

Thermal Diffusivity of Linear Alkanes and its Behaviour with the Size of the Chain: Study with a Photopyroelectric Technique

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Abstract: - Thermal transport properties of substances are fundamental for science and engineering. Among these properties, thermal diffusivity characterizes the way materials transport heat under non-stationary conditions. The manner in which this thermal property behaves with the size or molecular configuration is very important to understand the mechanisms involved in heat transport. It is a complicated work to study variations on this thermal property taking these two variables (size and configuration) together. Linear alkanes have essentially the same spatial configuration, varying only the molecular size (the number of involved carbon atoms in the molecule), so they are ideal substances to study the behaviour of thermal properties with the molecular size alone. In this work photopyroelectric technique, taking the sample's thickness as variable (the so-called TWRC method), is used for thermal diffusivity measurements of linear alkanes, from 1-heptane to 1-heptadecane. It is shown that this thermal property increases with the molecular size. This behaviour can be explained in a very simple way if it is considered that the increase in molecular size increases "routes" of heat transport.

Key-Words: - Linear alkanes, Photothermal techniques, Thermal characterization, Thermal diffusivity, TWRC method, Molecular size

Received: September 1, 2019. Revised: February 17, 2020. Accepted: March 25, 2020. Published: April 30, 2020.

1 Introduction

The knowledge of thermal properties, especially for substances in liquid phase, is very important since this state of matter is widely used in industry, particularly as heat exchangers. The knowledge of these properties is also important in basic science since this information can be used to support theoretical schemes concerning molecular configurations, for instance. Under this perspective is interesting to figure out how the size or molecular configuration influences thermal properties. Photopyroelectric (PPE) techniques are now widely used for thermal characterization of liquids; this can be done by measuring thermal diffusivity, effusivity and specific heat [1-5]. PPE techniques, taking the sample's thickness as variable (the so-called Thermal Wave Resonator Cavity (TWRC)) [4-5], provides high-precision measurements of thermal

diffusivity, for which is ideal to carry out empirical studies about the influence of size or molecular configuration on this thermal property. However, the ideal situation is when this study is carry out taking only one of these two possible variables and linear alkanes result in ideal substances since these organic molecules have a tree configuration with chemical formula C_nH_{2n+2} , where C atoms are the vertebral column of the structure. With this idea in mind, the TWRC method is used for measuring the thermal diffusivity for a series of linear alkanes, from 1-heptane to 1-heptadecane, to figure out the influence of the molecular size on this thermal property.

2 Theoretical Considerations

Figure 1 shows a cross section of the PPE experimental setup for thermal diffusivity

measurements. Monochromatic radiation, at fix modulation frequency f , strikes a thin silicon slab; thermal waves (temperature fluctuations) generated inside this material travel to the liquid sample and reach the pyroelectric material (a thin PVDF foil). The signal is proportional to the average temperature inside the pyroelectric material. At this way solving the corresponding set of differential equations to find the temperature profile inside the pyroelectric sensor and under the appropriate experimental conditions. It can be shown that, if the liquid sample's thickness, l , is took as variable this photopyroelectric signal takes the very simple form:

$V(l) = He^{-\sigma l}$, where $\sigma = (1 + i)(\pi f/\alpha)^{1/2}$ is a complex parameter involving sample's thermal diffusivity and H is a complex expression which is independent of the sample's thickness [4-5]. Linear fits to the amplitude and phase of this equation renders parameter M , from which sample's thermal diffusivity can be obtained as $\alpha = \pi f/M^2$.

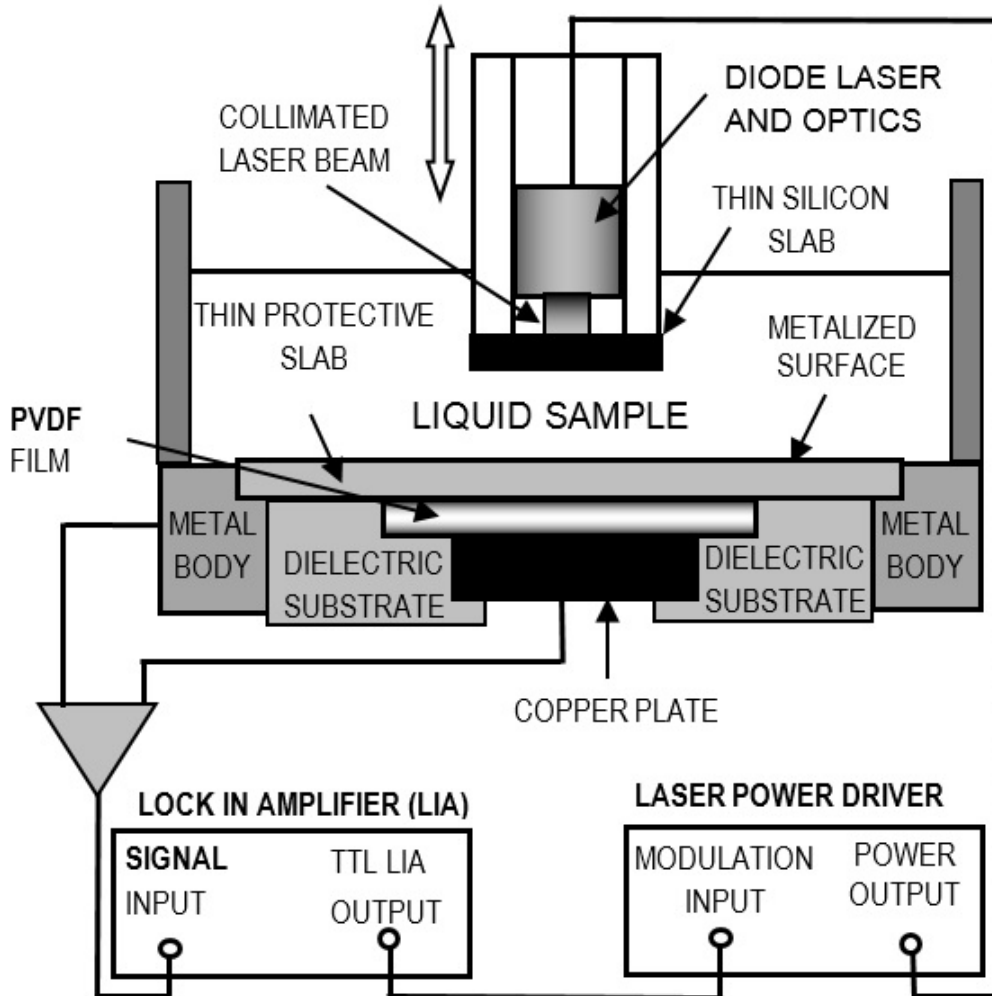


Figure 1. Cross section of the Photopyroelectric (PPE) set up for thermal diffusivity measurements.

3 Experimental Procedure

Ten linear alkanes, from 1-heptane to 1-heptadecane (Table I, column 1) were taken for the study. Thermal diffusivity measurements were carry out making the analysis on a set of 10 experimental data. These data consisted of PPE voltage amplitude for ten liquid sample's thicknesses, taken at increments of 0.0050 cm. Approximately 2 ml of liquid sample was required for each thermal diffusivity measurement. Linear fits were done to obtain slopes M for each sample from which the corresponding thermal diffusivity was calculated. All measurements were made at a fix modulation frequency of 1 Hz, setting the lock-in's time constant at 3 s and at room temperature of 23 °C.

4 Experimental Results

Figure 2 shows the linear behaviour of the photopyroelectric amplitude, as a function of the sample's thickness, for 1-undecane. The continuous line in this figure is the best linear fit as to obtain the parameter M , from which sample's thermal diffusivity can be obtained, as it was described above. All analytical procedures were carried out using commercial analytical software (Origin 6.1™) and the corresponding uncertainties were estimated by means of the usual formulas for error propagation. Thermal diffusivity values for all samples are summarized in Table 1, column 2. Figure 3 shows samples' thermal diffusivities as a function of the molecular size. It is evident that this thermal property increases with molecular size.

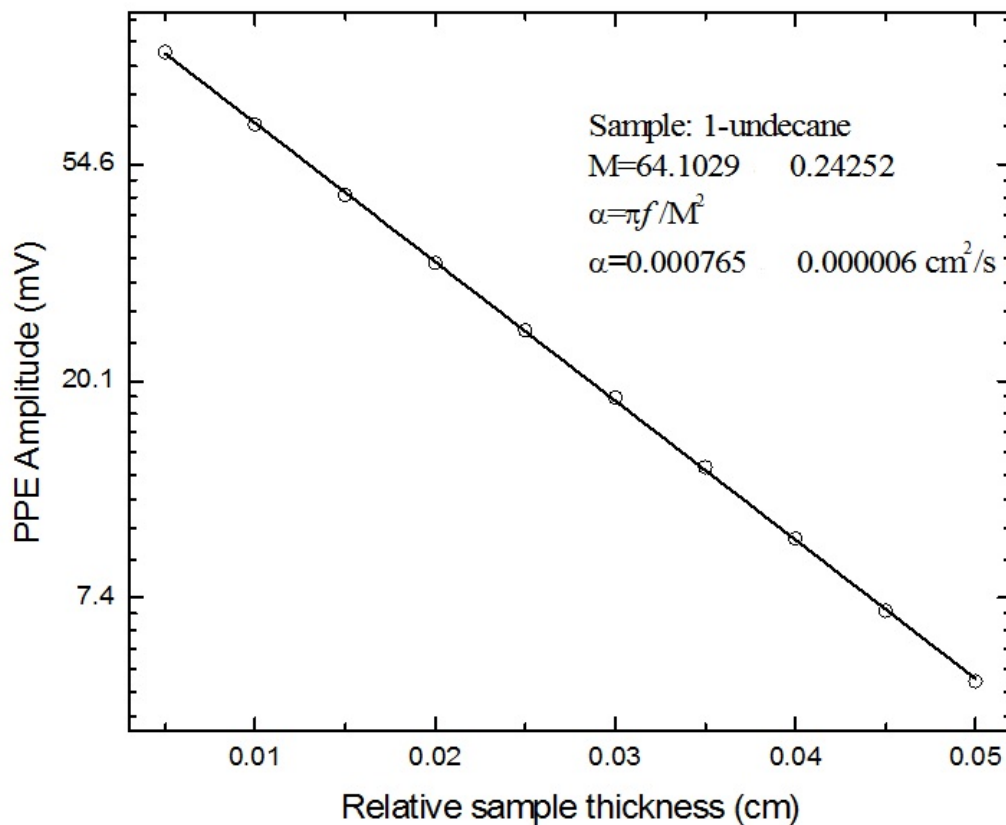


Figure 2. Photopyroelectric amplitude, as a function of the sample's thickness, for 1-undecane. The continuous line represents the best linear fit as to obtain parameter M , from which sample's thermal diffusivity can be obtained.

4 Conclusion

Photopyroelectric techniques (TWRC) were shown adequate for measuring thermal properties of 1-alkanes. It was empirically demonstrated that this thermal property increases with the molecular size, if molecular configuration is unchanged. This behaviour could be explained in a very simple form if it is considered that for this kind of molecules heat transport is due to vibrations or rotations of the C-H bonds. Increment of the molecular size increases the number of these bonds, providing at this way more “routes” of heat transport to the molecule and the final effect is an increment in thermal diffusivity. Similar behaviour for thermal conductivity could be expected, as suggested from thermal conductivities reported for 1-butane, 1-heptane and 1-decane [6]. The monotonic behaviour of this thermal property for 1-alkanes contrast with the one reported for 1-alcohols [7], which are linear molecules that differs from 1-alkanes only in an additional OH radical at one end. Thermal diffusivity decreases in this case

with the molecular size but this happens only for the first 5 alcohols (from methanol to 1-pentanol) then, starting at 1-hexanol, this thermal property increases with the increase of the molecular size. This peculiar behaviour of thermal diffusivity for linear alcohols can be explained as a “competition” of thermal properties between the OH-radical and the CH chain. For lineal alcohols of small size thermal diffusivity is driven for the OH radical meanwhile that for those ones of high molecular weight this thermal property is driven for CH bonds. In linear alkanes, the monotonic behaviour in thermal diffusivity can be then attributed to the thermal properties of the CH bonds and the chain’s size. These kind of molecules (alkanes and alcohols could be also used to figure out in what manner the molecular configuration influences the thermal properties) and the corresponding results could be complemented with computational simulations.

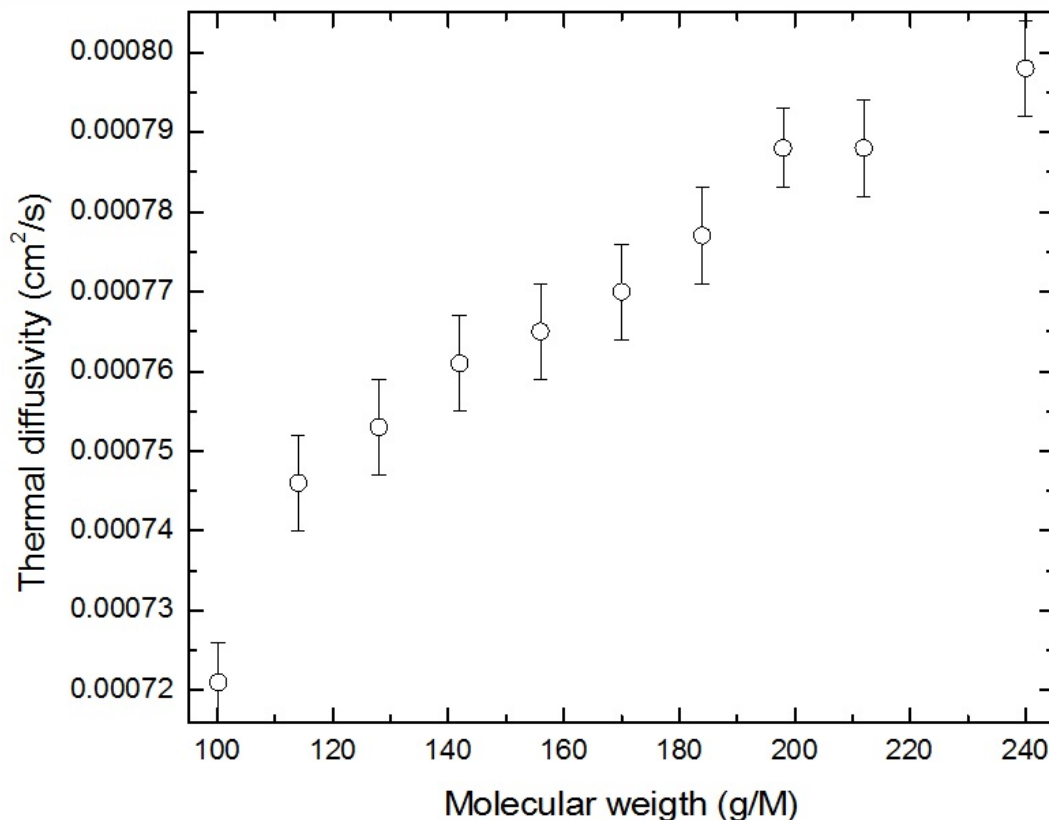


Figure 3. Thermal diffusivities, as a function of the sample’s molecular weight, for the 1-alkanes studied in this work.

Table 1. Thermal diffusivities, α , for the ten linear alkanes studied in this work.

Alkane	α (cm ² /s)
1-heptane	0.000721 ± 0.000005
1-octane	0.000746 ± 0.000006
1-nonane	0.000753 ± 0.000006
1-decane	0.000761 ± 0.000006
1-undecane	0.000765 ± 0.000006
1-dodecane	0.000770 ± 0.000006
1-tridecane	0.000777 ± 0.000006
1-tetradecane	0.000788 ± 0.000005
1-pentadecane	0.000788 ± 0.000006
1-heptadecane	0.000798 ± 0.000006

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