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Thermal transport properties of heptane-isooctane mixtures

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ABSTRACT

In this work, we perform measurements of the thermal transport properties of heptane-isooctane mixtures in the liquid phase at room temperature and atmospheric pressure. The thermal conductivity, k, was measured using the transient hot-wire (HW) method, and the thermal effusivity, e, was determined by the front photopyroelectric (FPPE) technique. Then, the thermal diffusivity, α, and the heat capacity per unit volume, C, were calculated using the well-known relationships $\alpha = (k/e)^2$ and $C = e^2/k$, respectively. We show that a correlation between these parameters and octane number exists, and that the obtained thermal parameters proved to be sensitive to detect molecular associations in binary hydrocarbon liquid mixtures. We also report about the thermal conductivity of mixtures of n-alkanes vapors and air showing that almost similar values are obtained for heptane and isooctane, so that octane number rating using the well-established binary mixtures of these substances becomes impossible with thermal properties measurements in the gas phase.

1. Introduction

There are four main thermal parameters involved in heat transport, namely the thermal conductivity, k, the thermal effusivity, e, the thermal diffusivity, α, and the heat capacity per unit volume, C (the product of mass specific heat and density). Accurate thermal properties data of fluids are important not only from the point of view of basic research, but also for many applications. In particular, measurement of thermal properties of n-alkanes (C_nH_{2n+2}) has deserved special attention because the importance of these parameters for improving the design of chemical plants and the energy efficiency of chemical processes [1]. For example, the development of a standard fuel rating system is based upon the fuel detonation characteristics on a special single engine with a variable compression ratio. Two pure substances were arbitrarily chosen to calibrate the test machines, namely isooctane ($n = 8$, one of the branched carbon chain isomers of octane, the straight chain of 8 carbon atoms with no branching) and n-heptane ($n = 7$), to which “octane” numbers of 100 and 0 have been assigned [2], respectively, being “octane” a general term used to indicate a fuel ability to resist engine knock. The sensitivity of the fuel rating parameters on the thermodynamic parameters has inspired the use of thermal properties, in particular the thermal diffusivity, as figure of merit for fuel characterization. Cardoso et al [3] and Lima et al [4] proposed the use of a thermal wave interferometer (TWI), also named thermal wave resonator cavity (TWRC) [5–7], to measure the thermal diffusivity of the air/fuel vapors mixture resulting from the fuel evaporation. These authors used hexane-isooctane mixtures to show that a correlation between thermal diffusivity of air saturated with vapor of this mixture and octane number exists. The use of hexane instead of the widely used heptane was justified by the simple reason that a larger variation of thermal diffusivity as a function of concentration was observed for mixtures of isooctane and hexane than for mixtures of isooctane and heptane [3]. The fact that very little difference was observed in the value of thermal diffusivity for air saturated with the heptane and isooctane vapors is further investigated in this work by measurements of the thermal conductivity for the same kind of samples. Here, we also performed measurements of the thermal transport properties of heptane-isooctane mixtures in the liquid phase at room temperature and atmospheric pressure. The thermal conductivity was measured using the transient hot-wire (HW) method [8,9] and the thermal effusivity was determined by the front photopyroelectric (FPPE) technique [10]. Then, the thermal diffusivity and the heat capacity per unit volume were calculated respectively using the well-known relationships $\alpha = (k/e)^2$ and $C = e^2/k$. We show that a correlation between these parameters and the relative concentration of the mixtures components (i.e. the octane number) exists, and that the obtained thermal parameters proved to be sensitive to detect molecular associations in binary hydrocarbon liquid mixtures.

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2. Experimental details

2.1. The hot wire technique

The hot wire apparatus used in this work is described in detail elsewhere [11,12]. It is based on the measurement of the temporal evolution of the temperature rise, ΔT, caused by a linear heat source (hot wire) embedded in a test sample. This temporal behavior depends on the thermal conductivity of the sample. In our approach this parameter is determined straightforwardly from the linear part of a graph of the voltage drop across the heated wire, which is proportional to ΔT, as a function of the natural logarithm of the measurement time, t. It can be straightforwardly demonstrated that this voltage drop is given by

$$\Delta V(t) = V(t) - V_0 = IR_0\sigma\left[\frac{q}{4\pi k}\ln\left(\frac{4t\alpha}{r^2 C}\right)\right] \tag{1}$$

where I is the heating electrical current, R_o is the electrical resistance of the wire when $\Delta T = 0$, σ is the temperature coefficient of the wire´s resistivity, k is the thermal conductivity of the sample, α is its thermal diffusivity, r is the wire radius, $\ln(C) = \gamma = 0.5772$ is the Euler`s constant and $q = I^2R_0/L$ is the heat flow per unit length of the source. It is easy to see from Eq. (1) that the slope of the ΔV versus ln (t) curve is

$$m = \frac{I^3R_0^2\sigma}{4\pi Lk} \tag{2}$$

A multi-current approach described elsewhere [11] is used here to allow that the selected linear region is the one that matches the conditions imposed by the theoretical model associated to the technique. In this approach, ΔV as a function of ln(t) curves are recorded for several values of the electrical current, I. Then, the slopes m of the linear regions of these curves are calculated and plotted as a function of I in a double logarithmic graph. If, according to Eq. (2) the slope of this graph is near to 3, then one can be sure that the selected linear regions in the curves of ΔV versus ln(t) are those in which the conditions imposed by the theoretical model are well satisfied. One can see from Eq. (2) that the m versus I^3 graph is a straight line, with a slope given by

$$b = \frac{R_0^2\sigma}{4\pi Lk} \tag{3}$$

from which the thermal conductivity can be obtained straightforwardly if R_0, L, and σ are well known.

The experimental set-up is shown schematically in Fig. 1(a).

The heat source is a 76.2 µm diameter platinum wire (*Alfa Aesar*) of length L = 70.5 mm, mounted on a Teflon support that is introduced into a 15 cm long and 3.54 cm diameter glass cylindrical container. For measurements in the liquid phase the whole wire is covered by the sample, whereas for vapor phase measurements 1 mL of the liquid sample are carefully deposited below the wire´s support as shown schematically in part b of the figure. The wire is heated by Joule´s effect using an electrical current stabilized power supply (Keithley 2400) and the voltage drops are measured with a nanovoltmeter (Keithley 2182 A). The sample container is thermally stabilized at 295 K (room temperature) using a commercial thermal bath (Julabo FP50) not shown in the figure. The experimental system was previously tested by thermal conductivity measurements in samples of air, distilled water, glycerol, ethylene glycol and methanol (see Table 1). Obtained values for these well-known samples are given in Table 2.

Table 1
Samples used. All samples were used as provided, without further purification.

Chemical name	Source	Initial mole fraction purity / mol%
Glycerol	J.T. Baker [13]	99.9
Ethylene glycol	J.T. Baker [13]	99.9
Methanol	J.T. Baker [13]	99.9
n-pentane	Sigma Aldrich [14]	98
n-hexane	Sigma Aldrich [14]	≥ 95
n-heptane	Sigma Aldrich [14]	99
n-octane	Sigma Aldrich [14]	98
n-nonane	Sigma Aldrich [14]	98
n-decane	Sigma Aldrich [14]	98
Isooctane	Sigma Aldrich [14]	≥ 99

Table 2
Thermal conductivity and effusivity measured with the Hot-wire and the Photopyroelectric Technique respectively for well-known samples at room temperature, T = 295 K and atmospheric pressure, p = 0.077 MPa. The numbers after the sign ± represent the standard uncertainties. The maximum value for the relative standard uncertainty of k is 2% for the liquid samples; while this value is increased to 4% for air (it is a typical result for our hot wire experiments that uncertainties are greater for measurements in the gas phase than for liquid samples). Maximum value for the relative standard uncertainty of e is 0.6%. The thermal effusivity of air is not reported because this substance was the reference sample used for thermal effusivity measurements in liquids. Standard uncertainties u are u (T) = 1 K, u (p) = 2 kPa.

Test sample	k/Wm^{-1}K^{-1}	k_{lit} /Wm^{-1}K^{-1}	e/Ws$^{1/2}$m^{-2}K^{-1}	e_{lit} /Ws$^{1/2}$m^{-2}K^{-1}
Distilled water	0.60 ± 0.01	0.59 [11]	1592 ± 10	1582 [16]
Glycerol	0.289 ± 0.005	0.288 [11]	931 ± 5	929 [17]
Ethylene glycol	0.254 ± 0.005	0.252 [11]	810 ± 4	805 [16]
Methanol	0.208 ± 0.004	0.208 [11]	621 ± 4	626 [17]
Air	0.026 ± 0.001	0.026 [15]	–	–

2.2. The front photopyroelectric technique

The photopyroelectric (PPE) technique in the front detection configuration [10] has been emerged as one of the most useful methods for measurements of thermal effusivity [18]. In this technique, the sample is located at the rear side of a pyroelectric (PE) sensor, while an intensity modulated light beam impinges on the PE front face, so that the sample acts as a heat sink, while the PE sensor acts as both, a source of heat propagating through the PE-sample system, and as the detector of them. Because of the induced temperature oscillations, a voltage, V, is

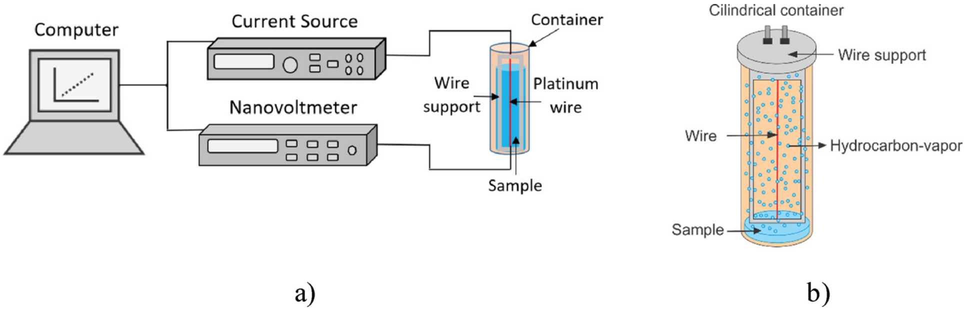

Fig. 1. a) The experimental set-up for the hot wire technique (schematically). b) Sample container for measurements in gas phase. (in color only in online version).