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Accurate Measurements of the Thermal Conductivity of *n*-Docosane, *n*-Tetracosane, 1,6-Hexanediol, and 1,8-Octanediol in the Solid and Liquid Phases

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Abstract

New measurements of the thermal conductivity of *n*-docosane, *n*-tetracosane, 1,6-hexanediol, and 1,8-octanediol, in the solid and liquid phase, are presented. The technique employed is the transient hot-wire technique, based on a full theoretical model. The technique is absolute and is characterized by an uncertainty of 1%. At the 95% confidence level, the standard deviations of the thermal conductivity measurements of *n*-docosane, are 0.40% for the solid phase (267 K to 308 K), and 0.60% for the liquid phase (330 K to 360 K); of *n*-tetracosane, 0.60% for the solid phase (265 K to 306 K), and 0.30% for the liquid phase (339 K to 363 K); of 1,6-hexanediol, 0.70% for the solid phase (263 K to 296 K), and 0.40% for the liquid phase (327 K to 351 K); and of 1,8-octanediol 1.1% for the solid phase (265 K to 312 K), and 0.50% for the liquid phase (344 K to 356 K), respectively.

Keywords 1,6-Hexanediol · *n*-Docosane · *n*-Tetracosane · 1,8-Octanediol · Solid and liquid phases · Thermal conductivity · Transient hot-wire

1 Introduction

In a recent article, reference correlations for the thermal conductivity of solid BK7, PMMA, Pyrex 7740, Pyroceram 9606 and SS304, were proposed [1]. It was made clear, that the thermal conductivity of reference solids over the widest possible range of conditions, is known with an uncertainty of no better than about 5% [1]. One of

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the main issues when measuring the thermal conductivity of a solid material, especially when employing methods based on thermal contact, whether they be the transient hot-wire technique (THW), or any other, is the thermal resistance between the solid sample(s) and the source of heat or thermometer. The resistance is often attributed to a thin layer of air that is present in the space between the imperfectly smooth surfaces of the test material and the other surfaces.

To avoid this thermal resistance, Velliadou et al. [2] for the first time, employed the THW technique, by immersing the wires directly into a melted organic Phase Changing Material (PCM) and letting the system cool down under a controlled temperature profile. In this way, upon solidification, the contact between the heating wire and the solid sample is excellent, and the value of the thermal conductivity can be attained directly from the analytical solution as well as from the numerical solution [2]. Hence, very accurate measurements of the thermal conductivity of 1-hexadecanol and 1-octadecanol in the solid and liquid phases, could be reported.

Solid–liquid PCMs have recently attracted a great deal of attention because of their ability to store the latent heat released or absorbed during repeated melting and crystallization cycles, while maintaining a relatively stable temperature, unlike conventional storage materials [3, 4]. In the present work, two high alkanes, *n*-docosane, and *n*-tetracosane, and two diols, 1,6-hexanediol, and 1,8-octanediol, were selected. The low melting points of these four materials, simplify their melting and solidification processes, while they can also easily be found in high purity and at relatively low cost, when compared to other similar compounds. They therefore have ideal characteristics for reference materials at moderate temperatures. Their thermal conductivity in both phases has been measured by an absolute THW instrument.

2 Theoretical

The transient hot-wire technique is based on the observation of the temporal temperature rise of a thin vertical, electrically conducting wire immersed in a single-phase homogeneous material whose thermal conductivity is to be determined. The wire is initially in thermal equilibrium with its surroundings and a step voltage is applied to it. In this way, electrical current flows through the wire and heats it up. Therefore, the wire acts as a line heat source of constant heat flux per unit length, producing a time-dependent temperature field inside the wire and the test material. The evolution of the wire's temperature depends in part on the thermal conductivity of the material around it.

In a recent paper Antoniadis et al. [5], examined very thoroughly the conditions that are necessary to secure accurate measurement of the thermal conductivity with a THW instrument. It was clearly shown that provided those conditions are satisfied, a GUM uncertainty analysis [5] proved that an absolute uncertainty of 0.5% can be achieved. Based on those criteria, an instrument was employed by Velliadou et al. [2] to measure very accurately the thermal conductivity of 1-hexadecanol and 1-octadecanol in the solid and liquid phases. In this paper, the work is extended to the accurate measurement of the thermal conductivity of *n*-docosane, *n*-tetracosane, 1,6-hexanediol, and 1,8-octanediol in both solid and liquid phases.

3 Experimental

The sensor employed is described in details in our previous publication [2], and will only be briefly presented here. A schematic drawing of the sensor, the wires and the shell can be seen in Fig. 1. To compensate for end-effects [6], two 25-μm-diameter Ta wires (Goodfellow Metals Ltd., U.K.) of 20 mm and 50 mm lengths (see 1 and 2 in Fig. 1) were employed. These were short enough to not require a large volume of test material, yet large enough to be workable and allow for a middle piece of the longer wire to act as a finite section of an infinitely long wire, as proven by Antoniadis et al. [5].

The two thin tantalum wires are supported by three 1 mm thick tantalum wires (see 3, 4 and 5 in Fig. 1). This arrangement ensures that as the temperature changes, each wire remains always under tension because it has the same linear expansion coefficient as its thick tantalum wire supports. Small pieces of Teflon (see 6 in Fig. 1) are used to hold the thick tantalum wires in place, as well as keep them apart to avoid contact. The sensor is attached through a screw to the front

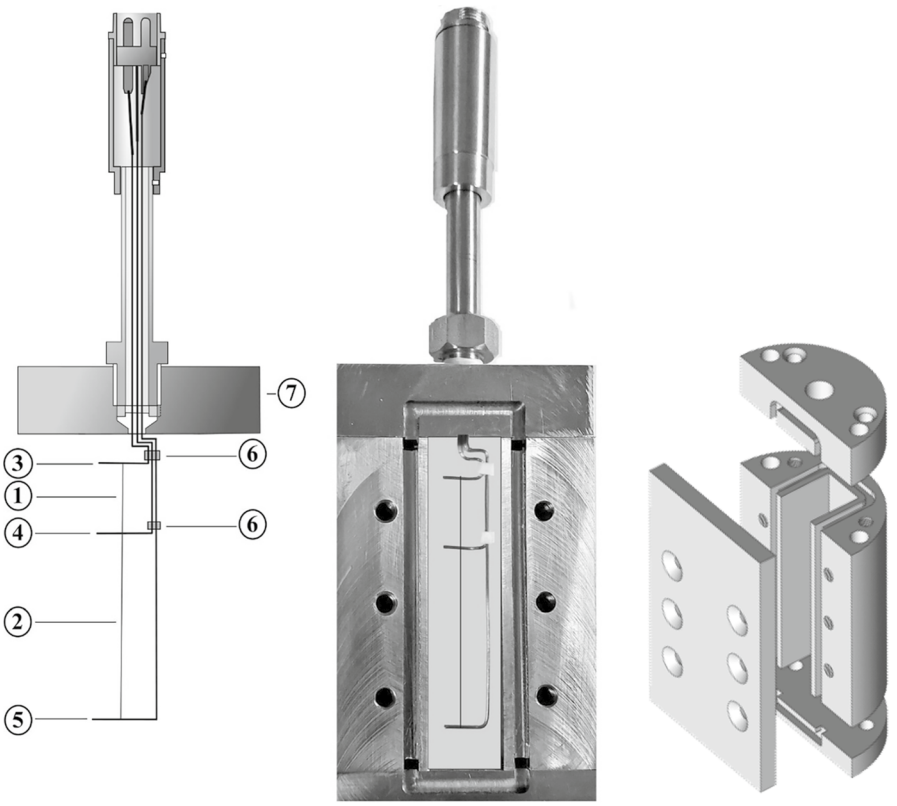

Fig. 1 Schematic diagram of wires, actual wires in the shell, and the shell decomposed

lid of the melt-containment shell (see 7 in Fig. 1). Thick tantalum wires are carried outside the front lid through a Conax-type plug.

The wires are connected through a plug and a cable to a computer-controlled Wheatstone-type bridge and the voltage across the circuit is directly measured upon transient heating. The voltage change of the wire is translated into resistance change and subsequently into temperature rise through the bridge equations. This process, as well as the deduction of the sample's thermal conductivity has been discussed elsewhere [7, 8].

Once the sample is melted, it is poured slowly and carefully into the shell placed in the horizontal position with the wires in place half-way down the channel, and it is allowed to cool down. Upon solidification, a top cover is placed over the filled cell. Two Pt resistance thermometers, calibrated to within 20 mK (via an NPL Class 1 thermometer) placed in the shell, are employed in order to register the temperature.

In addition to the measurements of the thermal conductivity in the solid phase, measurements in the liquid phase were also carried out. For these measurements a similar sensor to the one described above was employed, but in this case held in a glass vessel. Because its details have been described elsewhere [2, 5], they will not be repeated here.

3.1 Validation of the Technique

As described in Velliadou et al. [2], one of the greatest advantages of the present instrument is that its performance can be tested by measuring the thermal conductivity of toluene, a well-established reference liquid. More specifically, before pouring the melt into the shell, the sensor with the wires (see Fig. 1) was placed into a vessel containing toluene and its thermal conductivity measured. The value of the thermal conductivity obtained deviated by less than 0.2% (at the 95% confidence level) from the reference value for the thermal conductivity of toluene [9, 10]. This was repeated before each melt.

In order to ensure that there is no thermal resistance between the heating wire and the solid sample, we adopted the procedure described by Velliadou et al. [2], and Antoniadis et al. [7]. Accordingly, we employ a numerical solution of the full transient heat conduction equations using a finite element method (FEM) rather than an approximate analytic solution. In the present case, COMSOL Multiphysics Version 3.2 was employed to describe fully the complete geometry of the new sensor. The FEM approach was used to validate the thermal conductivity value obtained with the present THW instrument when measuring a solid sample. Hence, we ensure that there is a homogeneous solid body around the hot wire and that there is no thermal resistance between the heating wire and the solid sample. For more details on these procedures and validation, the reader is referred to Velliadou et al. [2]

3.2 Uncertainty Analysis

As already mentioned, the transient hot-wire technique employed is an absolute technique [5]. The final uncertainty of the method consists of two separated parts:

first the uncertainty arising from the experimental procedure and the electronic configuration used, and secondly the uncertainty owing to the use of the finite element method. These have been described in detail in our previous publication by Velliadou et al. [2], and will only be briefly mentioned here.

As far as the uncertainty of the experimental setup is concerned, it is associated with the uncertainty of the variables that affect the wires' resistances and the experimental time measurement. More specifically the related variables are:

(a) The supply voltage, is measured digitally with an uncertainty of about ±1 μV. The effect of this parameter on the temperature rise of the wire is estimated to be of the order of 10^{-4} %.
(b) The experimental time is measured and registered through the electronic circuit with an uncertainty of 1 μs. In the calculation of thermal conductivity value, the logarithm of time is used and therefore its influence on the uncertainty of the obtained value is lower than 10^{-3} %.
(c) The temperature coefficient of resistance is obtained by means of calibration over the relevant temperature range employing a Class I platinum resistance thermometer, with an uncertainty of ±1 mK. This has a negligible effect (< 0.01%) in the calculation of the temperature rise of the wire.
(d) The homogeneity of the solid sample is verified through the use of the FEM model. Thus, it does not affect the uncertainty of the technique.

Therefore, according to the Joint Committee for Guides in Metrology [12], the combined uncertainty of the aforementioned variables, results to an **uncertainty of the experimental setup** is no more than **0.1%**. Uncertainty owing to the use of the finite element method is obtained through a sensitivity analysis which evaluates the effects that the design parameters of the FEM model have on the calculated temperature rise and therefore on the calculated thermal conductivity value. Taking these into consideration, the estimated **uncertainty of the Finite Element Method applied** is no more than **1%**.

4 Measurement of the Thermal Conductivity of *n*-Docosane

n-Docosane (CAS number 629-11-8) is a straight-chain higher alkane with 22 carbon atoms, and the chemical formula $C_{22}H_{46}$. At room temperature it is a white solid, while when heated above its melting point (317 ± 1 K [11]), it becomes a colorless transparent liquid. For this work, 99% pure *n*-docosane was purchased from Sigma-Aldrich. The molar mass of the compound is 310.6006 g·mol^{-1} [11] and its density is 778 kg·m^{-3} at 298.15 K [13].

n-Docosane was received in the form of a bulk solid from the supplier. It was then melted by heating it above the melting point in a water bath, until all of the material was liquid. Subsequently,

(a) *For measurements in the solid phase*: The melted hydrocarbon was carefully poured into the stainless-steel, preheated instrument with the wires already horizontally in place. The configuration has been thoroughly presented in detail in our previous publication [2]. The system was then quickly placed in a freezer to solidify rapidly. In the particular case of the four solids studied here, it was observed that, rapid cooling facilitates the formation of an amorphous solid, whereas slow cooling results in the development of crystals and/or holes within the material, which are not desirable. Once solidified with the wires inside it, the configuration was placed in a 60:40 wt% ethane-1,2-diol/water bath, where the measurements were performed [2].

(b) *For the measurements in the liquid phase*: A two-wire 25-μm-diameter tantalum sensor presented in detail in our previous paper [2] was placed into a glass cell already containing the melted material. The configuration was subsequently quickly placed in a water-bath, at a temperature over the hydrocarbon's melting point, in order to keep it in the liquid phase throughout the duration of the experiment.

The evaluation of the thermal conductivity of the sample in either phase, using the THW technique, requires a knowledge of its density and heat capacity.. In the case of the density of the solid sample, we have used the value given by the manufacturer of the material [13]. For the liquid phase, we have adopted the equation of Dutour et al. [14], which is valid from 323 K to 393 K with an uncertainty of 0.1%. Finally, the heat capacity data, c_p, for the solid and liquid-phase measurement ranges, were obtained by fitting the experimental measurements of Yan et al. [15] as.

Solid phase (240 K to 300 K)

$$\left(c_p/\mathrm{J\cdot kg^{-1}\cdot K^{-1}}\right) = 3782.3 - 24.116(T/\mathrm{K}) + 0.0593\left(T^2/\mathrm{K^2}\right) \tag{1}$$

Liquid phase (345 K to 370 K).

$$\left(c_p/\mathrm{J\cdot kg^{-1}\cdot K^{-1}}\right) = 1353.8 + 2.7865(T/\mathrm{K}) \tag{2}$$

The heat capacity measurements of Yan et al. [15] are reported with an uncertainty of 3% in the solid phase and 1% in the liquid phase. Equations 1 and 2 represent the solid and liquid-state experimental data within 0.1% and 0.9%, respectively. We note that Eqs. 1 and 2 have been slightly extrapolated to obtain the heat capacity values at all of our measurement temperatures.

In Table 1 the results of the measurement of the thermal conductivity of *n*-docosane for the solid and liquid phases are collected, while Fig. 2 shows the thermal conductivity of *n*-docosane as a function of temperature. All measurements were performed at 0.101 MPa.

The measurements of the thermal conductivity of *n*-docosane, shown in Table 1, were fitted as:

Solid phase (267 K to 308 K)

$$\left(\lambda/\mathrm{mW\cdot m^{-1}\cdot K^{-1}}\right) = 786.08 - 1.3969(T/\mathrm{K}) \tag{3}$$

Table 1 Measurements of the thermal conductivity of *n*-docosane

T (°C)	T (K)	λ (mW·m^{-1}·K^{-1})	λ_{fit} (mW·m^{-1}·K^{-1})	$\Delta\lambda$ (%)
Solid phase				
− 6.41	266.74	414.0	413.5	0.1
− 0.84	272.31	404.6	405.7	− 0.3
3.92	277.07	399.3	399.0	0.1
8.51	281.66	392.4	392.6	− 0.1
13.48	286.63	385.7	385.7	0.0
18.42	291.57	379.4	378.8	0.2
24.52	297.67	371.4	370.3	0.3
28.73	301.88	363.1	364.4	− 0.4
35.23	308.38	355.3	355.3	0.0
Liquid phase				
56.20	329.35	150.4	150.6	− 0.1
61.84	334.99	150.1	149.5	0.4
66.75	339.90	148.2	148.5	− 0.2
71.62	344.77	147.0	147.5	− 0.4
76.89	350.04	146.8	146.5	0.2
81.92	355.07	145.8	145.5	0.2
86.86	360.01	144.4	144.6	− 0.1

The uncertainty in temperature $u(T)=0.02$ K, and the combined uncertainty in the thermal conductivity $U_r(\lambda)=1\%$ (at the 95% confidence level)

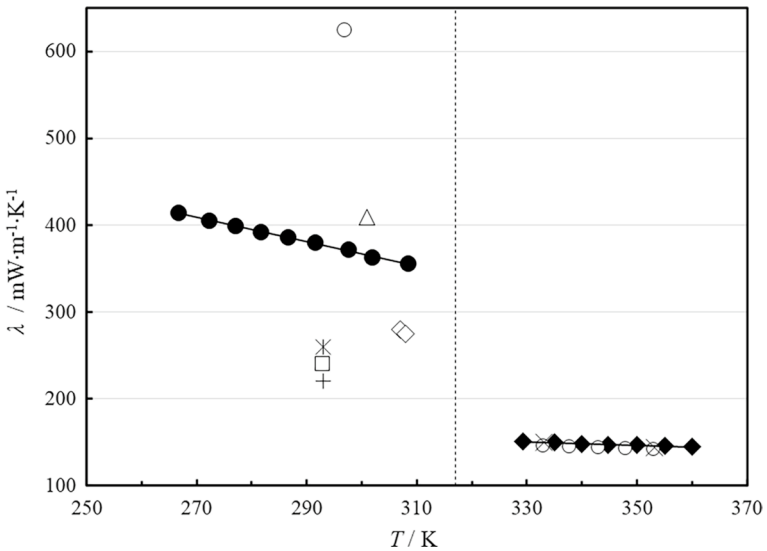

Fig. 2 Measurements of the thermal conductivity, λ, of *n*-docosane as a function of the temperature, T. Present measurements: solid phase (●), liquid phase (◆). Other investigators: Yan et al. [15] (△), Chang et al. [35] (□), Wang et al. [16] (◇), Fleming et al. [17] (○), Li et al. [18] (∗), Sari and Karaipekli [19] (+), and Rastorguev et al. [20] (x). Melting temperature (⋮)

Table 2 *n*-Docosane thermal conductivity values of other investigators, and their deviations from the present ones

Authors	Year	Technique	Purity (%)	Uncertainty (%)	T (K)	λ_{lit} (mW·m^{-1}·K^{-1})	λ_{fit} (mW·m^{-1}·K^{-1})	$\Delta\lambda$ (%)
Solid phase								
Yan et al. [15]	2021	TPS	99	5	301.00	409.1	365.6	12
Chang et al. [35]	2019	TPS	na	na	293.15*	240	376.6	− 36
Wang et al. [16]	2019	HFMA	na	3.8	307.65	280	356.3	− 21
Wang et al. [16]	2019	Hot-Disk	na	na	308.15	275	355.6	− 23
Fleming et al. [17]	2018	MTPS	99	5	297.60	624	370.4	68
Li et al. [18]	2014	Laser Flash	na	na	293.15*	260	376.6	− 31
Sari and Karaipekli [19]	2007	THW-1	na	5*	293.15*	220	376.6	− 42
Liquid phase								
Fleming et al. [17]	2018	MTPS	99	5	333.00	146	149.9	− 2.6
					337.70	145	148.9	− 2.6
					343.00	144	147.9	− 2.6
					347.90	143	146.9	− 2.7
					353.00	142	145.9	− 2.7
Rastorguev et al. [20]	1974	HFil	na	1.3	333.13	149.4	149.8	− 0.3
					353.13	143.4	145.9	− 1.7

H.Fil heated-filament, *HFMA* heat flow method analysis, *MTPS* modified transient plane source, *TPS* transient plane source, *na* not available, *THW-1* single-wire transient hot wire,

*Not clearly stated

Liquid phase (330 K to 360 K).

$$\left(\lambda/\mathrm{mW}\cdot\mathrm{m}^{-1}\cdot\mathrm{K}^{-1}\right) = 215.26 - 0.1964(T/K) \tag{4}$$

The fitted values, λ_{fit}, are also shown in Table 1, together with the percentage deviations of each measurement from the fitted ones, $\Delta\lambda$ (= 100 (λ–λ_{fit})/λ_{fit}). We note that at the 95% confidence level, the standard deviation for the solid phase is 0.4% and for the liquid phase 0.6%.

As we have thoroughly discussed in our previous publication [2], thermal-conductivity measurements of pure PCMs are rare in literature. Moreover, they are characterized by very large discrepancies between each other. This is mainly attributed to the fact that measurements are not usually performed in order to get accurate values for the thermal conductivity of the pure components, but mostly to investigate the enhancement of the property in composite PCMs. Table 2 shows all the measurements of the thermal conductivity of *n*-docosane we were able to find in the literature. These are also depicted in Fig. 2. In the case of the measurements in the solid phase, the disagreement between authors, is spectacular, ranging from − 42% to+68%. Analytically:

– In a very recent article Yan et al. [15] reported measurement of the thermal conductivity of *n*-docosane performed with a transient plane source instrument and

an associated uncertainty of 5%. These deviate from the present measurements by + 12%. A very similar instrument was employed by Chang et al. [35] to measure the thermal conductivity in the solid phase. The single measurement reported deviates by − 36% from the value calculated by Eq. 3.

- Wang et al. [16] employed the heat flow method analysis (HFMA) to measure the thermal conductivity of *n*-docosane with a quoted uncertainty of 3.8%. In order to compensate for thermal resistances the authors adopted a numerical solution, while in order to check the accuracy of their method, they also measured the thermal conductivity of *n*-docosane using a Hot-Disk instrument. Although their two values are in good agreement with each other, they deviate by − 21% (HFMA method) and -23% (Hot-Disk method) from the values calculated by Eq. 3, as shown in Table 2.
- In 2018, Fleming et al. [17] reported measurements of the thermal conductivity of *n*-docosane in both the solid and liquid phases, performed in a commercial modified transient-plane source instrument, with a quoted uncertainty of up to 5%. As it can be seen in Table 2, although in the liquid phase there is good agreement with deviations of about − 2.7%, the solid-phase measurement deviates by as much as + 68% from our fitted value.
- Li et al. [18] reported a single value for the thermal conductivity of *n*-docosane at room temperature, performed with a laser flash instrument. The uncertainty is not reported, and this value deviates by − 31% from the present value.
- Sari and Karaipekli [19] employed a single wire of 180 microns diameter, transient hot-wire instrument with a quoted uncertainty of 5%, and reported only one value for the thermal conductivity of *n*-docosane. Assuming that, the measurement was obtained at room temperature, it deviates by the present value calculated by Eq. 3, by − 42%, attributed to the fact that such thick wire should not be employed for proper operation of the THW technique [5].
- Finally Rastorguev et al. [20] in 1974 measured the thermal conductivity of a series of higher straight-chain alkanes, including *n*-docosane, in a wide range of temperatures and pressures, with a heated-filament method and a quoted uncertainty of 1.3%. These measurements deviate by − 0.3% and − 1.7% respectively, from Eq. 4.

Summarizing, it is interesting that some investigators do not even report the temperature at which the measurements were obtained. Furthermore, although most of the measurements were performed very recently, investigators do not find it necessary to compare their values with previously reported ones.

5 Measurement of the Thermal Conductivity of *n*-Tetracosane

n-Tetracosane (CAS Number 646-31-1) is a straight-chain higher alkane with 24 carbon atoms, and the chemical formula $C_{24}H_{50}$. It appears in the form of a white solid at room temperature and, when heated above its melting point (324 ± 3 K [11]), it transforms to a colorless transparent liquid. For this work, 99% pure

n-tetracosane (ThermoScientific®) was purchased from Sigma-Aldrich. The molar mass of the compound is 338.6538 g·mol^{-1} [11] and its density is 799 kg·m^{-3} at 298.15 K [21]. *n*-Tetracosane was supplied in the form of a bulk solid. The solid was melted by heating it above the melting point in a water bath, until all the amount of the material was liquid. The procedure of placing the sensor in the melted sample and cooling the system to obtain an amorphous solid with the wires in place was identical with that in the case of *n*-docosane. Moreover, the procedure of introducing the sensor in the liquid sample for the liquid-phase measurements was the same with that described for *n*-docosane. Finally, the performance of the THW instrument was continuously validated through the measurement of the thermal conductivity of toluene.

As already discussed, the calculation of low uncertainty thermal conductivity using the THW technique requires densities and heat capacities. In the case of the density of the solid, we have employed the value given by the supplier of the material [21], while for the liquid phase, we have adopted the equation of Dutour et al. [14], valid from 333 K to 393 K, with an uncertainty of 0.1%. As far as the solid heat capacity is concerned we have used the measurements given by Parks et al. [22] with an uncertainty of 0.7%, to produce a third order polynomial fit, Eq. 5, that represents the literature values within about 2%. Moreover, the heat capacity values in the liquid phase were adopted from the work of Höhne [23], by fitting the author's measurements (given with an uncertainty of 3%) to a straight line equation. Equation 6, represents the literature data within 0.2%. Hence.

Solid phase (250 K to 300 K)

$$\left(c_{\mathrm{p}}/\mathrm{J}\cdot\mathrm{kg}^{-1}\cdot\mathrm{K}^{-1}\right)=149323+1692.87\,(T/\mathrm{K})-6.34333\left(T^{2}/\mathrm{K}^{2}\right)+0.00794717\left(T^{3}/\mathrm{K}^{3}\right) \tag{5}$$

Liquid phase (350 K to 425 K)

$$\left(c_{\mathrm{p}}/\mathrm{J}\cdot\mathrm{kg}^{-1}\cdot\mathrm{K}^{-1}\right)=886+4.12(T/\mathrm{K}) \tag{6}$$

Table 3 shows the measurements of the thermal conductivity of *n*-tetracosane for the solid and liquid phases, while Fig. 3 depicts the thermal conductivity of *n*-tetracosane as a function of temperature. All the measurements were performed at 0.101 MPa.

The measurements of the thermal conductivity of *n*-tetracosane, shown in Table 3, were fitted as:

Solid phase (265 K to 306 K)

$$\left(\lambda/\mathrm{mW}\cdot\mathrm{m}^{-1}\cdot\mathrm{K}^{-1}\right)=879.19-1.7121\ (T/\mathrm{K}) \tag{7}$$

Liquid phase (339 K to 363 K)

$$\left(\lambda/\mathrm{mW}\cdot\mathrm{m}^{-1}\cdot\mathrm{K}^{-1}\right)=222.22-0.2046\ (T/K) \tag{8}$$

The fitted values, λ_{fit}, are also shown in Table 3, together with the percentage deviations of each measurement from the fitted ones, $\Delta\lambda$ ($=100\ (\lambda-\lambda_{\mathrm{fit}})/\lambda_{\mathrm{fit}}$). We note that at the 95% confidence level, the standard deviation for the solid phase

Table 3 Measurements of the thermal conductivity of *n*-tetracosane

T (°C)	T (K)	λ (mW·m^{-1}·K^{-1})	λfit (mW·m^{-1}·K^{-1})	$\Delta\lambda$ (%)
Solid phase				
− 8.40	264.75	428.1	425.9	0.5
− 4.82	268.33	419.7	419.8	0.0
− 0.12	273.03	410.2	411.7	− 0.4
4.31	277.46	403.6	404.2	− 0.1
9.14	282.29	396.5	395.9	0.2
13.58	286.73	387.1	388.3	− 0.3
18.34	291.49	379.3	380.1	− 0.2
23.72	296.87	371.2	370.9	0.1
25.15	298.30	367.7	368.5	− 0.2
28.14	301.29	364.5	363.4	0.3
32.99	306.14	355.9	355.1	0.2
Liquid phase				
65.46	338.61	152.8	152.9	− 0.1
70.76	343.91	152.0	151.9	0.1
75.66	348.81	150.8	150.9	0.0
80.66	353.81	149.9	149.8	0.0
85.74	358.89	149.1	148.8	0.2
90.76	363.91	147.5	147.8	− 0.2

The uncertainty in temperature $u(T) = 0.02$ K, and the combined uncertainty in the thermal conductivity $U_r(\lambda) = 1\%$ (at the 95% confidence level)

is 0.6% and for the liquid phase 0.3%. Table 4 shows all the measurements of the thermal conductivity in the solid and liquid phases that we were able to find in literature. As with most PCMs, experimental data for pure *n*-tetracosane are also rare in literature, and inconsistent with each other, especially in the solid phase. More analytically:

- In Table 4, and Fig. 3, the measurements of Fleming et al. [17] and Rastorguev et al. [20] and their deviations from the present ones, were discussed in Sect. 4, for *n*-docosane. In the case of n-tetracosane, they follow the same pattern so we do not repeat the discussion. Moreover, although Sari and Karaipekli [19] also measured that thermal conductivity of *n*-docosane with a thick transient hot-wire instrument, in this case Sari et al. [24] employed a commercially available needle probe (Decagon KD2 pro Devices), placed "tightly" into the sample. Their measurement is 32% lower than the present one.
- Shin et al. [25], very recently, investigated the thermal conductivity *n*-tetracosane as an energy storage material. The authors employed a modified transient plane source instrument (TCi Thermal Conductivity Analyzer, C-Therm Technologies Ltd.), to measure its thermal conductivity. No uncertainty was quoted. Table 4 shows that the thermal conductivity they measured at room temperature deviates by as much as -34% from the value predicted by Eq. 7.

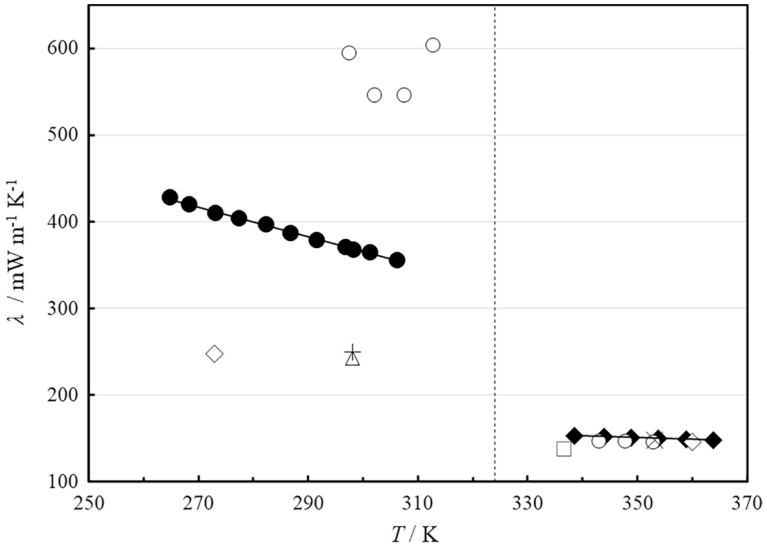

Fig. 3 Measurements of the thermal conductivity, λ, of *n*-tetracosane as a function of the temperature, *T*. Present measurements: solid phase (●), liquid phase (◆). Other investigators: Shin et al. [25] (△), Fleming et al. [17] (○), Sari et al. [24] (+), Tarzimanov et al. [26] (◇), O'Connor et al. [27] (□), and Rastorguev et al. [20] (x). Melting temperature (⋮)

– In 1992 Tarzimanov et al. [26] employed a pulse-heating instrument to measure the thermal conductivity of *n*-tetracosane around the phase transition temperature, with an uncertainty of about 5%. As shown in Table 4, although there is good agreement between the authors' results and the results of the present measurements in the liquid phase (the deviation is − 1.7%), the same is not true in the solid phase, where their measurement is 40% lower than the value predicted by Eq. 7.
– In a study performed in 2014 by O'Connor et al. [27] the thermal conductivity of four PCMs, including *n*-tetracosane, was measured by the transient plane source technique with an uncertainty of 5%. Their value is about 11% lower than ours.

In conclusion, deviations of other investigators from the present values follow the same pattern for both hydrocarbons studied. It is interesting that although deviations in the solid-phase measurements are very high, investigators seem to avoid t comparisons with previous measurements.

6 Measurement of the Thermal Conductivity of 1,6-Hexanediol

1,6-Hexanediol (CAS number 629-11-8), also known as hexane-1,6-diol, hexamethylene glycol, or 1,6-dihydroxyhexane is an organic compound with 6 carbon atoms, and the chemical formula $C_6H_{14}O_2$. It appears as a colorless solid at room

Table 4 *n*-Tetracosane thermal conductivity values of other investigators, and their deviations from the present ones

Authors	Year	Technique	Purity (%)	Uncertainty (%)	T (K)	λ_{lit} (mW·m^{-1}·K^{-1})	λ_{fit} (mW·m^{-1}·K^{-1})	$\Delta\lambda$ (%)
Solid phase								
Shin et al. [25]	2021	MTPS	99	na	298.15*	242.3	368.7	− 34
Fleming et al. [17]	2018	MTPS	99	5	297.60	594	369.7	61
					302.30	545	361.6	51
					307.70	545	352.4	55
					312.90	603	343.5	76
Sari et al. [24]	2015	Needle Probe	na	na	298.15*	250	368.7	− 32
Tarzimanov et al. [26]	1992	PHeat	na	5	273.00	248	411.8	− 40
Liquid phase								
Fleming et al. [17]	2018	MTPS	99	5	343.10	146	152.0	− 4
					348.00	146	151.0	− 3.3
					353.00	145	150.0	− 3.3
O'Connor et al. [27]	2014	TPS	Anal	5	336.80*	137	153.3	− 11
Tarzimanov et al. [26]	1992	PHeat	na	5	360.00	146	148.6	− 1.7
Rastorguev et al. [20]	1974	HFil	na	1.3	353.13	148.1	150.0	− 1.3

Anal analytical grade reagent, *HFil* heated-filament, *MTPS* modified transient plane source, *PHeat* pulse heating, *TPS* transient plane source, *na* not available

*Not clearly stated

temperature and a colorless, transparent liquid at temperatures above its melting point, 315 ± 2 K [11]. For this work, 99% pure hexane-1,6-diol was purchased from Sigma-Aldrich. The molar mass of the compound is 118.1742 g·mol^{-1} [11], and its density is 960 kg·m^{-3} at 298.15 K [28].

1,6-Hexanediol was received in the form of a bulk solid from the supplier, and it was melted by heating it above its melting temperature in a water bath. The sensor was introduced in the same way as already discussed in the case of n-docosane.

For the density of the solid phase, we used the value of 960 kg·m^{-3}, given by Sigma-Aldrich [28]. For the liquid phase, we have fitted the measurements of Bleazard et al. [29], given with an uncertainty of 0.2%, as

Liquid phase (318 K to 433 K)

$$\left(\rho/\ \mathrm{kg}\cdot\mathrm{m}^{-3}\right) = 1171.4 - 0.667(T/\mathrm{K}) \tag{9}$$

Equation 9 represents the data of Bleazard et al. [29] within 0.2%.

Table 5 Measurements of the thermal conductivity of 1,6-hexanediol

T (°C)	T (K)	λ (mW·m^{-1}·K^{-1})	λ_{fit} (mW·m^{-1}·K^{-1})	$\Delta\lambda$ (%)
Solid phase				
− 10.42	262.73	973.9	976.2	− 0.2
− 5.87	267.28	958.0	963.0	− 0.5
− 1.68	271.47	955.4	950.8	0.5
− 0.81	272.34	950.5	948.3	0.2
3.81	276.96	934.6	934.9	− 0.0
8.51	281.66	924.7	921.3	0.4
15.43	288.58	901.5	901.2	0.0
23.29	296.44	875.0	878.3	− 0.4
Liquid phase				
52.96	326.11	200.7	200.5	0.1
58.02	331.17	200.2	200.5	− 0.1
63.15	336.30	200.0	200.5	− 0.3
67.82	340.97	201.1	200.5	0.3
72.10	345.25	200.9	200.6	0.2
78.01	351.16	200.3	200.6	− 0.1

The uncertainty in temperature $u(T)=0.02$ K, and the combined uncertainty in the thermal conductivity $U_{\mathrm{r}}(\lambda)=1\%$ (at the 95% confidence level)

As far as the heat capacity is concerned, we used the measurements of Gatta et al. [30] for the solid phase (quoted uncertainty 2%), and the ones of Goralski and Tkaczyk [31] for the liquid phase (quoted uncertainty 0.2%), as.

Solid phase (280 K to 310 K)

$$\left(c_{\mathrm{p}}/\mathrm{J}\cdot\mathrm{kg}^{-1}\cdot\mathrm{K}^{-1}\right)=-349.27+6.5886(T/\mathrm{K}) \tag{10}$$

Liquid phase (318 K to 353 K)

$$\left(c_{\mathrm{p}}/\mathrm{J}\cdot\mathrm{kg}^{-1}\cdot\mathrm{K}^{-1}\right)=-350.02+8.6116(T/\mathrm{K}) \tag{11}$$

Equations 10 and 11 reproduce the corresponding data of Gatta et al. [30] and Goralski and Tkaczyk [31] within 0.6% and 0.1%, respectively.

Table 5 shows the measurements of the thermal conductivity of 1,6-hexanediol in the solid and liquid phases, while Fig. 4 depicts all these measurements. All measurements were performed at 0.101 MPa.

The measurements of the thermal conductivity of 1,6-hexanediol, shown in Table 5, were fitted as:

Solid phase (263 K to 296 K)

$$\left(\lambda/\mathrm{mW}\cdot\mathrm{m}^{-1}\cdot\mathrm{K}^{-1}\right)=1738.7-2.9023(T/\mathrm{K}) \tag{12}$$

Liquid phase (327 K to 351 K)

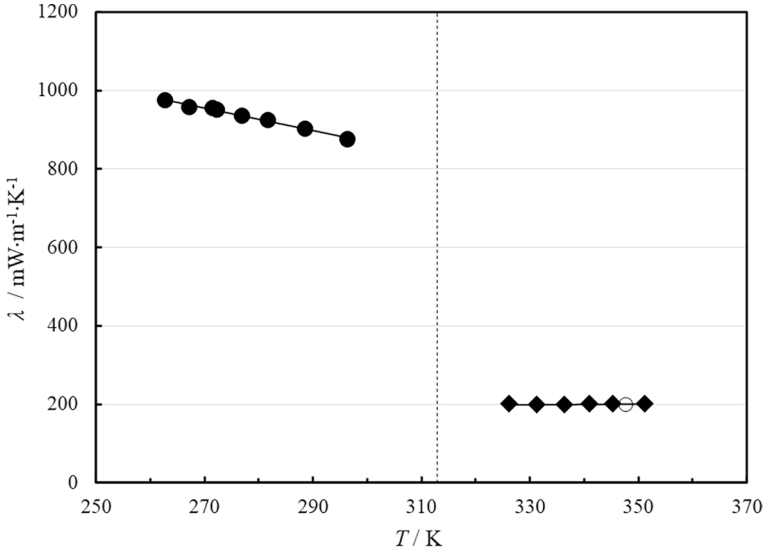

Fig. 4 Measurements of the thermal conductivity, λ, of 1,6-hexanediol as a function of the temperature, T. Present measurements: solid phase (●), liquid phase (◆). Other investigators: Bleazard et al. [29] (○) . Melting temperature (⋮)

$$\left(\lambda/\mathrm{mW}\cdot\mathrm{m}^{-1}\cdot\mathrm{K}^{-1}\right) = 198.56 + 0.0058(T/\mathrm{K}) \tag{13}$$

The fitted values, λ_{fit}, are also shown in Table 5, together with the percentage deviations of each measurement from the fitted ones, $\Delta\lambda$ (= 100 $(\lambda–\lambda_{\mathrm{fit}})/\lambda_{\mathrm{fit}}$). We note that at the 95% confidence level, the standard deviation for the solid phase is 0.7% and for the liquid phase 0.4%.

To the best of our knowledge, in the case of 1,6-hexanediol, there is only one other group of investigators that has ever studied its thermal conductivity. Specifically, in 1996, Bleazard et al. [29] employed a single-wire transient hot-wire instrument, operating in a relative way [32], to measure the thermal conductivity of a set of liquid diols, including 99% pure 1,6-hexanediol. The authors reported 7 values with an uncertainty of 2% in the temperature range 323 K to 471 K. From these values, only one at 347.9 K, is within the validity range of Eq. 13 and can be used hereby for comparison purposes. The reported value of Bleazard et al. [29], also shown in Fig. 4, at this temperature is 196.3 $\mathrm{mW}\cdot\mathrm{m}^{-1}\cdot\mathrm{K}^{-1}$ and deviates by − 2% from the equation proposed here (λ_{fit} = 200.6 $\mathrm{mW}\cdot\mathrm{m}^{-1}\cdot\mathrm{K}^{-1}$).

7 Measurement of the Thermal Conductivity of 1,8-Octanediol

1,8-Octanediol (CAS number 629-41-4), also commonly known as octane-1,8-diol, or octamethylene glycol is an organic compound with 8 carbon atoms, and the chemical formula $C_8H_{18}O_2$. It belongs in the family of diols and appears in the form of a white solid at room temperature and a colorless transparent liquid at temperatures above

its melting point, between 332 K ±2 K [33]. For this work, 98% pure 1,8 octanediol (ThermoScientific®) was purchased from Sigma-Aldrich. The molar mass of the compound is 146.2273 g mol^{-1} [11] and its density is 939 kg m^{-3} at 298.15 K [34].

Octane-1,8-diol was supplied in the form of solid white flakes, and it was melted by heating it above its melting point in a water bath. The procedure of measurements was identical to the previous three samples examined in this work. Similarly, the performance of the THW instrument was continuously validated with the measurement of the thermal conductivity of toluene, in the same way as in the case of the other materials.

The density value required to obtain the thermal conductivity of 1,8-octanediol in the solid phase was adopted from the work of Scott and Fiume [34]. For the liquid phase, we have fitted the measurements of Bleazard et al. [29], given with an uncertainty of 0.2%, to Eq. 14, which represents the literature values within 0.1%, as

Liquid phase (335 K to 433 K)

$$\left(\rho/\ \mathrm{kg}\cdot\mathrm{m}^{-3}\right) = 1147 - 0.679(T/\mathrm{K}) \tag{14}$$

Similarly to 1,6-hexanediol, the heat capacity data in the liquid and solid phases, were obtained by fitting the corresponding experimental data of Gatta et al. [30] (quoted uncertainty 2%) and Goralski and Tkaczyk [31] (quoted uncertainty 0.2%) to Eqs. 15 and 16, respectively, as.

Solid phase (280 K to 310 K)

$$\left(c_\mathrm{p}\ /\ \mathrm{J}\cdot\mathrm{kg}^{-1}\cdot\mathrm{K}^{-1}\right) = -207.64 + 6.1239(T/\mathrm{K}) \tag{15}$$

Liquid phase (333 K to 353 K):

$$\left(c_\mathrm{p}\ /\ \mathrm{J}\cdot\mathrm{kg}^{-1}\cdot\mathrm{K}^{-1}\right) = -365.33 + 8.7053(T/\mathrm{K}) \tag{16}$$

Equations 15 and 16 represent the corresponding literature data within 0.2% and 0.01%, respectively.

Table 6 shows the measurements of the thermal conductivity of 1,8-octanediol for the solid and liquid phase, while Fig. 5 depicts all these measurements. All measurements were performed at 0.101 MPa.

The measurements of the thermal conductivity of 1,8-octanediol, shown in Table 6, were fitted as:

Solid phase (265 K to 312 K)

$$(\lambda/\mathrm{mW}\cdot\mathrm{m}^{-1}\cdot\mathrm{K}^{-1}) = 1109 - 1.3445(T/\mathrm{K}) \tag{17}$$

Liquid phase (344 K to 356 K)

$$(\lambda/\mathrm{mW}^{-1}\cdot\mathrm{m}^{-1}\cdot\mathrm{K}^{-1}) = 205.71 + 0.004(T/\mathrm{K}) \tag{18}$$

The fitted values, λ_{fit}, are also shown in Table 6, together with the percentage deviations of each measurement from the fitted ones, $\Delta\lambda$ (= 100 $(\lambda - \lambda_{\mathrm{fit}})/\lambda_{\mathrm{fit}}$). We

Table 6 Measurements of the thermal conductivity of 1,8-octanediol

T (°C)	T (K)	λ (mW·m^{-1}·K^{-1})	λ_{fit} (mW·m^{-1}·K^{-1})	$\Delta\lambda$ (%)
Solid phase				
− 8.98	264.17	750.2	753.8	− 0.5
− 4.73	268.42	755.0	748.1	0.9
− 0.22	272.93	742.1	742.0	0.0
4.93	278.08	734.4	735.1	− 0.1
10.00	283.15	721.3	728.3	− 1.0
14.28	287.43	726.9	722.5	0.6
20.73	293.88	715.0	713.9	0.2
28.56	301.71	701.5	703.4	− 0.3
39.42	312.57	689.9	688.7	0.2
Liquid phase				
71.28	344.43	207.7	206.5	0.6
73.53	346.68	206.5	206.5	0.0
78.44	351.59	206.9	206.5	− 0.2
83.58	356.73	207.4	206.5	0.4

The uncertainty in temperature $u(T) = 0.02$ K, and the combined uncertainty in the thermal conductivity $U_r(\lambda) = 1\%$ (at the 95% confidence level)

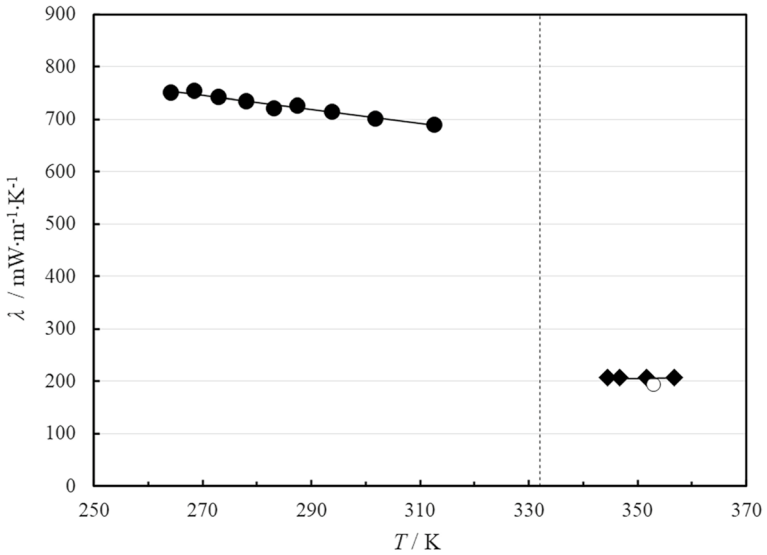

Fig. 5 Measurements of the thermal conductivity, λ, of 1,8-octanediol as a function of the temperature, T. Present measurements: solid phase (●), liquid phase (◆). Other investigators: Bleazard et al. [29] (○). Melting temperature (⋮)

note that at the 95% confidence level, the standard deviation for the solid phase is 1.1% and for the liquid phase 0.5%.

In the case of 1,8-octanediol, to our knowledge, only one other measurement existed in literature. Bleazard et al. [29], employed a single-wire transient hot-wire instrument, operated in a relative way with an uncertainty of 2% in the liquid phase. His value, also shown in Fig. 5, appears to underestimate the present thermal conductivity of liquid 1,8-octanediol, by about 7%.

8 Conclusions

In this work new measurements of the thermal conductivity of *n*-docosane, *n*-tetracosane, 1,6-hexanediol and 1,8-octanediol were presented in the solid and liquid phase. In all cases, the sample was melted by heating it above its melting point in a water bath, until all the amount of the material was liquid. Subsequently, for measurements in the solid phase, it was carefully poured into the instrument, preheated and placed in the horizontal position with the wires in place, and the system was cooled down rapidly. In this way the contact resistance between sample and wires was minimum as the finite elements comparison showed no sign of a temperature jump. For the measurements in the liquid phase, the liquid sample was poured in the glass cell and placed immediately in the bath at a temperature over its melting point, so as to keep it in the liquid phase. The technique is absolute and is characterized by an uncertainty of 1%.

At the 95% confidence level, the standard deviations of the thermal conductivity measurements of *n*-docosane, are 0.40% for the solid phase (267 K to 308 K), and 0.60% for the liquid phase (330 K to 361 K); of *n*-tetracosane, 0.60% for the solid phase (265 K to 306 K), and 0.30% for the liquid phase (339 K to 363 K); of 1,6-hexanediol, 0.70% for the solid phase (263 K to 296 K), and 0.40% for the liquid phase (327 K to 351 K); and of 1,8-octanediol 1.1% for the solid phase (265 K to 312 K), and 0.50% for the liquid phase (344 K to 356 K), respectively.

Author Contributions All authors contributed equally.

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Declarations

Competing interest The authors declare no competing interests of a financial or personal nature.

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