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Thermal Conductivity of Fourteen Liquids in the Temperature Range 298–373 K

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New experimental data on the thermal conductivity of 14 organic liquids at atmospheric pressure are presented in the temperature range from 25 to 100°C. The liquids measured are five n-alkanes (C_6, C_7, C_8, C_{10}, C_{12}), cyclohexane, six aromatic hydrocarbons (benzene, ethylbenzene, *o*-, *m*-, *p*-xylenes, isopropylbenzene) and two phenyl halides (chloro-, bromobenzenes). The measurements were performed by a transient hot-wire method on a relative basis. The thermal conductivity of toluene, which was selected as a reference liquid, was determined on an absolute basis with another transient apparatus. The precision of the present experimental results is within $\pm 1.2\%$. The uncertainty of the thermal conductivity values is estimated to be within $\pm 2\%$; this includes the uncertainty of the values of toluene as the reference liquid. The experimental results for each liquid are represented satisfactorily by a linear equation in temperature. At a reduced temperature $T/T_c = 0.5$, thermal conductivity has a simple relation with the molar density for each homologous series of liquids.

KEY WORDS: aromatic hydrocarbons; cyclohexane; n-alkanes; phenyl halides; thermal conductivity; toluene; transient hot-wire method.

1. INTRODUCTION

Measurements of transport properties of fluids provide valuable information on the molecular motion and interaction in the presence of a gradient. The thermal conductivity of fluids is a measure of the energy transport by heat conduction, and its study is of great scientific and technological importance. While thermal conductivity of monatomic gases at low density is satisfactorily represented by rigorous molecular theory [1], it is difficult to estimate theoretically the thermal conductivity of liquids due to the fact that the problem of multiple collision of molecules must be considered.

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Accurate experimental data on the thermal conductivity of liquids are necessary to interpret the typical behavior of the thermal conductivity as functions of temperature, pressure, or density. Another problem is the establishment of an accurate method for measuring thermal conductivity over a wide range of temperature and pressure.

This paper describes a precise instrument of the transient hot-wire type, yielding results on a relative basis, and presents new experimental data of the thermal conductivity for 14 organic liquids at temperatures from 25.00°C (298.15 K) to 100.00°C (373.15 K) at atmospheric pressure. The liquids measured are as follows: five n-alkanes (n-hexane, n-heptane, n-octane, n-decane, and n-dodecane), one cycloalkane (cyclohexane), six aromatic hydrocarbons (benzene, ethylbenzene, *o*-, *m*-, *p*-xylenes, and isopropylbenzene) and two phenyl halides (chlorobenzene and bromobenzene). The thermal conductivity of toluene, as a reference liquid, is determined on an absolute basis with another transient hot-wire instrument. The experimental results of the present work are compared with those reported in the literature. The effects of temperature, molecular weight, chemical structure, and density on the thermal conductivity are also discussed.

2. EXPERIMENTAL

2.1. Principle of Measurements

In the past, the transient hot-wire method was considered to be an easy and rapid technique with a simple instrument for measuring thermal conductivity of fluids, yet somewhat inferior to the conventional steady methods [2, 3]. Recent rapid progress in the electronics field has made it possible for the transient method to become a technique of high precision. A theoretical analysis of the transient measurments for gases at high pressures has been given by Kestin and his coworkers [4–6]. The transient hot-wire method has the following advantages:

1. The measurement is performed in a short time period before the onset of free convection; that is, no convective error affects the results.
2. The influence of radiative heat transfer is negligibly small because of the small surface of the hot wire.
3. There is no need to account for various heat losses in the measuring system.
4. It is not necessary to maintain a uniform temperature gradient for a long period of time.
5. The construction of the hot-wire cell is extremely simple.

In the ideal case, that an infinitely thin and long straight wire with negligible heat capacity and infinite thermal conductivity is vertically suspended in a medium of infinite extent under thermal equilibrium, the wire provides a line source of constant heat generation by an electric current. The solution of the thermal conduction equation is simplified by using some boundary conditions. If it is assumed that the physical properties of the fluid (density ρ, isobaric specific heat C_p, and thermal conductivity λ) do not vary during a measurement, the temperature rise $\Delta T(r,\theta)$ at r, a radial distance from the center of wire, and at time θ is

$$\Delta T(r,\theta) = \frac{q}{4\pi\lambda} \ln \frac{4\alpha\theta}{r^2 C} \tag{1}$$

where q is the heat flux per unit length of wire, $\alpha = \lambda/(\rho C_p)$ is the thermal diffusivity, and $\ln C$ is Euler's constant. Based on the assumption that a temperature jump between the wire surface and the adjacent fluid, the Knudsen effect, does not occur, the temperature rise at the wire surface of radius a is given by substituting $r = a$ in Eq. (1). Then a linear relation between ΔT and $\ln\theta$ should be obtained experimentally. The thermal conductivity of the fluid can be determined from the slope of this straight line.

In the present investigation, a relative method has been employed in order to account for the practical departure of the operation of the present apparatus from the ideal conditions described above. Two identical hot-wire cells are prepared: one is for the sample liquid to be measured and the other for the reference liquid. When a constant current flows in both wires simultaneously, Eq. (1) should express the temperature increments of each wire. Then the following equation is obtained:

$$\Delta T(a,\theta)_s = \left(\frac{q_s}{q_r}\right)\left(\frac{\lambda_r}{\lambda_s}\right)\Delta T(a,\theta)_r + \frac{q_s}{4\pi\lambda_s} \ln \frac{\alpha_s}{\alpha_r} \tag{2}$$

where subscripts s and r denote the sample and the reference fluid, respectively. If the quantities q, λ, and α for each fluid are constant during a measurement under a given experimental condition, the temperature rise of the wire in the sample $\Delta T(a,\theta)_s$ shows a linear relation with respect to $\Delta T(a,\theta)_r$ in the reference fluid. Thus, when $q_s = q_r$ is realized experimentally, the thermal conductivity of the sample liquid can be determined from the slope of the straight line based on the results of the simultaneous measurements of only the temperatures of the two wires.

2.2. Apparatus and Procedures

Figure 1 shows the cross-section of the cell. The hot wire, 5, made of platinum (30 μm in diameter and 150 mm long) is placed in the inner tube, *1*, made of stainless steel, SUS 410, (16 mm inner diameter). The platinum wire is suspended tautly by a spring, *7*, and is connected to an electric system through copper leads, *4*, and electrodes, *3*. The spacers, *2*, made of reinforced phenol resin, support the wire coaxially and insulate it electrically.

As described above, two identical cells were constructed. One was for the sample and was mounted in a high pressure vessel made of Cr-Mo steel, SCM3. The other was for the reference and was placed in a brass vessel. Both were placed vertically in an oil bath, which was thermostat controlled to within ± 10 mK. Temperature was determined with a standard thermometer calibrated by the National Research Laboratory of Metrology. Accuracy in temperature measurements is estimated to be better than ±20 mK.

The temperature rise of the wire was determined from the measurement of its resistance change. Figure 2 shows a schematic diagram of the electric circuit, which is mainly composed of a battery, an X-Y recorder, and two Wheatstone bridges. The entire circuit was placed in an air bath controlled at 40.0 ± 0.1 °C. The platinum wires are connected to one of the arms of each bridge. The adjustable resistors R_3 and R_3' compensated for the resistance changes of the platinum wires due to various temperature conditions and kept the entire resistance of the bridges constant. R_5 is a resistor which was to adjust the current flowing in the bridges. R_6 was connected to the circuit for balancing the bridges before the initiation of a measurement; its high resistance (5 kΩ) prevented the temperature rise of the wires. R_7, whose resistance was matched to that of the bridges, forms a dummy circuit so as to stabilize the output voltage of the battery before the measurement.

The resistance change of the platinum wire due to its temperature rise unbalanced the bridge. However, the change in resistance was so small that its temperature coefficient was considered to be constant. The change in the current flowing through the wire was also negligible during a measurement. Therefore, the unbalanced voltages generated in both bridges were

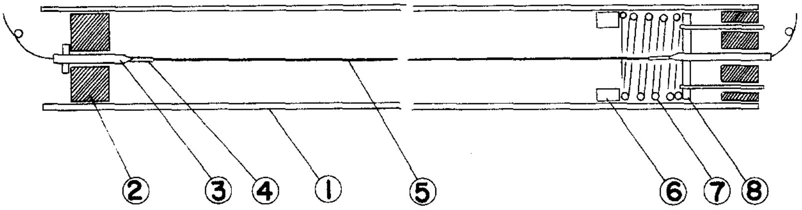

Fig. 1. The hot-wire cell: *1*, inner tube; *2*, insulating spacers; *3*, electrodes; *4*, copper leads; *5*, hot wire; *6*, spring supporter; *7*, spring; *8*, electrode supporting disk.

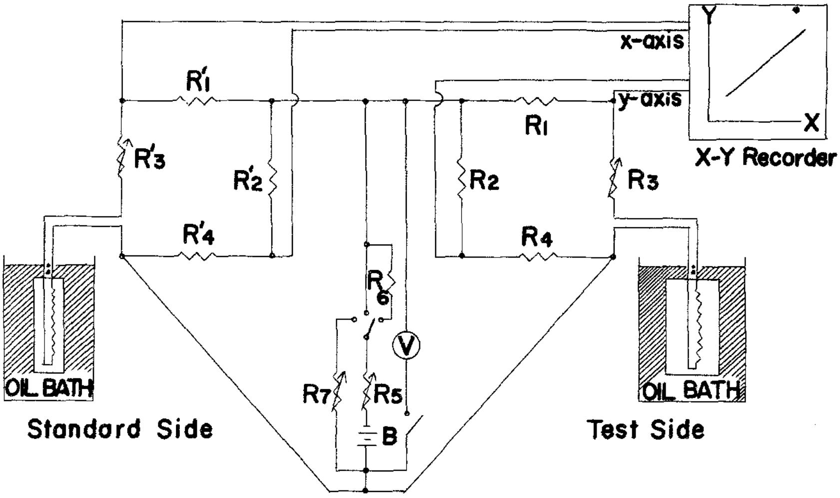

Fig. 2. The electric circuit diagram: B, battery; R, resistors (R1, 2, 4, R'1, 2, 4, 50Ω; R3, R'3, 0–50Ω; R5, 0–30Ω; R6, 5kΩ; R7, 0–50Ω).

proportional to the temperature increases in the wires and were recorded on each axis of the X-Y recorder. The thermal conductivity of the liquid was determined from the slope ($\Delta T_s/\Delta T_r$) as given by Eq. (2). Since the trace on the recorder was somewhat curved at each end, only the middle portion of the line was suitable in the determination of thermal conductivity.

For a given experimental condition, several measurements were performed at different voltages in order to confirm the reproducibility of the results. Each measurement took approximately 10 s when the temperature of the wire increased by 0.05–0.2°C. Half an hour or more was required to attain thermal equilibrium after each measurement.

2.3. Standard Reference Liquid

As described above, the experimental data on the thermal conductivity of liquids are insufficient and, in general, most of them are of questionable accuracy. Toluene and water are two exceptions which have been studied by many investigators at atomospheric pressure and have been recommended as standard reference liquids [7, 8]. Water was not adequate for the present work because of its unfavorable electric conductivity. Therefore, toluene was selected as the reference liquid for this investigation.

Over 50 investigations have been reported in the literature on the thermal conductivity of liquid toluene. The discrepancy among the reported values of different authors is large, even near room temperature at atmospheric pressure. There is a marked tendency for the recent data, obtained by advanced experimental techniques, to be lower than those obtained earlier. Among several recommended values [8–11], the same tendency is observed. However, the low values do not always signify their reliability because of an overestimation of heat losses, such as convective and radiative effects.

Because of the existing discrepancy in the literature values, it was difficult to evaluate critically the thermal conductivity of toluene. Therefore, the absolute thermal conductivity values were determined with a transient hot-wire apparatus constructed recently in this laboratory. This program is in progress and its details will be published in the near future. The experimental results obtained are represented by the following relation:

$$\lambda_{\text{toluene}} = 137.9_2 - 0.282_7 t \tag{3}$$

where λ is in $\mathrm{mW \cdot m^{-1} \cdot K^{-1}}$ and t is in °C. This equation is valid in the temperature range from 0 to 100°C. Figure 3 shows the deviations of the literature values from Eq. (3). The present results are in good agreement with those in other recent work obtained with the transient hot-wire method [12, 14]. In the present measurements, the values of toluene calculated from Eq. (3) were used as the thermal conductivity of the reference fluid λ_s in Eq. (2). The uncertainty of the values represented by Eq. (3) was estimated to be less than 1.0%.

2.4. Instrument Constant

Although it was desirable that heat emissions from the two wires were equal, that is, $q_s = q_r$ as described in Section 2.1, the small differences in the length of the wires and in the resistance of the bridges were not avoidable in the present apparatus. Therefore, the ratio q_s / q_r in Eq. (2) was treated as the instrument constant, which was determined from experiments where both of the cells were filled with toluene. It was found that the instrument constant was independent of temperature over the entire experimental range.

2.5. Uncertainties of Measurements

The reliability of the measurements can be easily checked from the linearity of the recorded curve. If the straight portion of the line is extremely short, it implies that the ideal condition has not been achieved. The uncertainty in the measurements is ascribed to the following causes: the departure from the basic assumption in the derivation of Eq. (1), the uncertainty in the evaluated thermal conductivity of toluene, and the inaccuracy of the instruments such as X-Y recorder, thermometer, etc.

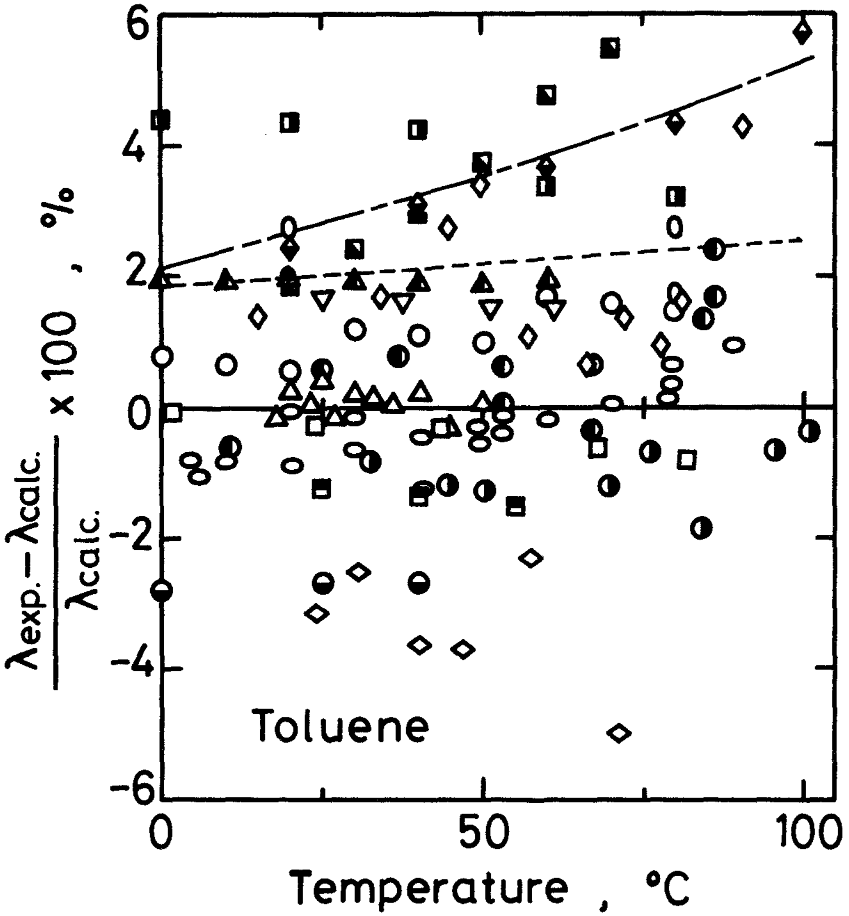

Fig. 3. Comparison of thermal conductivity of toluene with earlier work. The "zero" line indicates the results according to Eq. (3). □ Nagasaka [12]; ◪ Ogiwara [13]; △ Nieto de Castro [14]; ⊖ Trump [15]; ◑ Mani [16]; ◐ McLaughlin [17]; ◇ Davis [18]; ▲ Brykov [19]; ⧫ Rastorguev [20]; ⬭ Tree [21]; ⊟ Poltz [22]; ○ Venart [23]; ▽ Horrocks [24]; ◊ Ziebland [10]; ◨ Challoner [25]; 0 Riedel [9]; —— TPRC [11]; --- Ziebland [10].

The inevitable problem in the measurements of the thermal conductivity of fluids with a steady-state method is the evolution of natural convection. The transient method, however, almost entirely eliminates this effect. The onset of convection is detected by the gradual departure from the linear relation between ΔT_s and ΔT_r [as predicted by Eq. (2)] with the passage of time. Therefore, the results obtained in this investigation should be free from errors due to natural convection.

The finite physical properties, C_p and λ, of the platinum wire cause a curvature in the plot of ΔT_s versus ΔT_r at the beginning of the measurement. That portion is eliminated from the determination of the slope. Another problem is the end effect of the hot wire; that is, the heat loss at each end causes a longitudinal temperature gradient in the wire and in the fluid. The use of two identical hot wires should compensate for and minimize its effect.

Although it is assumed that the heat flux per unit length of the wire is constant during a measurement, in practice the resistance and the heat flux vary with time. However, the variation is estimated to be less than 0.02% for a temperature increase of 0.2°C. In the present measurements, there was no evidence of heat transfer by radiation. Since it was difficult to estimate quantitatively the effects of radiative heat transfer, no correction due to radiation was applied to the thermal conductivity results. It is very likely that calibration of the instrument would have compensated for part of these effects.

Based on the above discussion of errors and the reproducibility of the measurements, the maximum uncertainty in the measured thermal conductivity is estimated to be less than 1.2%. The uncertainty in the reference values of toluene is not included in this figure.

2.6. Materials

The 15 liquids were supplied as "reagent-grade" from commercial sources. Although they were used in "as received" condition without further purification, their purities were in excess of 99%; thus small amounts of impurities would not have affected the present results.

3. RESULTS AND DISCUSSION

The experimental data for the thermal conductivity of 14 organic liquids at atmospheric pressure are presented in Table I. Measurements have been performed two to eight times under the same experimental conditions, and only the mean values of these runs are listed in the table.

It is well known that thermal conductivity of liquids at atmospheric pressure decreases linearly with increasing temperature. The present results for each liquid are fitted by the following equation:

$$\lambda = a + bt \tag{4}$$

where λ is in $\mathrm{mW \cdot m^{-1} \cdot K^{-1}}$ and t is in °C. The coefficients of this equation, determined by means of the least squares method, are listed in Table II with the mean and the maximum deviations. Figure 4 shows the

Table I. Thermal Conductivity of 14 Organic Liquids[a] in mW · m^{-1} · K^{-1}

	Temperature (°C)						
Substance	25.00	40.00	50.00	60.00	75.00	85.00	100.00
n-Hexane	121.5	115.7	113.0	108.3			
n-Heptane	124.5	120.2	116.9	113.1[c]	108.5	105.9	
n-Octane	127.3	122.5	119.0	116.4	111.7		
n-Decane	130.4[b]	127.7	124.3	121.2	117.8	114.4	109.9
n-Dodecane	135.0	129.4	127.1	124.0	120.5	116.7	112.3
Cyclohexane	120.1[b]	117.8	116.3	112.8			
Benzene	137.2[b]	133.2	130.5	127.2	122.5		
Ethylbenzene	129.1	125.1	122.3	119.3	114.1	112.2	
o-Xylene	132.3	127.0	125.2	121.4	117.6	113.8	
m-Xylene	130.6	127.2	124.8	122.0	117.9	114.5	
p-Xylene	129.9	125.2	123.1	119.7	115.3	112.8	
Isopropylbenzene	123.8	120.1	116.0	133.2	109.0	105.7	
Chlorobenzene	126.9	121.3	118.6	116.1	112.2		
Bromobenzene	114.9	110.8	108.2	106.5	102.9	99.58	95.88

[a] In mW · m^{-1} · K^{-1}.
[b] Values at 30.00°C.
[c] Value at 65.00°C.

Table II. Coefficients *a* and *b* in Eq. (4)

Substance	*a* (mW · m^{-1} · K^{-1})	*b* (mW · m^{-1} · K^{-2})	Mean dev. (%)	Max dev. (%)
n-Hexane	130.6_5	-0.366_0	0.44	0.80
n-Heptane	132.5_5	-0.311_4	0.37	1.15
n-Octane	135.0_5	-0.313_4	0.23	0.56
n-Decane	139.0_7	-0.288_2	0.27	0.66
n-Dodecane	141.9_1	-0.294_4	0.33	1.17
Cyclohexane	127.2_5	-0.233_4	0.80	1.90
Benzene	146.2_7	-0.316_4	0.22	0.75
Ethylbenzene	136.8_3	-0.296_3	0.39	1.07
o-Xylene	139.4_8	-0.296_9	0.36	0.90
m-Xylene	138.0_3	-0.271_3	0.33	0.96
p-Xylene	137.0_7	-0.287_8	0.25	0.46
Isopropylbenzene	131.5_9	-0.303_9	0.26	0.64
Chlorobenzene	133.4_8	-0.288_6	0.46	0.96
Bromobenzene	121.0_6	-0.249_6	0.38	0.83

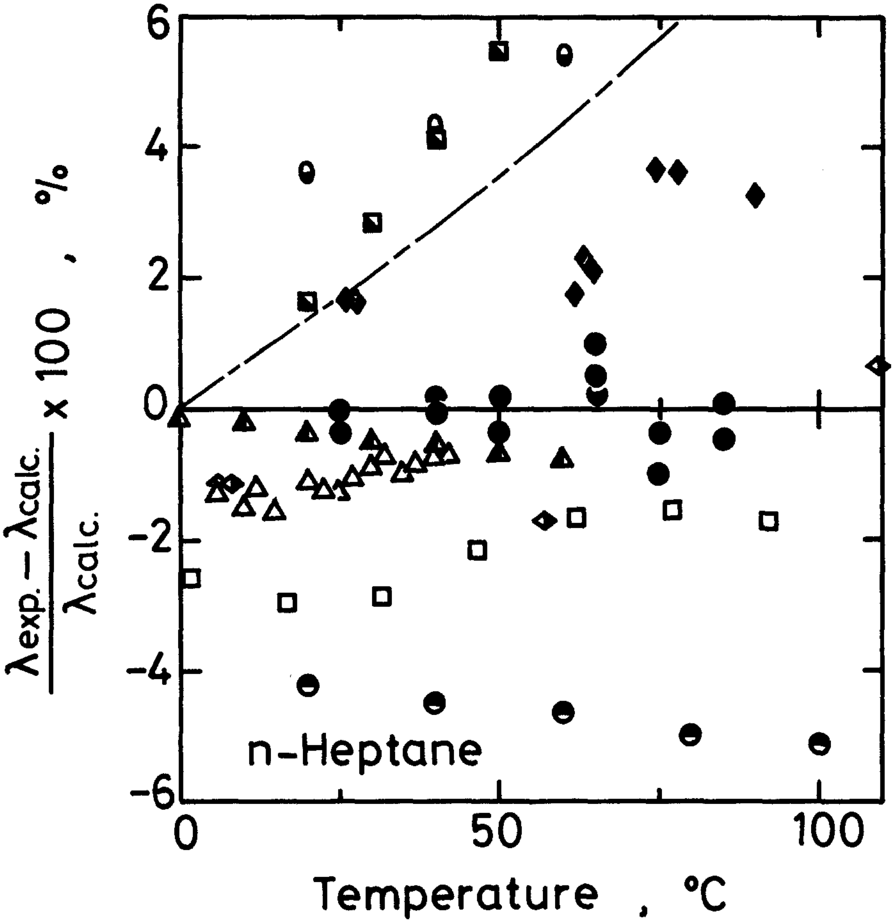

Fig. 4. Comparison of thermal conductivity of n-heptane with earlier work. The "zero" line indicates the result according to Eq. (4). ● This work; □ Nagasaka [12]; ◪ Ogiwara [13]; △ Nieto de Castro [14]; ⬖ Kandiyoti [26]; ◐ Naziev [27]; ◭ Brykov [19]; ◒ Rastorguev [28]; ♦ Mukhamedzyanov [29]; --- TPRC [11].

deviations of the typical literature values from Eq. (4) for n-heptane. Although the present results are slightly higher than some of the other recent data, the discrepancies with those of Nieto de Castro et al. [14] and Brykov et al. [19] are within the combined estimated uncertainties.

The thermal conductivity of normal alkanes is plotted against temperature in Fig. 5, where the thermal conductivity is found to increase with

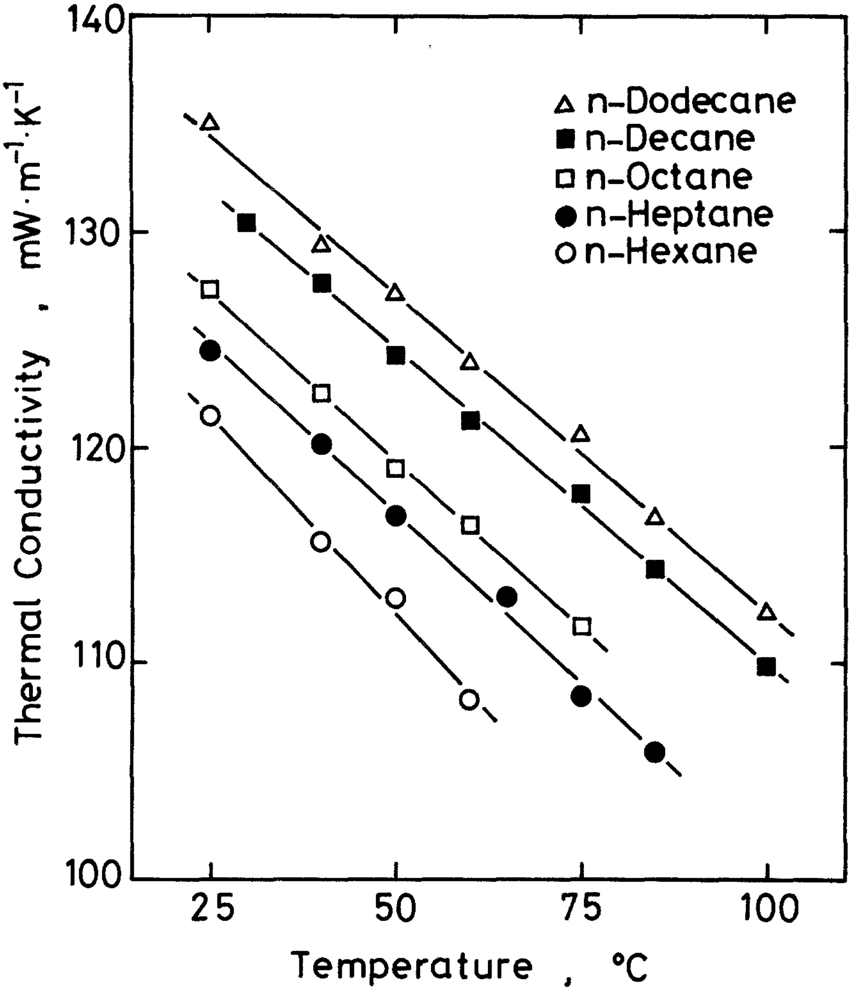

Fig. 5. Temperature dependence of thermal conductivity of n-alkanes.

increasing molecular weight. On the other hand, that of aromatic hydrocarbons, including phenyl halides, decreases with the molecular weight, as shown in Figs. 6 and 7. It is found that *o*-, *m*-, and *p*-xylenes and ethylbenzene, which have the same molecular weight, exhibit nearly a similar behavior, and that the effect of the chemical structure is not so predominant among these isomers. As seen in Fig. 7, a halogen substituent has affected thermal conductivity considerably in the phenyl halide series.

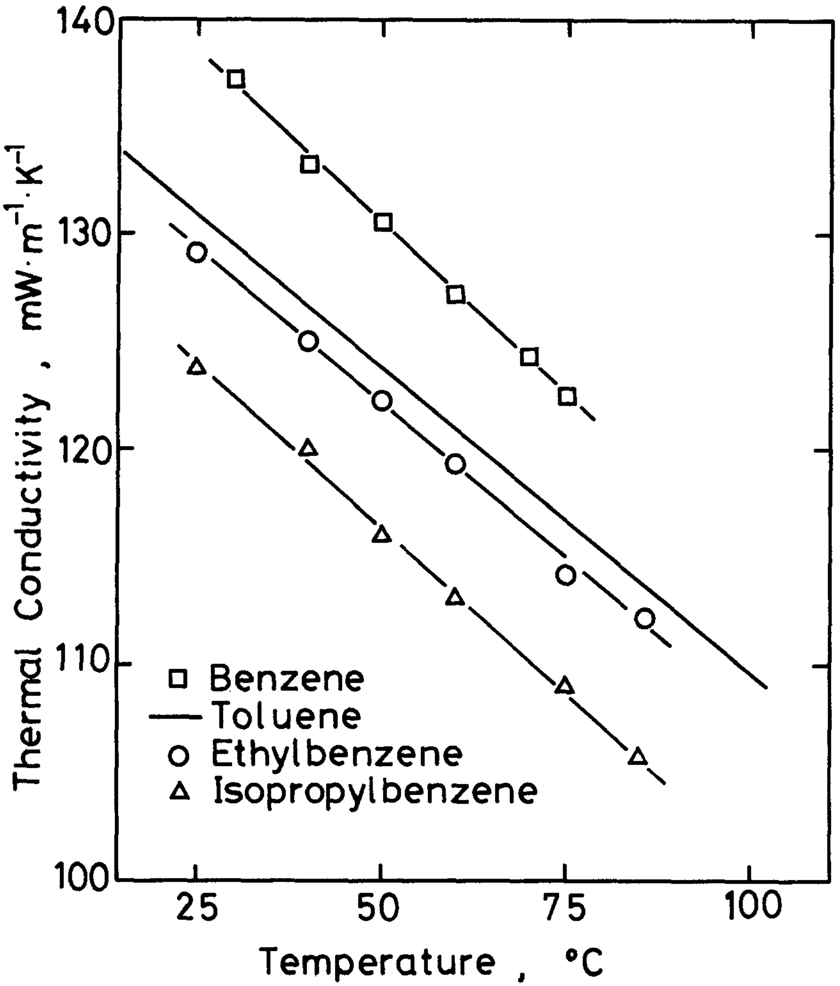

Fig. 6. Temperature dependence of thermal conductivity of aromatic hydrocarbons I.

Thermal conductivity of liquids should relate to molecular structure such as shape, size, weight, and intermolecular force, as well as chemical structure of the molecule. Among macroscopic properties, molar density would be a measure of these effects. Figure 8 represents the density dependence of the thermal conductivity for the hydrocarbons at atmospheric pressure at the same reduced temperature $0.5T_c$, where T_c is the critical temperature. The thermal conductivity at $0.5T_c$ is estimated by interpolation or extrapolation using Eq. (4). It is quite evident from Figure 8 that the plot is divided into three groups along each homologous series,

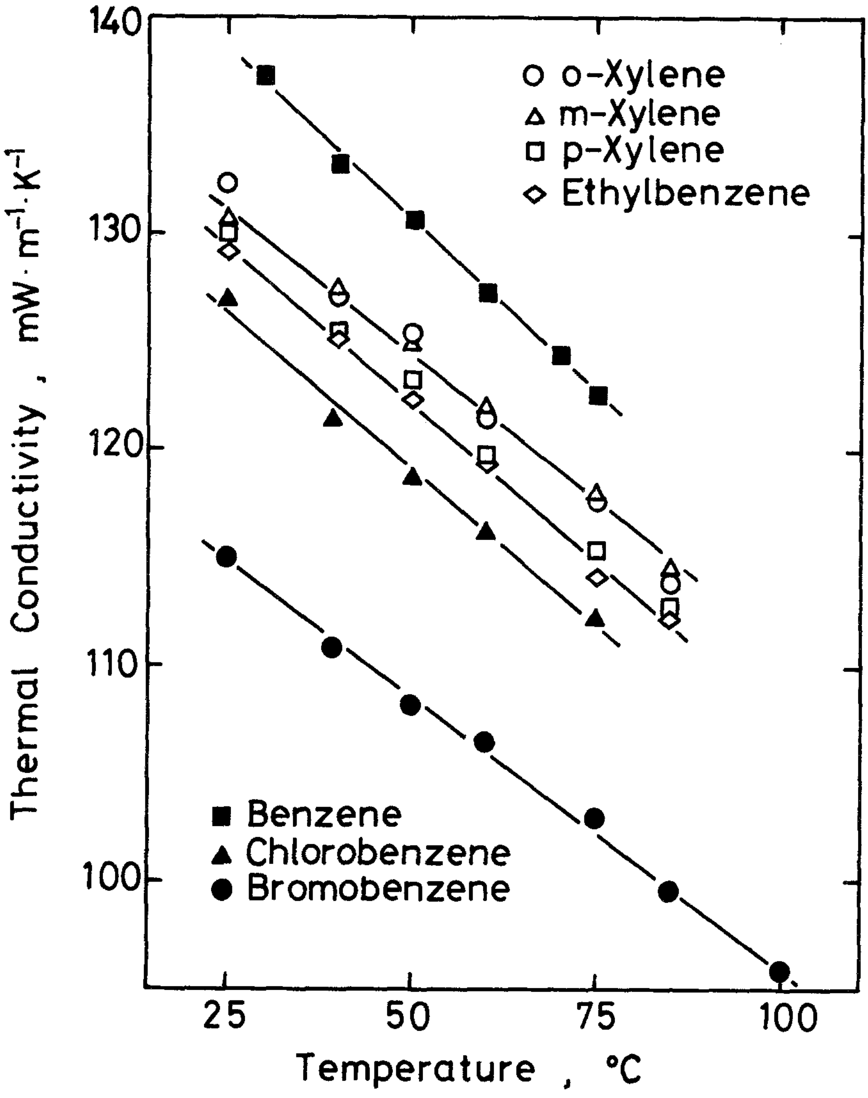

Fig. 7. Temperature dependence of thermal conductivity of aromatic hydrocarbons II.

the thermal conductivity of which increases linearly with increasing density. In a homologous group, the number of molecules per unit volume, rather than molecular weights, plays an important role in heat conduction. On the other hand, the difference in the thermal conductivity between the groups of the same molar density is significant.

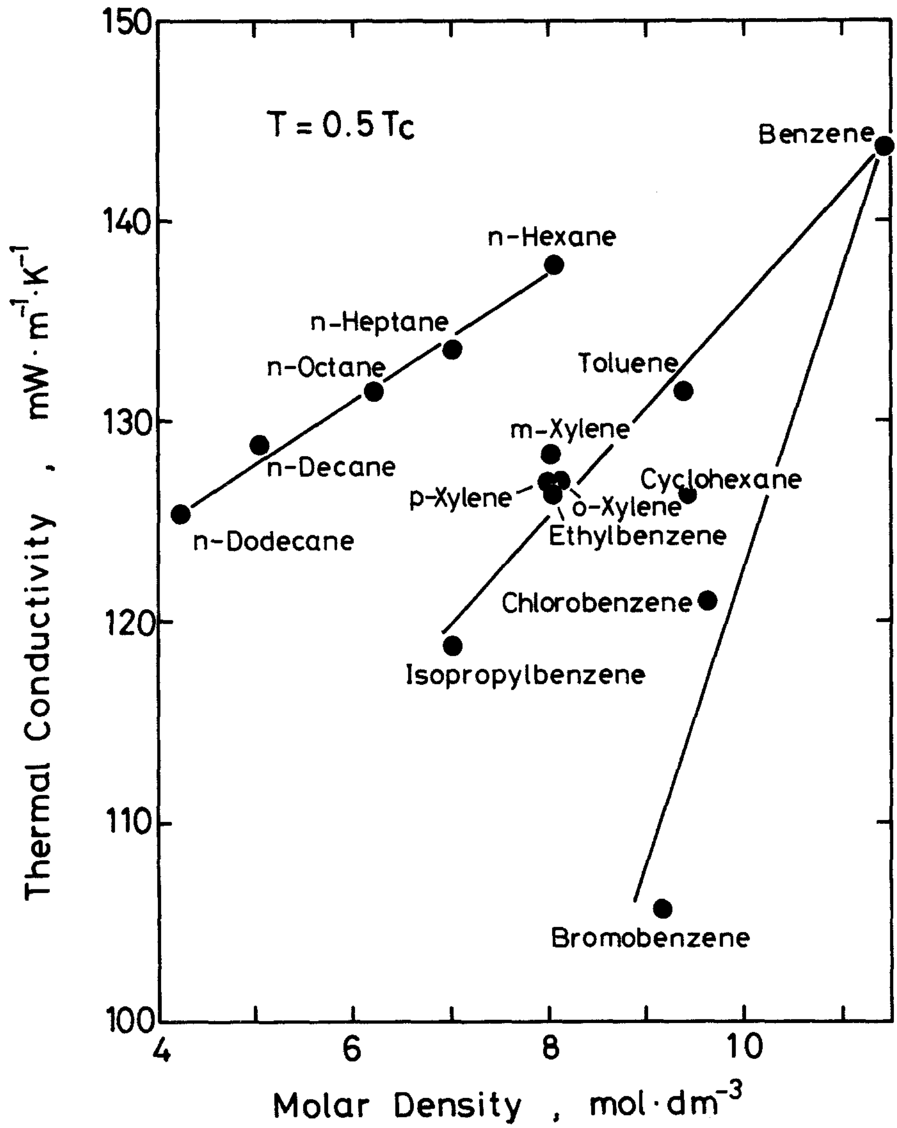

Fig. 8. Molar density dependence of thermal conductivity of organic liquids at a reduced temperature, $T/T_c = 0.5$.

4. CONCLUSIONS

An experimental study on the thermal conductivity of 14 organic liquids has been conducted at atmospheric pressure and at temperatures in the range from 25 to 100°C by a transient hot-wire method on a relative basis. The thermal conductivity obtained decreases with increasing temperature and is represented by a linear expression.

The dependence of the thermal conductivity on the molecular weight of liquids is positive for the normal hydrocarbons, while it is negative for the aromatic ones, including the phenyl halides. At the same reduced temperature, a simple relation between the thermal conductivity and the molar density holds for each homologous series of liquids. Further measurements on various other liquids need to be performed in order to discuss the effect of chemical structure on thermal conductivity.

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