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The Thermal Conductivity of Toluene and Water

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A new instrument is presented to measure the thermal conductivity of polar and electrically conducting liquids based on the transient coated hot-wire method. The performance of the apparatus has been assessed with toluene and water, which are recognized as standard reference materials for nonpolar and polar fluids, respectively. New results are reported fort the thermal conductivity of these liquids between 298 and 370 K and at pressures slightly above the saturation. The results show that the instrument is capable of an accuracy better than ±0.5%, while the precision and reproducibility are better than ±0.3%.

KEY WORDS: thermal conductivity; toluene; transient hot-wire; water.

1. INTRODUCTION

The transient hot-wire method is recognized as a standard technique for the measurement of the thermal conductivity of electrically nonconducting fluids over most of the phase diagram, except near the critical point and at very low densities. This success stems largely from the fact that the technique allows the determination of the thermal conductivity from exact working equations including a full set of well-known, small corrections to its ideal model and because of its capability to eliminate or to detect modes of heat transfer other than conduction. Accurate thermal conductivity data on fluids are more important for industrial processes which involve heat transfer. Furthermore, in view of the fact that it is impractical to measure

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the thermal conductivity of all fluids over their phase diagram, accurate values of thermal conductivity in a part of the diagram allow the implementation of consistent prediction schemes based on theory.

The application of the transient hot-wire method to electrically conducting liquids is not straightforward because the hot wires are normally bare. Using a bare metallic wire in contact with the fluid, simultaneously as a power source and as a resistance sensor, leads to current leakage, and consequently to ambiguity in the definition of some fundamental parameters necessary for the determination of the thermal conductivity. Furthermore, polarisation effects occur on the surface of the wire and the small signals to be observed are distorted because of the electrical contact between the wire and the cell walls through the liquid.

The first attempt to apply transient hot-wire method to measure the thermal conductivity of electrically conducting liquids was performed by van der Held and van Drunen [1], who used a lacquered wire to provide the heating effect together with a thermocouple for temperature measurement contained in a narrow glass capillary tube. However, the effect of the thermal contact resistance, between the heating wire and the glass capillary, on the temperature change was not analyzed, therefore degrading the accuracy of the data obtained.

More recently, with the appearance of more sophisticated electronic devices, instruments have been designed in order to overcome the problems of using a bare metallic wire in conducting fluids. Dietz et al. [2] applied the transient hot-wire method using alternating current instead of direct current on bare platinum wires, avoiding in this manner, the polarization effects on their surface. Nagasaka and Nagashima [3] proposed the use of a coating in order to insulate the wire from the fluid. They used a platinum wire of 40 μm coated with a layer of polyester, impervious to chemical attack, with adequate electrical and physical properties. These authors also developed a working equation for the new measuring cells, including an accurate analysis of the heat transport through the insulation layer. The thermal conductivity of water and sodium chloride solutions [3, 4] was obtained with this instrument with an estimated accuracy of $\pm 0.5\%$.

Nevertheless, this particular arrangement presents significant disadvantage because it requires the use of large diameter wires, which gives rise to large corrections owing to their finite physical properties. To avoid this problem, Alloush et al. [5] proposed a new method for the insulation of the hot-wires. These authors used a tantalum wire with a diameter of 25 μm, anodized with a uniform thin layer of tantalum pentoxide, which is resistant to chemical attack and mechanically stable.

In the present paper we describe the application of coated tantalum hot-wires to toluene and water at temperatures from 290 to 370 K, near the saturation line. The results are compared with values of other authors and with values recommended by IUPAC [6]. The accuracy of the present data is estimated to be one of ±0.5%.

2. APPARATUS AND PROCEDURE

The principle and the working equations for the transient hot-wire technique for the measurement of the thermal conductivity of fluids have been fully discussed in Ref. 7. Details of the coated wire corrections are available elsewhere [3], and so we confine ourselves in this section to the description of the present experimental apparatus.

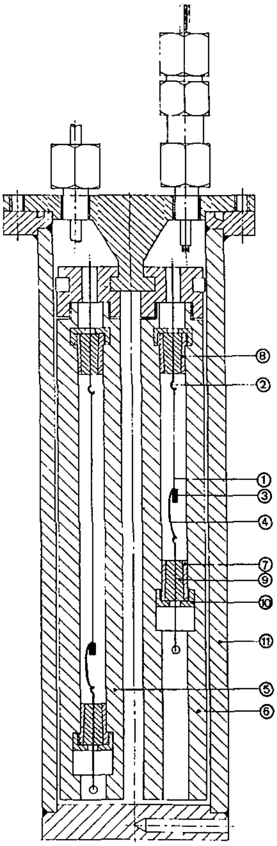

Fig. 1. Liquid vessel with the hot-wire cells.

2.1. The Hot-Wire

Figure 1 shows the hot-wire cells containing the long and the short wires. The hot-wire, used both as a linear heat source and as a resistance thermometer, is a tantalum (99.9%) wire with a nominal diameter of 25 μm coated with an anodic layer of tantalum pentoxide. At its upper end, the tantalum wire (1) is spot-welded to a hook of the same material (2). At its lower end the wire is spot-welded to a tantalum weight of approximately 200 mg (3) to ensure its verticality without introducing any deformations. The electrical connection between the wire and the lower hook is made through a strip of tantalum (4) which is spot-welded at both ends to the weight and to the hook, respectively.

Before assembling, the long and short wires are prepared for anodization by chemical polishing in a mixture of 98% sulfuric acid, 70% nitric acid, and 40% hydrofluoric acid at the proportions of 10:4:3 for a few seconds. They are subsequently washed in boiling deionized water for several minutes to remove any trace of the film formed during the polishing process.

The anodization is performed in a 0.2 M solution of sulfuric acid with a current density of about 0.2 $\text{mA} \cdot \text{cm}^{-2}$ (maximum applied voltage, 50 V), thus producing a layer of about (835 ± 5) Å according to Vermilyea's studies [8].

2.2. The Hot-Wire Cells

The hot-wire cells (5, 6) are similar in design except in the length of the wire's cavities and are made from Iconel 625 to avoid corrosion when used with agressive environments. Each cell consists of a cylindrical cavity with a 10-mm internal diameter and 208 mm long. The cylinder is divided axially in two halves; one half carries the hot-wire (1) and its suspension mechanisms (7, 8), while the other serves as a cover that permits an easy access to the interior. The top and bottom suspension mechanisms are identical and they are designed in a way as to provide the compression of the hook that carries the wire between two halves of a Teflon cone (9) placed inside a conical cavity in the suspension mechanism and compressed by means of a threaded cap (10). To place and fix the hot-wire's suspension mechanisms in the cell, two cavities, 7 and 17 mm long, respectively, 16 mm in diameter, were made by electroerosion in its top and bottom. The two halves of the cell are held together with two M3 screws in a way that permits the suspension of the cell in a liquied vessel (11) represented in Fig. 1.

The entire assembly is immersed in a well-stirred thermostat oil bath controlled by a PD temperature controller that secures a stabilization of ±0.001 K during the period necessary to perform a measurement. The temperature of the sample is measured with a platinum resistance thermometer (Degussa Pt 100) whose calibration was checked to comply with ITS-90 with an accuracy of ±0.002 K.

The Wheatstone bridge circuit used to record the resistance change and thus the temperature rise of the wires is similar to that described by Charitidou et al. [9]. In order to ensure the stability of the oxide layer on the long and short wires, a bias must be applied to them so that they are maintained positive with respect to the vessel walls, which are maintained at ground potential.

The determination of the temperature coefficient of the tantalum wire resistance was obtained by means of an *in situ* calibration procedure. The results were represented by a quadratic polynomial function of the resistance of tantalum, R (Ω), versus the absolute temperature T (K), over the temperature range 298–361 K as

$$\frac{R(T)}{R(273.15)} = 1 + 3.454 \times 10^{-3}(T - 273.15) - 8.731 \times 10^{-7}(T - 273.15)^2 \qquad (1)$$

with a standard deviation of 0.045%. The standard deviations of the coefficients of first and second order are $2.4 \times 10^{-5}\ \mathrm{K}^{-1}$ and $2.04 \times 10^{-7}\ \mathrm{K}^{-2}$, respectively.

The liquids were purified, using standard techniques. Toluene (Merck p.a.) was dried under reflux with calcium hydride under nitrogen and further distilled and degassed. Water was obtained from a Millipore purification device and degassed prior to its use.

3. RESULTS AND DISCUSSION

In order to demonstrate the accuracy of the new instrument, a number of measurements of the thermal conductivity of toluene were performed. They were carried out near the gas–liquid saturation line of the liquid but at pressures slightly above their vapor pressure in order to avoid vaporization near the wires. The values of the heat capacity and density of the fluids used in corrections to be applied in the analysis of the data were obtained from the compilation of Vargaftik [10].

Figure 2 shows a plot of the deviations of a set of corrected experimental data (ΔT, ln t) from a linear fit to them. The experiment was carried out at a reference temperature of 361.996 K, near the saturation line, and it can be seen that no datum departs from the straight line by more than

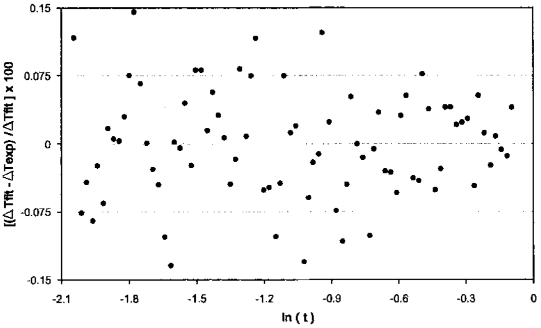

Fig. 2. Percentage deviations of the measured temperature rise as a function of the logarithm of time (time in seconds), from the linear fit for toluene, at 361.996 K and near the saturation line.

±0.15%. Furthermore, no systematic curvature was found in the lines, indicating the absence of radiation [7, 11] and convection.

Table I contains the experimental results for the thermal conductivity of toluene at the reference temperature T_{ref} and near the saturation line together with the deviations from the fitting equation [Eq. (2)].

The temperature dependence of the thermal conductivity of toluene has been represented by a linear function with a standard deviation of 0.2%, of the form

$$\lambda = 0.2184 - 0.00029(T - 273.15) \qquad (2)$$

where λ is in $\mathrm{W \cdot m^{-1} \cdot K^{-1}}$ and T is in K. In Table I, it can be seen that the maximum deviation amounts to no more than ±0.4%. The deviations

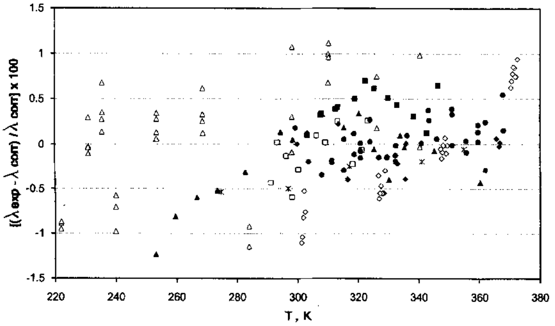

Fig. 3. Comparison of the experimental measurements of the thermal conductivity of toluene with the correlation recommended by IUPAC [6] (baseline): ∗ [11]; □ [13]; ■ [9]; ◆ [14]; ● (p.w.); ◇ [16]; ▲ [17]; △ [18].

Table I. Thermal Conductivity of Toluene Near the Saturation Line; Deviations from Eq. (2)

T_{ref} (K)	λ $(\mathrm{W \cdot m^{-1} \cdot K^{-1}})$	$\Delta\lambda/\lambda$ (%)
299.183	0.1310	−0.31
303.558	0.1292	0.05
307.927	0.1277	0.21
311.227	0.1269	0.07
311.301	0.1269	0.07
315.185	0.1256	0.23
315.303	0.1260	−0.12
318.563	0.1251	−0.16
318.614	0.1248	0.03
320.753	0.1242	0.02
320.781	0.1241	0.10
320.792	0.1243	−0.06
323.858	0.1234	−0.10
323.863	0.1237	−0.31
326.815	0.1223	0.12
329.473	0.1215	0.10
329.504	0.1215	0.14
332.252	0.1207	0.11
332.303	0.1206	0.21
332.349	0.1208	0.04
336.133	0.1198	−0.09
340.795	0.1183	0.04
343.212	0.1180	−0.29
343.443	0.1178	−0.22
345.980	0.1168	0.01
350.911	0.1157	−0.26
351.012	0.1156	−0.20
351.046	0.1152	0.14
355.560	0.1139	0.11
355.736	0.1137	0.24
359.515	0.1127	0.10
359.545	0.1129	−0.03
359.585	0.1128	−0.03
361.998	0.1122	−0.10
362.013	0.1116	0.40
367.761	0.1108	−0.33
367.984	0.1103	0.07

Table II. Thermal Conductivity of Water Near the Saturation Line; Deviations from Eq. (3)

T_{ref} (K)	λ ($\mathrm{W \cdot m^{-1} \cdot K^{-1}}$)	$\Delta\lambda/\lambda$ (%)
298.788[a]	0.6096	−0.36
298.845[a]	0.6081	−0.10
302.270	0.6127	0.07
302.354	0.6137	−0.09
302.395	0.6113	0.33
303.145[a]	0.6150	−0.09
303.186[a]	0.6131	0.24
307.020	0.6185	0.31
309.683	0.6257	−0.23
309.902	0.6269	−0.37
312.005	0.6274	0.03
312.022	0.6280	−0.06
312.037	0.6248	0.45
317.441	0.6336	0.20
319.983[a]	0.6387	−0.12
322.855	0.6408	0.08
327.245	0.6481	−0.29
327.453	0.6456	0.14
327.466	0.6473	−0.13
332.666	0.6530	−0.20
332.674	0.6488	0.44
334.060[a]	0.6535	−0.08
337.818	0.6571	−0.12
337.861	0.6599	−0.55
338.765[a]	0.6580	−0.15
343.027	0.6567	0.55
343.051	0.6580	0.36
345.292[a]	0.6648	−0.42
345.323[a]	0.6649	−0.45
345.341[a]	0.6623	−0.04
347.662	0.6614	0.31
351.957	0.6640	0.30
352.040	0.6652	0.12
352.097	0.6641	0.29
357.209	0.6713	−0.41
357.209	0.6679	0.09
363.538	0.6700	0.11
363.702	0.6719	−0.17

[a] Values obtained with a different set of wires.

of the present experimental data from the correlation proposed by IUPAC [6] are plotted in Fig. 3, and in no case do the deviations exceed ±0.6%. The accuracy assigned to the IUPAC correlation is one of ±1.0%. The same figure includes the deviation of the present results from those obtained by other authors [9, 12–18]. It can be seen that the agreement is excellent, within the mutual uncertainties of the various sets of data and the accuracy of the correlation. Therefore, we can conclude that our instrument operates in accordance with the theoretical model of it, and we estimate that the precision of the thermal conductivity measurements is one of ±0.2%, while an absolute uncertainty of better than ±0.5% may be assigned to our instrument for nonpolar fluids.

In order to test the operation of the new instrument with polar fluids, we have performed measurements of the thermal conductivity of water in the temperature range 298 to 365 K, along the saturation line. Two different sets of hot-wires were used in order to test the reproducibility of the instrument.

Water is the only polar liquid for which thermal conductivity standard reference data have been recommended by IUPAC, and being so it permits a test of operation of our apparatus for such fluids.

Table II shows our experimental data for the thermal conductivity of water near its saturation vapor pressure as a function of temperature. The values obtained with the different sets of hot-wires are distinguished. The values for the heat capacity and density for water were obtained from the compilation of Sato et al. [19].

Figure 4 shows a plot of the deviations of a set of corrected experimental data (ΔT, ln t) from a linear fit to them. The experiment was carried out at a reference temperature of 363.702 K, at a pressure slightly above the

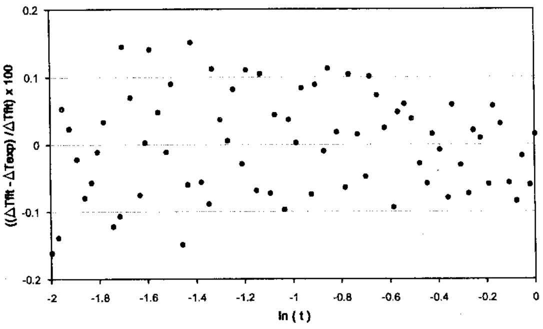

Fig. 4. Percentage deviations of the measured temperature rise as a function of the logarithm of time (time in seconds), from the linear fit for water, at 363.702 K and near the saturation line.

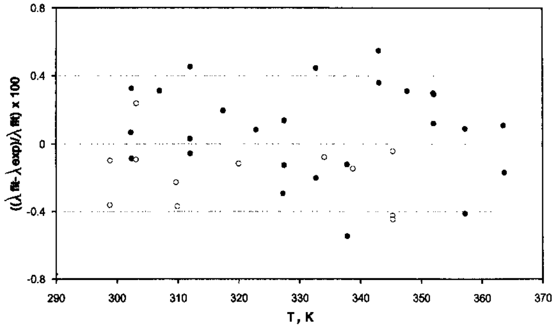

Fig. 5. Percentage deviation of the experimental measurements of the thermal conductivity of water from Eq. (3); ●, first set of wires; ○, second set of wires.

saturation line, and it can be seen that, once again, almost no point departs from the straight line by more than ±0.15% and that there is no evidence of systematic curvature.

The temperature dependence of the thermal conductivity of water has been represented by a quadratic polynomial function, with a standard deviation of 0.2%, of the form

$$\lambda = 0.5575 + 0.00222(T - 273.15) - 1.1 \times 10^{-5}(T - 273.15)^2 \qquad (3)$$

where λ is in $W \cdot m^{-1} \cdot K^{-1}$ and T is in K. In Fig. 5 the deviations of the present results from the above equation are plotted, from which it can be seen that they do not exceed ±0.6%.

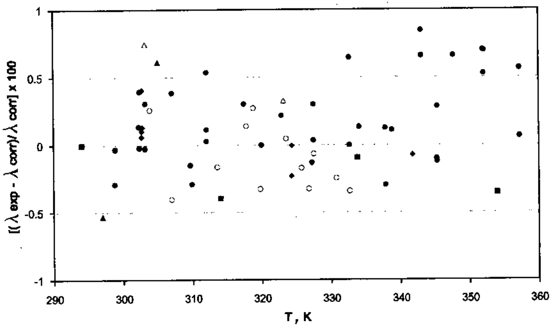

Fig. 6. Comparison of the experimental measurements of the thermal conductivity of water with the correlation recommended by IUPAC [6] (baseline): ● (p.w.); ■ [4]; ▲ [2]; △ [5]; ○ [20]; ◆ [21].

Allowing for the reproducibility of the measurements as well as the uncertainty arising from the resistance characteristics of the wire, it is estimated that the accuracy of the reported data is one of ±0.5%.

Figure 6 shows a comparison of values of thermal conductivity obtained by several earlier authors and those of the present work with values recommended by IUPAC [6]. As can be seen, within the accuracy of the IUPAC correlation (±1.1%) the agreement is excellent (±0.8%). However, there is a systematic trend toward higher temperatures. This may be the result of the fact that only two sets of data were used to establish the IUPAC correlation at high temperatures, and there the correlation is estimated to have an inferior accuracy of ±0.5% [2].

4. CONCLUSIONS

New thermal conductivity data have been reported for toluene and water in the temperature range 290–370 K, near the saturation line. The experimental results were obtained with the transient coated hot-wire technique and have been shown to be consistent with other accurate measurements along the saturation line, as well as with standard reference data. Therefore we can claim for our present instrument an accuracy of ±0.5%.

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