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Application of the Multi-current Transient Hot-Wire Technique for Absolute Measurements of the Thermal Conductivity of Glycols

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Experimental measurements of the thermal conductivity of mono-, di-, tri-, and tetra-ethylene glycol are presented. The experiments were carried out at atmospheric pressure and at temperatures ranging from 25 to 65°C. The multi-current transient hot-wire technique has been used with a platinum wire of 25 μm diameter; the electrical current varied from 25 to 75 mA. For all studied glycols, it was found that the thermal conductivity increases with temperature and decreases with the glycol molar mass. The random uncertainty of the reported experimental thermal conductivity data is less than 0.9%. The estimated systematic errors affecting the obtained data are at most 2%. The values obtained in this study were compared with previously published results for the four glycols, finding deviations of the order of 2%.

KEY WORDS: glycol; multi-current method; polyethylene glycol; thermal conductivity; transient hot-wire technique.

1. INTRODUCTION

One of the most difficult thermophysical properties to measure accurately is the thermal conductivity of liquids. This is due to the coupling of both convection and radiation to the conductive heat transfer. Various experimental techniques, steady-state or transient, have been historically employed. Today, the transient hot-wire method has been accepted as the most precise and reliable method to measure the thermal conductivity of fluids, over a wide range of temperatures and pressures. The measurements give absolute values (do not require comparison with any standard, or

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calibration); only a knowledge of the hot-wire geometry, the applied power, and the electrical resistance of the wire are required. For the best experimental setups, the uncertainty of the results is estimated to be ±0.5% [1–6]. The hot-wire technique can be used to measure simultaneously both thermal conductivity and thermal diffusivity. However, the uncertainty of the thermal diffusivity is about an order of magnitude higher than that of the thermal conductivity [1, 6]. Moreover, there are two regions of the thermodynamic phase diagram where the application of the hot-wire technique for thermal-conductivity measurements is not recommended: (i) first region is near the critical point and (ii) in the region where fluids exhibit high thermal diffusivity values (i.e., low-density region).

Glycols are widely used as antifreeze liquids in car engines and solar heating systems. Hence, accurate values for the thermal conductivity of glycols are required in heat exchanger design and process engineering. In this study, the transient hot-wire technique is employed to measure the thermal conductivity of the first four polyethylene glycols, at atmospheric pressure and at various temperatures ranging from 25 to 65°C.

2. EXPERIMENTAL

2.1. Materials

Mono-ethylene glycol of molar mass, $M_W = 62.07\,\mathrm{g \cdot mol^{-1}}$ and boiling point, $T_b = 196$ to $198^\circ\mathrm{C}$, was purchased from Panreac Química S.A.; di-ethylene glycol ($M_W = 106.12\mathrm{g \cdot mol^{-1}}$, $T_b = 245^\circ\mathrm{C}$), tri-ethylene glycol ($M_W = 150.17\mathrm{g \cdot mol^{-1}}$, $T_b = 285^\circ\mathrm{C}$), and tetra-ethylene glycol ($M_W = 194.23\mathrm{g \cdot mol^{-1}}$, $T_b = 314^\circ\mathrm{C}$) were obtained from Aldrich. All glycols are of the highest purity (i.e., a nominal purity of 99.9%) and were used as supplied. The maximum water content as quoted by the manufacturer is 0.1%.

2.2. Equipment

The core of our experimental setup is a platinum wire of 25 μm diameter and 10.76 ± 0.01 cm length. The wire is supported by a set of stainless steel rods to keep it straight, and two Teflon isolated leads are connected to each one of the wire ends by clamping small connectors. The four connectors were electrically insulated by coating with chemically resistant epoxy. A Keithley 2400 source-meter, which can act simultaneously as a current source and voltage meter, was employed. This instrument is interfaced to a personal computer, and a software code was written to record the measurement points, to fit the data, and to calculate the thermal conductivity. For each thermal conductivity measurement, various current values, from 25 to

75 mA, were applied. The electrical current is inputed by two of the leads connected to the wire ends, while voltage measurements are acquired simultaneously using the other two leads. The supported wire is placed vertically inside a double-wall glass cell, which is connected to a thermostatic bath to control the temperature at which the experiments are performed within ±0.05 K. The liquid under test was loaded in the inner volume of the glass cell. The whole assembly, glass cell with the wire, is then placed inside a controlled atmospheric chamber. The humidity of the chamber was maintained at low values (~40%). A platinum thermometer placed inside the cell is used to measure the temperature of the liquid under study. A typical heating run last for 1.6 s, during which 75 voltage measurements are acquired. Thermal conductivity values are obtained by repeating heating cycles, which included 20–30 heating runs at each electrical current value. To stabilize the system, a waiting period of a minimum of 300 s was established among the heating runs. Moreover, before each heating run, a resistance measurement is performed using the four-wire configuration of the Keithley-2400, which compensates for the electrical resistance of the connecting leads.

3. PRINCIPLE OF MEASUREMENT

The system under study is a thin metal wire of radius r_0 and length L surrounded by a liquid. When an electrical current I is circulated through the wire, its temperature increases because of Joule heating, depending on both the thermal conductivity and the thermal diffusivity of the liquid surrounding the wire. As a consequence, the electrical resistance of the wire R increases, as does the voltage drop ΔV between the wire ends. For an infinite cylindrical straight wire, the voltage difference between two points, separated by a distance L, can be approximated by [7]

$$\Delta V(t) \simeq I R_0 \left\{ 1 + \alpha \, \frac{I^2 R_0}{4\pi \lambda L} \left[\ln\left(\frac{t}{\beta}\right) - \gamma \right] \right\} \tag{1}$$

where R_0 is the electrical resistance of the wire at $t = 0$, γ is Euler's constant ($\gamma = 0.5772$), α is the temperature resistance coefficient of the material of the wire, λ is the thermal conductivity of the liquid surrounding the wire, and parameter β (units of time) is given by

$$\beta = \frac{r_0^2}{4 a_T}, \tag{2}$$

where a_T is the thermal diffusivity of the liquid surrounding the wire. Equation (1) is valid as an asymptotic expansion for long times, $t \gg \beta$. In deducing Eq. (1), the wire is assumed as an infinite line source, self-heating effects are neglected, and the liquid surrounding the wire is assumed to be in a quiescent state (no convection). The most important systematic error that might be present when analyzing experimental data with Eq. (1) is convection, but this is easily detected as long-time deviations [1]. A second important systematic error source is finite size effects (i.e., nonzero wire radius and finite length). For wires of similar aspect ratio ($r_0/L \simeq 10^{-4}$) to the wire used in this study, Kestin and Wakeham [7] estimated the temperature increase (voltage drop) in the wire to be 1–2% lower than that corresponding to an infinite line source. Other systematic effects, such as heat transfer by radiation [8], thermal conduction through the wire, electrical noise and timing of the voltage measurements, current leakage through the medium, and the precision of the voltage and current measurements, are at least one order of magnitude lower.

To obtain the thermal conductivity of the liquid, the following procedure was applied: First, following Eq. (1), the data pairs $\{\Delta V, \ln(t)\}$ acquired in each heating run are fitted to a straight line, and a slope b is obtained. Since Eq. (1) is actually an asymptotic expansion for large t, only the points acquired after 213 ms are used for this fitting. For a constant temperature (i.e., same value of R_0), the slope b is proportional to the cube of the current, $b = B\,I^3$ (see Eq. (1)), with the proportionality constant given by

$$B = \alpha \frac{R_0^2}{4\pi\lambda L}. \tag{3}$$

Hence, the thermal conductivity λ of each liquid at each temperature was calculated by fitting the slopes b of the $\{\Delta V, \ln(t)\}$ lines to the cube of the corresponding intensity and using Eq. (3). In this case, the average of R_0 values measured before each heating run was used.

4. EXPERIMENTAL RESULTS

As an example of the heating runs, Fig. 1 shows, on a semi-logarithmic scale, $(\Delta V - R_0 I)$ as a function of time, for mono-, di-, tri-, and tetra-ethylene glycol at $T \cong 35°\mathrm{C}$ and $I = 45\,\mathrm{mA}$. The solid lines represent fits to Eq. (1) of the experimental points at long times ($t \geqslant 213\,\mathrm{ms}$, much larger than β, which is typically around a few ms for the tested glycols). Some deviations at short times are visible, which can be ascribed to both the wire-finite-size effects and to the fact that Eq. (1) is actually an asymptotic expansion for large t. Most importantly, no deviations were observed at long times, indicating that convection is absent in our measurements [1]. We note in Fig. 1 that the slope b is higher for the glycol having a

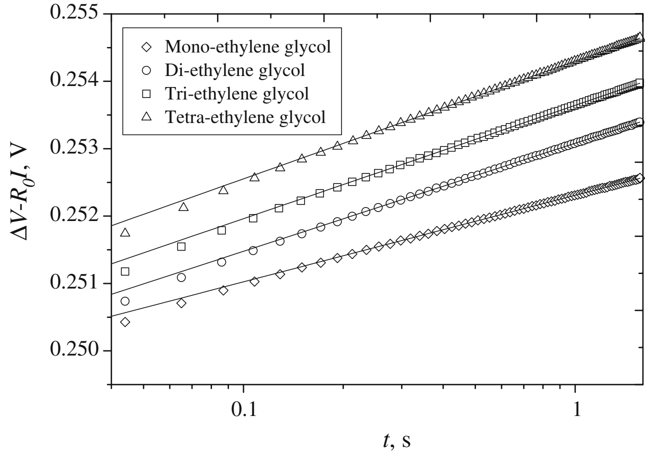

Fig. 1. ΔV-$R_0 I$ *vs.* time for typical heating runs with mono-, di-, tri- and tetra-ethylene glycol at $T \simeq 35°C$ and $I = 45\,mA$. Solid lines are fits with Eq. (1) of experimental points at long times ($t \geqslant 213$ ms).

higher molar mass. This indicates that the thermal conductivity of glycols decreases with an increase in the degree of polymerization.

As stated earlier, the resistance of the wire R_0 was measured just before each heating run. In addition to being required for the calculation of λ, this parameter is also a probe of the temperature stability in the experimental setup. In our case, the dispersion of R_0 values in each series of measurement is less than 0.3%. Then, for each liquid and each temperature, the average wire resistance was calculated for using it in the calculation of λ. It was found that the electrical resistance of the wire increases linearly with temperature, and is independent of the liquid used as expected. The value of the resistance temperature coefficient, α, for the wire was obtained from a linear fit of the averaged R_0 values versus temperature. The calculated mean experimental value was $\alpha = 0.00361\,K^{-1}$, which agrees well with the tabulated value for the temperature resistance coefficient of platinum over our temperature range. By knowing the voltage drop at the end of a heating run and the wire resistance coefficient, the total wire-temperature increase ΔT_E was estimated for each heating run. Depending on both the initial temperature and electrical current applied, ΔT_E ranged from 0.2 to 2.8 K.

Figure 2 shows a representation of the slope b of the lines $\{\Delta V, \ln(t)\}$ as a function of the intensity I, on a double logarithmic scale, for mono-ethylene glycol and tetra-ethylene glycol at $T = 45°C$. Similar figures may be plotted for the other temperatures and glycols. It is worth noting

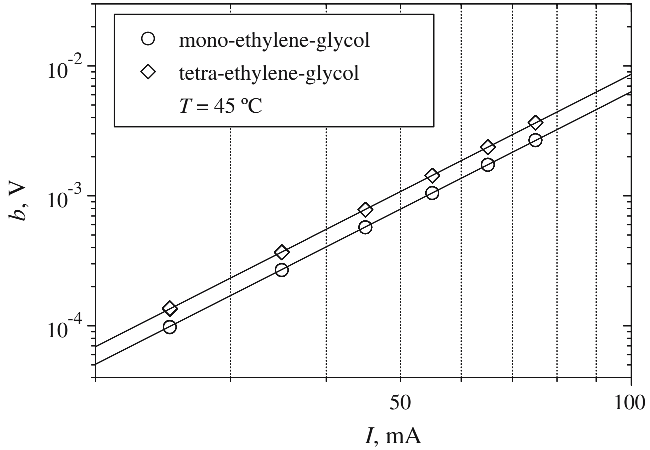

Fig. 2. Double logarithmic plot of experimental slopes b as a function of the intensity I. Data are for mono- and tetra-ethylene glycol at $T = 45°\mathrm{C}$. Solid lines have a slope of 3 (on double logarithmic scale).

that the data points shown in Fig. 2 are actually the superposition of 20–30 slope measurements obtained at each intensity, which, on the scale of the graph, become indistinguishable. The solid lines have a slope equal to three (on a double logarithmic scale), and represent the fit of the b values to the cube of the intensity. From such fits, values for the proportionality constant B are obtained, from which the thermal conductivity was calculated by using Eq. (3). It is worth noting that, for all glycols, measurements were repeated by cycling different temperatures in order to check that the possible water intake by the glycols was negligible and does not affect the λ measurements.

Table I displays the obtained λ values for the four glycols at the various temperatures employed in this work. The random error of λ is also shown in Table I, where it may be verified that the random uncertainty of our data is less than 0.9%. Temperatures quoted in Table I correspond to an average of the temperatures measured with the platinum resistance thermometer placed inside the measurement cell. As indicated, temperature values were constant within $\Delta T = \pm\ 0.1\,\mathrm{K}$.

5. DISCUSSION

The obtained thermal conductivity values of the first two polyethylene glycols, together with their standard errors are plotted in Fig. 3a1, b1 as a function of temperature. The two lower panels of Fig. 3 show the deviations

Table I. Experimental Thermal Conductivities Measured in this Study for the First Four Polyethylene Glycols, Together with their Random 2σ-Standard Errors

Glycol	T (K), ±0.1 K	λ ($\mathrm{mW{\cdot}m^{-1}{\cdot}K^{-1}}$)
Mono-ethylene glycol	298.2	249.6±1.8
	308.1	251.8±1.8
	318.3	253.9±1.9
	328.3	256.1±1.9
	338.3	258.0±1.8
Di-ethylene glycol	298.1	199.4±1.5
	308.0	201.2±1.5
	318.2	203.8±1.7
	328.4	205.0±1.5
	338.2	206.8±1.5
Tri-ethylene glycol	298.1	192.3±1.4
	308.2	193.2±1.4
	318.4	193.9±1.4
	328.4	194.5±1.4
	338.4	194.5±1.5
Tetra-ethylene glycol	298.2	184.9±1.4
	308.2	185.6±1.4
	318.3	186.4±1.4
	328.2	187.5±1.4
	338.2	187.7±1.4

(in %) of the measured values with respect to a linear correlation of our data, as stated in Ref. 9. The two left panels of Fig. 3a1, a2 correspond to mono-ethylene glycol, while the two right panels (b1, b2) correspond to di-ethylene glycol. Furthermore, we add data from literature sources to Fig. 3 for comparisons [9–13]. In Fig. 4 we display in a similar way the data for tri-ethylene glycol (a1, a2) and tetra-ethylene glycol (b1, b2).

We find that the maximum deviation of our measurements from literature results is +3%, for mono-ethylene glycol and with respect to the (somewhat older) λ values reported by Touloukian et al. [10]. However, in comparison to the λ values given by Assael et al. [9], our present values are within the limits of the experimental errors. It is worth noting that Assael et al. [9] present a comprehensive review of previous values for the thermal conductivity of mono-ethylene glycol. For di-ethylene glycol and tri-ethylene glycol, our present results are in good agreement with those of Obermeier et al. [13], measured by a horizontal concentric cylinder device. This confirms the reliable operation of our experimental setup. Agreement

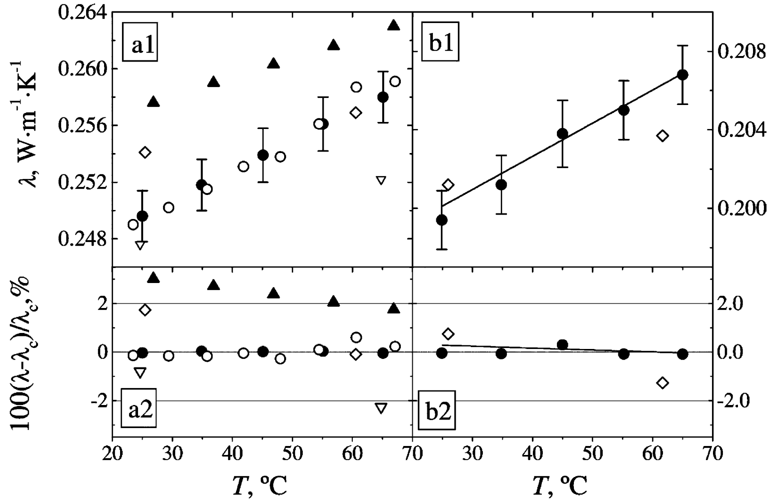

Fig. 3. Comparison of our present measurements (solid circles) with literature values. (a1) shows data for mono-ethylene glycol and (b1) for di-ethylene glycol. (a2) shows deviations (%) of measured values from a linear correlation of our present data for mono-ethylene glycol. (b2) shows the same for di-ethylene glycol. Open circles represent data from Assael et al. [9]; solid triangles from Touloukian et al. [10]; open down triangles from Bohne et al. [12]; open diamonds from DiGuilio and Teja [11]; while the solid curves in (b1) and (b2) represent the correlation proposed by Obermeier et al. [13].

with the most recent data of DiGuilio and Teja [11], who also employed the transient hot-wire technique, is within 2%.

From Table I, and Figs. 3 and 4, it can be observed that our λ values increase with temperature for all studied glycols. For the two first poly-ethylene-glycols plotted in Fig. 3, such an increase is well represented by a simple linear trend. However, for the glycols plotted in Fig. 4, deviations from a linear trend are observed at the higher temperatures. In this respect it should be noted that DiGuilio and Teja [11], Bohne et al. [12], and Obermeier et al. [13] represented their experimental data for glycols with quadratic equations, although for a temperature range wider than ours. Moreover, for the data of DiGuilio and Teja [11] it can be clearly observed that the thermal conductivity of poly-ethylene-glycols, as a function of temperature, exhibits a maximum. The temperature corresponding to the maximum λ decreases with the degree of polymerization, but it is always located at values above the ambient. Our experimental setup does not allow us to measure λ at temperatures above 65°C; however, our data seem to indicate, at least for the glycols with the higher molar mass (i.e.,

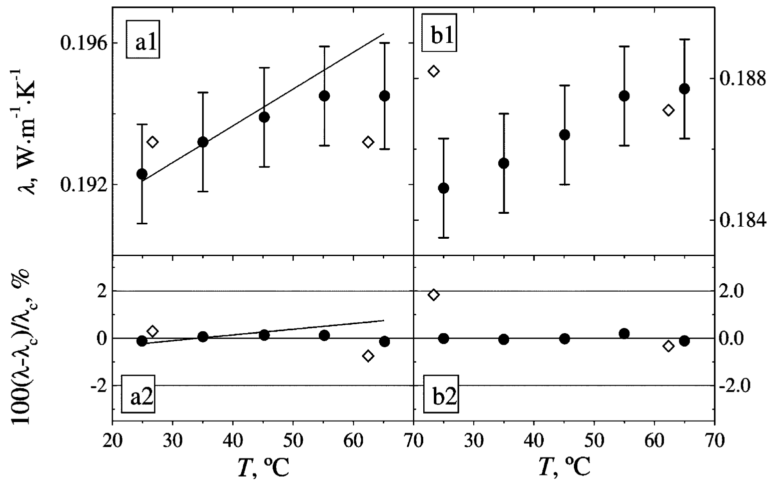

Fig. 4. Comparison of our present measurements (solid circles) with literature values. (a1) shows data for tri-ethylene glycol and (b1) for tetra-ethylene glycol. (a2) shows deviations (%) of measured values from a linear correlation of our present data for tri-ethylene glycol. (b2) shows the same for tetra-ethylene glycol. Open diamonds represent data from DiGuilio and Teja [11]; while the solid curves in (a1) and (a2) represent the correlation proposed by Obermeier et al. [13].

tri- and tetra-ethylene glycol), that we are not far from such a maximum. The quadratic correlations suggested by Obermeier et al. [13] also have a maximum in λ, but for temperatures systematically higher than those of DiGuilio and Teja [11]. Evidently, the presence of a maximum in the thermal conductivity of poly-ethylene glycols is an interesting feature, and an accurate determination of its location as a function of temperature is worthy of further experimental work.

We conclude by noting that, for poly-ethylene-glycols of low molar mass, λ decreases with increasing degree of polymerization. Such a decrease is nonlinear, in the sense that there is a large decrease (~20%) between mono-ethylene glycol and di-ethylene glycol, while the decrease between glycols of higher molar mass is moderate (~4%).

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