffusivity is tabulated as the ratio of the measured value to the reference value $\kappa_{\rm ref}$ of Eq. (1). From it, with the aid of the tabulated density and thermal conductivity, we have derived the isobaric heat capacity $C_{\rm p}$ by means of the definition

$$\kappa = \lambda / \rho C_{\rm p} \tag{2}$$

The thermal diffusivity determined by the transient hot-wire technique refers to the density and temperature of the fluid under the equilibrium

	<u> </u>		
P (MPa)	$\frac{\lambda(T_{\text{nom}}, P)}{(W \cdot m^{-1} \cdot K^{-1})}$	$\kappa/\kappa_{ m ref}$	$\frac{C_{p}}{(kJ \cdot kg^{-1} \cdot K^{-1})}$
$T_{\rm norm}$	a = 308.15 K	T_0	= 305.80 K
0.1	0.1280	0.967	1936
0.1	0.1278	0.907	2008
0.1	0.1279	0.925	2098
6.8	0.1302	0.929	1952
11.9	0.1321	0.946	2022
20.3	0.1351	0.991	1959
33.5	0.1393	1.027	1930
51.2	0.1445	1 079	1884
51.2	0.1441	1.034	1961
T_{nom}	= 317.65 K	T_0	= 315.75 K
0.1	0.1254	0.991	1869
3.0	0.1264	1 030	1807
13.0	0.1303	1.090	1745
23.7	0.1339	1.068	1813
38.7	0.1387	1.050	1887
T _{nom}	= 330.65 K	T _o	= 328.50 K
0.1	0.1215	1.000	1971
3.0	0.1215	0.004	1821
12.8	0.1251	1.030	1047
12.0	0.1260	0.870	2154
23.5	0.1209	0.940	2134
36.1	0.1350	1.034	1802
37.4	0.1354	1.034	1892
$T_{\rm nom}$	= 347.15 K	To	= 345.00 K
0.1	0 1 1 6 9	0.040	1949
4.1	0.1187	0.909	1040
12.0	0.1225	0.955	1071
22.0	0.1223	0.241	1009
37.1	0.1311	1 042	1900
51.2	0.1362	0.982	2015
67.5	0.1406	1 023	1974
0.12	0.11.000	1.025	17/7

 Table I.
 Thermal Conductivity, Thermal Diffusivity, and Isobaric Heat Capacity of Toluene

P (MPa)	ρ_r (kg·m ⁻³)	$\dot{\lambda}(T_{\text{nom}}, \rho)$ $(\mathbf{W} \cdot \mathbf{m}^{-1} \cdot \mathbf{K}^{-1})$	$\lambda(T_{\text{nom}}, P)$ $(\mathbf{W} \cdot \mathbf{m}^{-1} \cdot \mathbf{K}^{-1})$	κ/κ_{ref}	$\begin{array}{c}C_{\rm p}\\(\rm kJ\cdot \rm kg^{-1}\cdot \rm K^{-1})\end{array}$
	$T_{\rm nom} = 308$.15 K	T ₀	= 305.55	ĸ
$\begin{array}{c} 3.4\\ 13.3\\ 25.6\\ 40.2\\ 44.0\\ 56.6\\ 75.4\\ 95.1\\ 96.4\\ 122.6\\ 147.3\\ 172.5\\ 173.0\\ 203.9\\ 233.1\\ 238.0\\ 264.6\\ 294.5\\ 321.9\\ 322.0\\ 323.3\\ 354.2\\ 354.4\\ 381.9\\ 381.9\end{array}$	854.8 862.2 870.6 879.8	0.1288 0.1324 0.1362 0.1401	0.1288 0.1323 0.1361 0.1401 0.1408 0.1446 0.1495 0.1538 0.1546 0.1603 0.1653 0.1699 0.1701 0.1755 0.1803 0.1810 0.1853 0.1892 0.1892 0.1892 0.1931 0.1931 0.1931 0.1933 0.1973 0.1971 0.2007 0.2004	$\begin{array}{c} 1.016\\ 0.974\\ 1.077\\ 0.994\\ 0.943\\ 1.107\\ 1.003\\ 1.007\\ 1.003\\ 1.096\\ 1.031\\ 1.223\\ 1.198\\ 1.294\\ 1.305\\ 1.155\\ 1.354\\ 1.285\\ 1.155\\ 1.354\\ 1.285\\ 1.155\\ 1.354\\ 1.285\\ 1.175\\ 1.364\\ 1.293\\ 1.272\\ 1.320\\ 1.320\\ 1.352\\ \end{array}$	1857 1972 1817 2004
	$T_{\rm nom} = 318$.15 K	T_0	= 315.65	ĸ
$\begin{array}{c} 3.9\\ 3.9\\ 15.0\\ 23.9\\ 9.5\\ 57.9\\ 76.2\\ 76.2\\ 76.2\\ 96.9\\ 119.2\\ 123.5\\ 147.3\\ 172.6\\ 202.9\\ 233.9\\ 264.2\\ 265.5\\ 292.1\\ 323.3\\ 323.9\\ 355.5\\ 383.0\\ \end{array}$	847.0 847.3 855.8 862.2 872.4	0.1259 0.1261 0.1297 0.1328 0.1377	0.1261 0.1261 0.1297 0.1328 0.1376 0.1428 0.1427 0.1474 0.1476 0.1526 0.1575 0.1588 0.1636 0.1634 0.1684 0.1793 0.1840 0.1842 0.1842 0.1842 0.1885 0.1927 0.1929 0.1972 0.2004	$\begin{array}{c} 0.937\\ 0.929\\ 0.971\\ 0.967\\ 0.951\\ 1.041\\ 0.988\\ 1.113\\ 1.087\\ 1.088\\ 1.130\\ 1.174\\ 1.150\\ 1.216\\ 1.216\\ 1.218\\ 1.227\\ 1.219\\ 1.300\\ 1.341\\ 1.296\\ 1.336\\ 1.404 \end{array}$	1988 2006 1954 1993 2076

 Table II.
 Thermal Conductivity, Thermal Diffusivity, and Isobaric Heat Capacity of m-Xylene

P (MPa)	$ ho_r$ $(kg \cdot m^{-3})$	$\lambda(T_{\text{nom}}, \rho)$ $(\mathbf{W} \cdot \mathbf{m}^{-1} \cdot \mathbf{K}^{-1})$	$\lambda(T_{\text{nom}}, P)$ $(\mathbf{W} \cdot \mathbf{m}^{-1} \cdot \mathbf{K}^{-1})$	$\kappa/\kappa_{ m ref}$	$\begin{array}{c}C_{\rm p}\\(\rm kJ\cdot kg^{-1}\cdot K^{-1})\end{array}$
	$T_{\rm nom} = 337$.65 K	T _{non}	n = 360.1	5 K
4.4 4.6 14.7 26.5 40.4 55.4 76.5 96.3 122.8 146.5 173.7 202.6 206.7 206.8 233.1 265.3 295.9 323.7 326.5 353.4 382.5 414.2	831.9 832.3 840.8 849.9 859.6	0.1210 0.1211 0.1247 0.1289 0.1333	$\begin{array}{c} 0.1212\\ 0.1211\\ 0.1248\\ 0.1290\\ 0.1333\\ 0.1377\\ 0.1440\\ 0.1489\\ 0.1554\\ 0.1604\\ 0.1662\\ 0.1718\\ 0.1721\\ 0.1717\\ 0.1771\\ 0.1771\\ 0.1826\\ 0.1873\\ 0.1914\\ 0.1916\\ 0.1955\\ 0.1995\\ 0.2038\\ \end{array}$	0.874 0.897 0.979 1.020 1.030 1.021 1.008 1.021 1.008 1.021 1.008 1.146 1.207 1.261 1.150 1.176 1.184 1.252 1.314 1.288 1.298 1.331 1.291	2088 2031 1897 1861 1883
	$T_{\rm nom} = 360$.15 K	$T_{\rm nom}$	a = 357.8	5 K
$\begin{array}{c} 3.2\\ 3.2\\ 3.1\\ 3.2\\ 3.3\\ 14.9\\ 24.4\\ 24.4\\ 24.4\\ 39.6\\ 56.2\\ 56.3\\ 76.9\\ 97.2\\ 123.4\\ 147.2\\ 173.6\\ 203.6\\ 203.6\\ 203.6\\ 203.6\\ 203.6\\ 204.0\\ 264.0\\ 264.0\\ 264.0\\ 264.0\\ 264.1\\ 294.1\\ 354.2\\ 378.5\\ \end{array}$	812.0 812.3 812.2 812.3 812.2 823.4 831.6 831.6 831.6 831.8 843.5	0.1149 0.1150 0.1152 0.1151 0.1150 0.1194 0.1228 0.1228 0.1228 0.1228 0.1228	$\begin{array}{c} 0.1150\\ 0.1150\\ 0.1151\\ 0.1151\\ 0.1151\\ 0.1150\\ 0.1194\\ 0.1228\\ 0.1228\\ 0.1227\\ 0.1283\\ 0.1334\\ 0.1334\\ 0.1393\\ 0.1449\\ 0.1515\\ 0.1572\\ 0.1630\\ 0.1630\\ 0.1690\\ 0.1738\\ 0.1798\\$	$\begin{array}{c} 0.908\\ 0.902\\ 0.878\\ 0.914\\ 0.875\\ 0.909\\ 0.920\\ 0.945\\ 1.047\\ 1.328\\ 1.030\\ 1.029\\ 1.115\\ 1.140\\ 1.185\\ 1.167\\ 1.220\\ 1.130\\ 1.138\\ 1.160\\ 1.271\\ 1.141\\ 1.141\\ 1.141\\ 1.287\\ 1.215\\ 1.310\\ \end{array}$	1953 1966 2023 1943 2027 1997 2010 1948 2004 2014

 Table II. (Continued)

P (MPa)	$\rho_{\rm r}$ (kg·m ⁻³)	$ \lambda(T_{\text{nom}}, \rho_r) (\mathbf{W} \cdot \mathbf{m}^{-1} \cdot \mathbf{K}^{-1}) $	$\frac{\lambda(T_{\text{nom}}, P)}{(W \cdot m^{-1} \cdot K^{-1})}$
	T _{nom}	= 308.15 K	
0.3	869.5	0.1309	0.1307
8.9	875.7	0.1338	0.1336
24.1	885.6	0.1383	0.1381
43.3	897.0	0.1436	0.1434
58.3		0.1471	
76.6		0.1517	
93.4		0.1558	
122.9		0.1610	
143.5		0.1651	
147.8		0.1655	
169.2		0.1699	
194.3		0.1740	
224.7		0.1786	
244.2		0.1816	
	$T_{\rm nom}$	= 318.15 K	
27	863.2	0.1282	0.1282
16.0	872.7	0.1320	0.1320
26.0	879.7	0.1326	0.1356
41.3	889.1	0.1396	0.1396
57.1		0.1437	0.1070
77.0		0.1488	
96.9		0.1536	
122.2		0.1589	
148.2		0.1642	
150.2		0.1645	
173.7		0.1688	
204.0		0.1742	
228.8		0.1781	
228.8		0.1779	
253.3		0.1817	
253.3		0.1818	
279.7		0.1853	

Table III. Thermal Conductivity of o-Xylene

P (MPa)	ρ_r (kg·m ⁻³)	$\frac{\lambda(T_{\text{nom}}, \rho_{\text{r}})}{(\mathbf{W} \cdot \mathbf{m}^{-1} \cdot \mathbf{K}^{-1})}$	$ \begin{aligned} \lambda(T_{\text{nom}}, P) \\ (\mathbf{W} \cdot \mathbf{m}^{-1} \cdot \mathbf{K}^{-1}) \end{aligned} $
	$T_{\rm nom} =$	= 337.65 K	
8.7	850.8	0.1254	0.1255
8.7	850.8	0.1253	0.1254
24.9	863.4	0.1308	0.1308
30.5	867.4	0.1322	0.1322
41.2	874.7	0.1358	0.1358
41.2	874.7	0.1357	0.1357
57.5		0.1403	
77.2		0.1455	
98.6		0.1508	
123.7		0.1563	
148.9		0.1616	
173.8		0.1661	
184.2		0.1677	
204.8		0.1715	
234.9		0.1769	
263.7		0.1818	
263.7		0.1819	
295.1		0.1861	
306.5		0.1875	
319.7		0.1896	
353.0		0.1943	
	Т	- 260 15 V	
	I nom =	= 500,15 K	
6.0	828.0	0.1183	0.1184
16.1	837.2	0.1120	0.1221
24.0	843.9	0.1249	0.1250
42.4	857.9	0.1308	0.1309
42.4	857.9	0.1307	0.1308
56.8		0.1351	
74.8		0.1403	
97.4		0.1462	
123.1		0.1523	
150.7		0.1580	
171.3		0.1622	
176.3		0.1630	
203.9		0.1684	
233.7		0.1738	
262.6		0.1/86	
291.6		0.1833	
325.8		0.1884	
338.U		0.1899	
304.8 280.7		0.1921	
382.7		0.1900	
419.2		0.2006	

Table III. (Continued)

р (MPa)	ρ_r (kg·m ⁻³)	$ \begin{aligned} \lambda(T_{\text{nom}}, \rho_{\text{r}}) \\ (\mathbf{W} \cdot \mathbf{m}^{-1} \cdot \mathbf{K}^{-1}) \end{aligned} $	$\lambda(T_{\text{nom}}, P)$ $(\mathbf{W} \cdot \mathbf{m}^{-1} \cdot \mathbf{K}^{-1})$	$\kappa/\kappa_{ m ref}$	$\begin{array}{c}C_{p}\\(kJ\cdot kg^{-1}\cdot K^{-1})\end{array}$
	$T_{\rm nom} = 308.$.15 K	T_{0}	= 305.55	K
4.4 8.8 15.9 22.4 41.0 53.8	850.8 854.2 859.5 864.1 876.2	0.1257 0.1273 0.1296 0.1319 0.1373	0.1257 0.1273 0.1296 0.1319 0.1373 0.1407	1.000 0.972 1.039 1.075 1.031 1.115	1851 1920 1817 1776 1900 1784
	$T_{\rm nom} = 318$.15 K	T_0	= 315.55	5 K
3.9 4.0 4.1 14.6 14.7 24.2 39.2 57.8 78.7	842.5 842.6 842.7 851.2 851.2 858.2 868.5	0.1232 0.1231 0.1232 0.1270 0.1268 0.1300 0.1347	0.1231 0.1231 0.1232 0.1269 0.1268 0.1299 0.1345 0.1397 0.1453	0.918 0.923 0.920 0.930 0.959 0.954 0.983 1.020 1.032	1992 1982 1990 2006 1944 1986 1973
	$T_{\rm nom} = 337$.65 K	$T_0 = 335.25 \text{ K}$		
5.4 15.1 24.3 39.0 39.0 55.1 55.5 56.5 76.6 96.4 121.3 147.4	827.3 835.9 835.9 843.4 854.3 854.3	0.1185 0.1219 0.1218 0.1249 0.1300 0.1300	$\begin{array}{c} 0.1185\\ 0.1219\\ 0.1218\\ 0.1248\\ 0.1299\\ 0.1300\\ 0.1347\\ 0.1348\\ 0.1349\\ 0.1405\\ 0.1456\\ 0.1456\\ 0.1521\\ 0.1576\end{array}$	$\begin{array}{c} 0.848\\ 0.882\\ 0.904\\ 0.941\\ 0.945\\ 0.992\\ 0.991\\ 1.000\\ 0.980\\ 1.002\\ 1.094\\ 1.044 \end{array}$	2113 2069 2066 2049 2022 2013
	$T_{\rm nom} = 360.$	15 K	T_0	= 358.25	K
$\begin{array}{c} 3.5\\ 3.6\\ 14.5\\ 15.5\\ 24.2\\ 40.6\\ 40.0\\ 40.0\\ 55.3\\ 76.5\\ 97.0\\ 118.1\\ 124.6\\ 148.6\\ 173.3\\ 197.8 \end{array}$	805.2 805.3 816.5 817.4 825.4 838.7 838.3 838.4	0.1122 0.1122 0.1163 0.1169 0.1197 0.1253 0.1253 0.1255	$\begin{array}{c} 0.1123\\ 0.1124\\ 0.1165\\ 0.1170\\ 0.1199\\ 0.1255\\ 0.1254\\ 0.1256\\ 0.1304\\ 0.1366\\ 0.1421\\ 0.1473\\ 0.1491\\ 0.1547\\ 0.1600\\ 0.1650\\ \end{array}$	$\begin{array}{c} 0.867\\ 0.844\\ 0.857\\ 0.920\\ 0.920\\ 0.994\\ 0.953\\ 0.919\\ 0.977\\ 1.008\\ 1.061\\ 1.049\\ 1.113\\ 1.077\\ 1.148\\ 1.146 \end{array}$	2013 2068 2080 2000 1973 1881 1962 2039

 Table IV.
 Thermal Conductivity, Thermal Diffusivity, and Isobaric Heat Capacity of p-Xylene

conditions prior to a run (T_0, P) . Thus, in order to evaluate the heat capacity under these conditions, the thermal conductivity is corrected to that state and the density evaluated from the available equations of state [11, 12]. This process introduces only a very small additional error into the reported heat capacity for the state (T_0, P) . It is estimated that the overall error in the thermal diffusivity ratio and in the heat capacity is one of $\pm 6\%$.

Figure 1 shows the deviations of the repeated measurements of the thermal conductivity of toluene from the correlation of our earlier measurements [2]. The standard deviation of the data is one of $\pm 0.6\%$, which is commensurate with the mutual uncertainty of the present data and the correlation. In general, the pressure dependence along an isotherm is rather more consistent between the two sets of data than in the absolute thermal conductivity. This is a reflection of the fact that the precision of the experimental method is superior to the accuracy.

For the purposes of interpolation, the thermal conductivity has been represented as a function of pressure along each isotherm by means of the equation



$$\lambda = \lambda' \left[1 + \sum_{i=1}^{4} a_i \frac{p - p'}{p'} \right]$$
(3)

Fig. 1. A comparison of the new measurements of the thermal conductivity of toluene with a correlation of earlier results [2]. (\blacktriangle) 308.15 K; (\blacktriangleleft) 320.15 K; (\blacksquare) 330.15 K; (\bigcirc) 345.15 K.

		and the second se			
Т (К)	$\frac{\lambda'}{(\mathbf{m}\mathbf{W}\cdot\mathbf{m}^{-1}\cdot\mathbf{K}^{-1})}$	10 <i>a</i> ₁	$10^2 a_2$	$10^2 a_3$	$10^2 a_4$
		o-Xylene; p	′ = 250 MPa		
308.15	182.39	1.9512	-7.7619	-6.1889	-7.2386
318.15	181.22	1.9957	7,9077	-1.4013	- 3.3111
337.65	179.29	2.2372	-4.8354	0.30786	-4.2433
360.15	176.40	2.3554	-4.8825	2.1394	- 3.4978
		<i>m</i> -Xylene; <i>p</i>	o' = 250 MPa		
308.15	182.88	2.0726	-5.4278	2.4636	- 1.4461
318.15	181.87	2.2039	-4.9685	1.1018	3.3227
337.65	179.82	2.3116	-5.1852	2.7240	-2.4975
360.15	177.40	2.4847	-5.7717	2.1210	-3.1284
		p-Xylene; p	∞′ = 50 MPa		
308.15	139.70	0.94453	0.87091	6.0582	3.5757
318.15	137.61	1.0109	-1.0722	0.61962	0.21557
337.65	133.15	1.1081	-1.1622	0.37688	-0.10747
360.15	128.64	1.2242	-1.3211	0.17849	-0.01311

 Table V.
 Coefficients of the Correlation of the Pressure Dependence of the Thermal Conductivity Eq. (3)



Fig. 2. Deviations of the thermal conductivity of the three isomers of xylene from the correlation of Eq. (3). (\blacktriangle) *o*-xylene; (\checkmark) *m*-xylene; (\checkmark) *p*-xylene.

The coefficients a_i of this equation are listed in Table V for the three xylene isomers.

The deviations of the experimental data from this correlation are plotted in Fig. 2. Taken over all three isomers the standard deviation of the data from the correlation is about ± 0.1 %, while the maximum deviation is ± 0.4 %.

4. DISCUSSION

4.1. The Density Dependence of the Thermal Conductivity

In the case of normal alkanes [4] it has proved possible to develop a reliable scheme for the representation and prediction of the thermal conductivity based upon the results of a rigid-sphere model of the fluids. The essence of the representation is that the experimental group

$$\lambda^* = 1.936 \times 10^7 \,\lambda V^{2/3} (M/RT)^{1/2} = F(V/V_0) \tag{4}$$

is, for a particular fluid, a function only of the ratio of the molar volume V to a characteristic molar volume V_0 , which is itself but weakly temperature dependent. In Eq. (4), M is the molar mass and R is the universal gas constant.

In the case of alkanes it has been found not only is λ^* a function only of V/V_0 , but also that it is universal among alkanes from ethane to tridecane [4]. It is therefore worthwhile to examine whether a similar representation of the data for the three isomers of xylene can be achieved.

For this purpose, and guided by the results of the earlier work on alkanes [4, 6], we have represented λ^* by the equation

$$\ln \lambda^* = A + B \ln[V/V_{0}(T)]$$
⁽⁵⁾

in which A and B are coefficients universal among the three isomers of xylene and V_{0_i} is a species and temperature-dependent characteristic volume. The adoption of a single reference value of V_0 for *n*-xylene at T = 308.15 K,

$$V_{0_{\text{ref}}} = V_0(308.15 \text{ K}) = 79.88 \times 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$$
 (6)

then allows the experimental thermal conductivity for the three isomers along all isotherms to be employed to determine the optimum values of the coefficients A and B as well as the values of $V_{0,}(T)$ for other species and temperatures. In this way the optimum correlation has been determined as

$$\ln \lambda^* = 4.675 - 2.234 \ln[V/V_{o}(T)]$$
⁽⁷⁾

The corresponding values of the ratio $V_{o_i}(T)/V_{0_{ref}}$ are listed in Table VI.

Т		$V_0(T)/V_{0_{ m ref}}$	
7 (K)	o-Xylene	<i>m</i> -Xylene	<i>p</i> -Xylene
308.15	0.9854	1.0	0.9955
318.15	0.9777	0.9949	0.9913
337.65	0.9732	0.9868	0.9838
360.15	0.9676	0.9800	0.9787

Table VI. Characteristic Volumes for the xylenes, $V_{0_{ref}} = 79.88 \times 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$

Figure 3 displays the deviations of all the experimental thermal conductivity data for the xylenes (within the range of the available density data) from the universal correlation of Eq. (7). It can be seen that the maximum deviation amounts to no more than ± 0.4 %, while the standard deviation is one of ± 0.15 %. This result provides ample confirmation of the universality of Eq. (7) among the three xylene isomers and, as usual [4], permits ready and reliable interpolation *and* extrapolation of the present thermal conductivity data to other conditions.



Fig. 3. Deviations of the thermal conductivity of the three isomers of xylene from the correlation of Eq. (7). (\blacktriangle) *o*-xylene; (\blacksquare) *m*-xylene; (\blacklozenge) *p*-xylene.

4.2. The Variation of the Thermal Conductivity Among the Isomers

In the case of alkanes, previous investigations [5, 6] have revealed a difference between the thermal conductivity of normal and that of branched isomers of as much as 30% at the same density and temperature. The structural changes among the xylene isomers studied here are obviously considerably less than those encountered in the alkanes. It is therefore of some interest to examine the differences in the thermal conductivity among the xylenes. Use of the correlation of the previous section with the parameters in Table VI immediately shows that the maximum differences between the thermal conductivity of the isomers at the same temperature and density amounts to some 3%. We therefore find that the differences of thermal conductivity reflect the relatively small conformational changes among the isomers of xylene.

4.3. The Isobaric Heat Capacity

The accuracy claimed for the thermal diffusivity and isobaric heat capacities listed in Tables I to IV is modest by comparison with that attainable by a purpose-built apparatus. Nevertheless, the values reported for C_p of the xylenes are the first reported over a range of pressures. Within the estimated accuracy of the data there is no evidence of a pressure dependence of C_p and the three isomers have the same heat capacity.

5. CONCLUSIONS

The thermal conductivity of the three xylene isomers—m-xylene, o-xylene, and p-xylene, has been determined over a range of temperature and pressure. The density dependence of the thermal conductivity of all three isomers has been represented by one equation characterized by a single parameter specific to the isomer. The correlation permits reliable evaluation of the thermal conductivity for thermodynamic states beyond those covered in the present study.

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