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Absolute Measurements of the Thermal Conductivity of Alcohols by the Transient Hot-Wire Technique[1]

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New absolute measurements of the thermal conductivity of methanol, ethanol, propanol, butanol, pentanol, and hexanol at atmospheric pressure and in the temperature range 290–350 K are reported. The overall uncertainty in the reported thermal conductivity data is estimated to be better than ±0.5%, an estimate confirmed by the measurement of the thermal conductivity of water. The measurements presented in this paper have been used to develop a consistent theoretically based correlation for the prediction of the thermal conductivity of alcohols. The proposed scheme, based on an extention of the rigid-sphere model, permits the density dependence of the thermal conductivity of alcohols, for temperatures between 290 and 350 K and atmospheric pressure, to be represented successfully by an equation containing just one parameter characteristic of the fluid at each temperature.

KEY WORDS: alcohols; prediction; thermal conductivity; transient hot-wire technique.

1. INTRODUCTION

The transient hot-wire technique has now become established as a very accurate technique for the measurement of the thermal conductivity of fluids [1]. In a series of papers [2–4] a new computer-controlled instrument for the absolute measurement of the thermal conductivity of liquids by the transient hot-wire method was described. The technique involves the measurement of the temporal evolution of the temperature of a thin, metallic wire immersed in the liquid following the stepwise application

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of a voltage across its ends. The resulting heat pulse is conducted radially by the liquid surrounding the wire in a fashion that depends on the liquid thermal conductivity. When dealing with electrically conducting liquids, this approach cannot be used unaltered because electrical contact between the liquid and the bare metal wire causes the former to polarize and leads to distortion of the small electrical signals to be measured. In a recent paper [5], a modified transient hot-wire instrument for measuring electrically conducting liquids has been described. The novelty employed in that instrument was the use of an anodized tantalum wire instead of the bare wire. When tantalum is anodized a very thin layer of insulating tantalum oxide is formed on its surface and thus electrical contact with the liquid is prevented.

The measurement of the thermal conductivity of the alcohols with transient hot-wire instruments of the bare metal wire type has been very difficult, due primarily to the alcohols' high affinity to moisture. Even such a small water content can lead to distortion of the small electrical signals. In this paper, measurements of the thermal conductivity of the alcohols performed in the transient hot-wire instrument of the tantalum type, described in detail elsewhere [5], are presented. The measurements have subsequently been used to develop a consistent correlation, based on an extention of the rigid-sphere model, for the prediction of the thermal conductivity of alcohols.

2. EXPERIMENTAL

The transient hot-wire instrument employed in these measurements has been described in detail elsewhere [5]. Consequently we confine ourselves here to a brief description of the present installation and the experimental procedure adopted.

In Fig. 1, the thermal conductivity cell employed is presented. The material employed for the cell and the vessel was Inconel 625, a high-strength, very good, oxidation-resistant nickel alloy. The cell employs two 25-μm-diameter, tantalum wire heat sources, differing only in length, mounted within two cylindrical compartments machined within a single cylinder of 20-cm length and 3-cm diameter. The wires are isolated from the supports and held in position by thin PTFE strips. Verticality and constant tension of the wires are ensured by spot welding a tantalum weight at the bottom end of each wire. A thin, flat tantalum strip provides the bottom electrical connection as shown in Fig. 1. Thick tantalum wires (0.5-mm diameter) provide the electrical connections with the measuring bridge. The four electrical connections come out of the cell top, each through a PTFE conical seal as shown in Fig. 1.

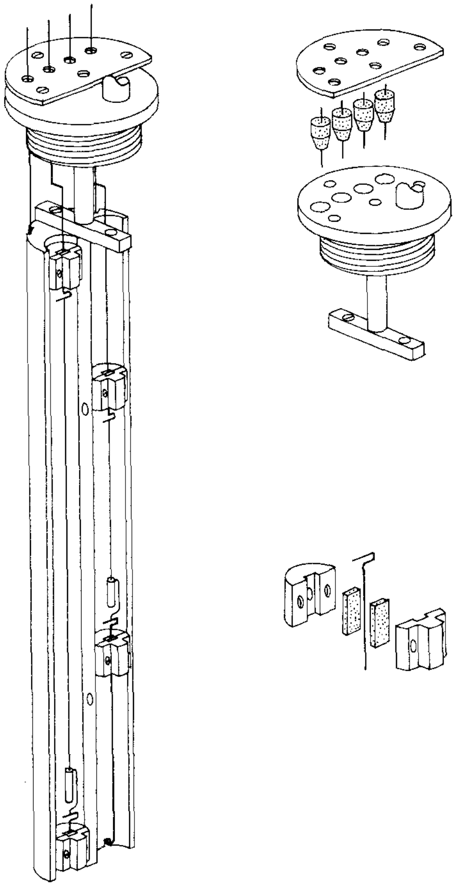

Fig. 1. The thermal conductivity cell.

The wires were chemically polished by immersing the whole cell in a bath containing 95% H_2SO_4, 70% HNO_3, and 40% HF at a ratio of 5:2:1.5. Following this the wires were immediately leached in boiling water for 15 min to remove the film formed during the polishing process. To form the insulating layer, the cell with the wires was placed in a 0.2 *M* H_2SO_4 solution in demineralized water. The tantalum wires were connected as the anode, while the Inconel cell itself provided the cathode. The voltage applied was 50 V and it was held constant until the current density fell to about $30\,\mu A \cdot cm^{-2}$. Under these conditions a layer of tantalum pentoxide (Ta_2O_5) with a thickness of about 70 nm is formed on the surface of the wires [5]. The cell with the oxidized wires was then placed in a supporting vessel, and the vessel in a thermostat enclosure.

The resistance change and thus the temperature change of the wires are recorded by incorporating the two wires in the arms of a Wheatstone type computer-controlled bridge [2, 5]. One arm of the bridge is arranged to provide a preset sequence of balance points as the resistance difference of the two wires in the bridge increases. The time at which these preset balances occurs yields a series of temperature rise-time data for the regression analysis [2, 5]. In order to ensure stability of the oxide layer on both wires, a bias was applied to them by means of a DC supply, so that the wires are positive with respect to the vessel which itself is maintained at ground potential.

The samples of the alcohols were supplied by B.D.H. Chemicals Ltd., with a nominal purity of 99.8% for methanol, 99.7% for ethanol, 99.8% for propanol, 99.8% for butanol, 99% for pentanol, and 99% for hexanol. These samples were treated for a long period of time with molecular sieves to reduce the water content and the vessel was subsequently filled under vacuum. The purity of all the alcohols analysed with gas chromatography after the measurements was found to be better than 99.9%.

3. RESULTS

The overall uncertainty in the reported thermal conductivity data is estimated to be better then ±0.5%, an estimate which is confirmed by measuring water [5] after every alcohol. Table I shows the experimental thermal conductivity values of the alcohols at atmospheric pressure as a function of temperature. The measurements of methanol and ethanol have also been reported previously [5] and are included here for comparison purposes. The thermal conductivity values for each alcohol have been represented by a linear function of the absolute temperature T, as

$$\lambda = a_0 + a_1 T \qquad (1)$$

The coefficients a_i for each alcohol, together with the standard deviation of the fits, are represented in Table II. The maximum deviation of all measurements is ±0.25%, whereas the maximum standard deviation, displayed by the methanol measurements, is ±0.2%. Figures 2 and 3 show the deviations from Eq. (1) of the experimental measurements of other investigators. The high discordancy of the literature data can be seen in all figures. The measurements of Mallan et al. [6], Powell and Groot [7], Golubev and Vasilkovskaya [8], Venart and Krishnamurthy [12], and Abas-Zade et al. [13, 14] were all performed in transient type of equipment. The full theory of the transient-type technique was not available at that time, and hence the high scatter of experimental values. The

Table I. The Thermal Conductivity of the Alcohols as a Function of Temperature at Atmospheric Pressure

T (K)	λ ($mW \cdot m^{-1} \cdot K^{-1}$)
Methanol	
301.30	198.3
304.28	197.8
306.32	197.4
310.37	197.4
313.07	197.1
316.01	197.4
318.97	196.9
323.07	196.0
325.41	196.4
Ethanol	
305.74	160.7
311.13	160.0
312.69	160.1
316.15	159.6
319.87	159.1
323.96	159.0
325.82	158.7
328.95	159.0
331.43	158.3
335.06	158.0
Propanol	
300.44	149.1
304.59	148.9
309.87	148.0
312.18	148.2
316.12	147.4
322.01	147.2
326.43	146.0
331.22	145.9
335.26	145.4
340.74	145.5
Butanol	
301.64	147.1
307.24	146.6
312.57	145.9
317.59	145.3
323.85	144.3
329.48	144.2
333.81	144.1
335.44	143.3
345.12	143.0

Table I. (*Continued*)

T (K)	λ ($\mathrm{mW \cdot m^{-1} \cdot K^{-1}}$)
Pentanol	
303.14	144.8
307.13	145.3
311.00	144.3
315.94	143.7
321.00	143.5
325.18	142.9
328.41	142.3
332.55	141.8
338.76	140.9
342.77	140.7
344.37	140.4
Hexanol	
300.48	144.4
305.75	143.0
310.95	142.6
311.66	142.4
314.87	141.6
316.81	140.7
322.02	139.8
326.36	139.3
333.63	138.0
339.46	136.9

measurements of Rastorguev et al. [9–11], Poltz and Jugel [15, 16], Tufeu et al. [17, 18], Mukhamedzyanov et al. [19], Filippov [20, 21], Eldarov [22, 23], Vargaftik [24], Sakiadis and Coates [25], and Riedel [26] were taken in various types of steady-state instruments.

4. DISCUSSION

A heuristic modification of the Enskog theory [27] to the van der Waals model of a dense fluid [28] suggests that the experimental quantity [29, 30]

$$\lambda^* = 1.9362 \times 10^7 (M/RT)^{1/2}\, \lambda V^{2/3} \tag{2}$$

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

	a_0 ($\mathrm{mW \cdot m^{-1} \cdot K^{-1}}$)	a_1 ($\mathrm{\mu W \cdot m^{-1} \cdot K^{-2}}$)	σ (%)
Methanol	220.7 ± 3.7	-75 ± 11	± 0.13
Ethanol	186.4 ± 2.2	-84 ± 6	± 0.11
Propanol	179.2 ± 2.4	-100 ± 7	± 0.20
Butanol	179.2 ± 2.5	-106 ± 7	± 0.17
Pentanol	181.2 ± 1.9	-118 ± 5	± 0.18
Hexanol	201.9 ± 2.3	-192 ± 7	± 0.18

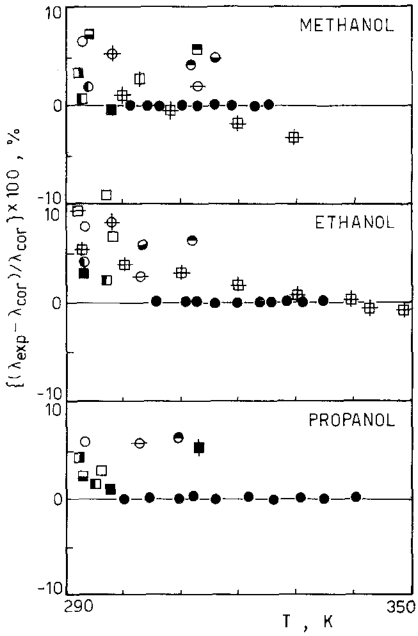

Fig. 2. Deviations of the experimental thermal conductivity values of methanol, ethanol, and propanol from Eq. (1). (●) Present work; (□) Ref. 6; (◫) Ref. 7; (⊞) Ref. 8; (⬓) Ref. 9; (⬒) Ref. 10; (▮) Ref. 11; (◧) Ref. 12; (◨) Ref. 13; (⊟) Ref. 14; (■) Ref. 15; (○) Ref. 17; (⊖) Ref. 21; (⊕) Ref. 23; (◒) Ref. 24; (◓) Ref. 25; (◐) Ref. 26.

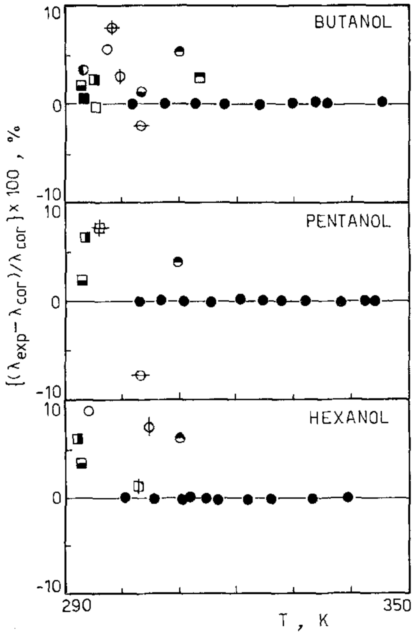

Fig. 3. Deviations of the experimental thermal conductivity values of butanol, pentanol, and hexanol from Eq. (1). (●) Present work; (□) Ref. 6; (⎅) Ref. 7; (⬓) Ref. 9; (⬒) Ref. 10; (◨) Ref. 13; (■) Ref. 16; (⊞) Ref. 17; (○) Ref. 18; (⦶) Ref. 19; (⊖) Ref. 20; (⊕) Ref. 22; (◒) Ref. 24; (◓) Ref. 25; (◐) Ref. 26.

for a particular liquid is a function only of the ratio of the molar volume, V, to an effective core volume, V_0, so that

$$\lambda^* = F(V/V_0) \tag{3}$$

Here M is the molecular weight and R is the gas constant. The effective core volume, V_0, is characteristic of the fluid and displays a weak dependence on temperature only, as a result of the softness of the real repulsive wall of the intermolecular potential compared with that of a rigid sphere. Equation (3) implies that it should be possible to superimpose plots of experimental curves of λ^* against ln V for a single fluid at a series of temperatures merely by imposing relative shifts along the ln V axis. The amount of shift required will produce the values of V_0 at every temperature. Assigning an arbitrary, but realistic value to the core volume at the lowest temperature for which accurate measurements of the thermal conductivity exist, Li et al. [29] used the accurate measurements of 11 hydrocarbon liquids over the temperature range 112–370 K and for pressures up to 700 MPa to determine the function $F(V/V_0)$ of Eq. (3). The single curve of λ^* as a function of reduced molar volume can be represented by the equation,

$$\lambda^* = 4.8991 - 2.2595 \ln(V/V_0) \tag{4}$$

For the present measurements of the alcohols, we have used Eqs. (2) and (4) to calculate the effective core volume values for the alcohols. Required density values were obtained from Vargaftik [31]. The effective core volume values obtained were subsequently represented by a linear function of the absolute temperature T, as

$$V_0 = b_0 + b_1 T \tag{5}$$

The values of b_0 and b_1 for the six alcohols are shown in Table III. It can be seen that the coefficient b_1 for hexanol is negative, while for the lower alcohols it is positive. One of the basic assumptions of the rigid-sphere model, however, is that the core volume decreases with temperature to account for the finite steepness of the repulsive region of the intermolecular potential. Therefore the coefficient b_1 cannot be positive. Nevertheless, it was decided to examine the applicability of the scheme described by Eqs. (2), (4), and (5) as an empirical correlating scheme where V_0 represents an effective system volume. Using this scheme and Table III, the experimental thermal conductivity values were found to differ by less than ±1% from the theoretical values. Consequently, the effective system volume values for all alcohols were fitted as a function of the alcohol carbon number, C, and the absolute temperature. The resulting least-squares fit is

$$V_0 = A(C) + B(C)T \tag{6}$$

Table III. Coefficients of the Least-Squares Straight-Line Fit of the Effective System Volume, Eq. (5), as a Function of Temperature

	b_0 $(10^{-6}\,\text{m}^3\cdot\text{mol}^{-1})$	b_1 $(10^{-9}\,\text{m}^3\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$
Methanol	12.4948	1.1866
Ethanol	20.7622	1.5559
Propanol	31.2223	1.5678
Butanol	45.3815	1.0796
Pentanol	60.1046	0.7708
Hexanol	81.1866	−1.3127

where

$$A(C) = (6.2 + 3.45C + 1.51C^2) \times 10^{-6}$$

$$B(C) = (6.24 + 12.1C - 2.55C^2) \times 10^{-9}$$

Therefore, the scheme described by Eqs. (2), (4), and (6) can be used to calculate the thermal conductivity of the alcohols as a function only of the alcohol carbon number, for a given temperature and density. Values calculated by this scheme differ form our experimental results by ±2% as shown in Fig. 4.

Another very interesting fact that confirms the validity of this scheme is the following. If we substitute the value of zero for C ($n = 0$ in $C_nH_{2n+2}O$), then we ought to get values that correspond for the thermal conductivity of water. Indeed, substituting $C = 0$ in the above scheme, the values obtained for the thermal conductivity of water are within ±0.5% of our experimental values for water reported earlier [5]. Furthermore, using this scheme we can predict the high-pressure values of the thermal conductivity of water (40 MPa) of Nagasaka et al. [32] with a maximum deviation of ±2.5% and a standard deviation of ±1.3%. This fact not only confirms the applicability of this scheme, but also indicates, in relation to similar work for the hydrocarbons [29] and the aromatic hydrocarbons [4], that it should be able to express the effective system volume V_0 as a function of group contributions.

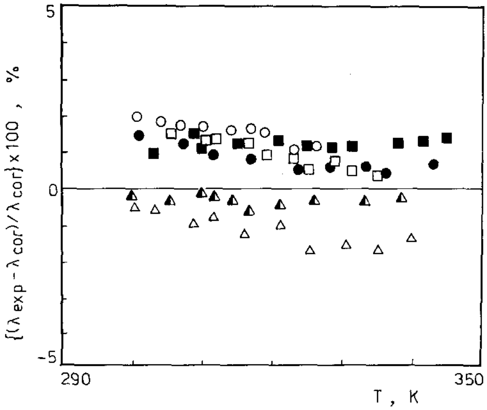

Fig. 4. Deviations of the experimental thermal conductivity values of the alcohols from the correlation scheme, Eqs. (2), (4), and (6). (○) Methanol; (□) ethanol; (△) propanol; (●) butanol; (■) pentanol; (▲) hexanol.

5. CONCLUSIONS

New absolute measurements of the thermal conductivity of the alcohols are presented. The measurements have an estimated overall uncertainty of ±0.5%. The proposed scheme developed allows the thermal conductivity of methanol, ethanol, propanol, butanol, pentanol, and hexanol, over the temperature range 290–350 K, to be represented successfully by an equation containing just one parameter characteristic of the fluid at each temperature. The validity of this scheme was confirmed by employing it to predict successfully, high-pressure thermal conductivity data for water.

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