Trends in Heat & Mass Transfer
Vol. 13, 2013

Original Communication

Thermal characterization of Diglyme by using photopyroelectric spectroscopy

A. Cruz-Orea[1,*], F. Sánchez-Sinencio[1], M. A. Algatti[2], J. L. Jiménez-Pérez[3], Z. N. Correa-Pacheco[3] and A. García-Quiroz[4]

[1]Departamento de Física, Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional, Av. Instituto Politécnico Nacional 2508 Col. San Pedro Zacatenco, C.P. 07360 México, D.F., México. [2]FEG-DFQ-UNESP, Campus de Guaratinguetá, Av. Ariberto Pereira da Cunha 333, CEP: 12516-410, Guaratinguetá, S.P., Brazil. [3]Unidad Profesional Interdisciplinaria en Ingeniería y Tecnologías Avanzadas, Avenida Instituto Politécnico Nacional No. 2580, Col. Barrio la Laguna Ticomán, C.P. 07340, México D.F., México, [4]Universidad Autónoma de la Ciudad de México, Fray Servando Teresa de Mier 92, Col. Centro, C.P. 06080, México D.F., México

ABSTRACT

Photopyroelectric spectroscopy was used for thermal characterization of the solvent diethylene glycol dimethyl ether (Diglyme). Photopyroelectric detection is based on the measurement of an electrical signal due to temperature variations in a pyroelectric detector. In this work, two configurations of the photopyroelectric technique were used. The sample thermal diffusivity (α_s) was measured by using the thermal-wave resonator cavity (TWRC) configuration and the thermal effusivity (e_s) was obtained by using the inverse photopyroelectric (IPPE) configuration. From the obtained values of α_s and e_s the thermal conductivity (k) and heat capacity per unit volume (ρc) were calculated through the relationships $k = e_s (\alpha_s)^{1/2}$ and $\rho c = e_s/(\alpha_s)^{1/2}$. On comparing the obtained k value for the Diglyme sample with some reference data reported in the literature, it was found that the reported k value for diethylene glycol diethyl ether (compound with a similar structure to Diglyme) is similar to the obtained k value for Diglyme in the present study. To our knowledge the thermal characterization of Diglyme has not been reported until now.

*Corresponding author: orea@fis.cinvestav.mx

KEYWORDS: photopyroelectric technique, Diglyme, thermal diffusivity, thermal effusivity, thermal conductivity

INTRODUCTION

Photothermal techniques are based on the measurement of temperature fluctuations in a sample due to a process of non-radiative de-exitation after modulated light beam absorption. The thermal wave propagation depends on the thermal diffusivity in the material [1]. These techniques have been used for the optical and thermal characterization in a wide variety of materials ranging from solids [2-3], liquids [4-5] to gases [6-7]. The first use of a pyroelectric (PE) detector for the measurement of the photothermal response of a sample in contact with a PE sensor and excited by a laser beam, at different modulation frequencies, was reported by Mandelis and Coufal [8-10]. There are several configurations of the photopyroelectric technique, including the thermal-wave resonator cavity (TWRC) and inverse photopyroelectric (IPPE) configurations.

TWRC is a simple and highly accurate experimental photothermal technique and some modifications have been used to measure thermal diffusivity of gases such as air, nitrogen, hydrogen, methane, helium [7, 11-13] and gasoline vapors [11], and liquids including mixtures such as water-ethanol [13] and also silicone oil [14]. Its high sensitivity to thermal diffusivity inside the cavity is due to the exponential dependence of the photopyroelectric (PPE) signal with the sample thickness at a fixed modulation frequency. The evaluation of thermal diffusivity by using TWRC involves the fitting of the experimental data as a function of the cavity length or the modulation frequency [7, 11].

The concept of inverse photopyroelectric configuration (IPPE) was introduced by Dadarlat [15] and the thermal effusivity is a physical property that can be directly measured by using this technique. This thermal property is defined as $e_s = (k\ \rho\ c_p)^{1/2}$, where k, ρ and c_p are the thermal conductivity, density and the specific heat at constant pressure, respectively [16]. For a given sample, the thermal efussivity is related to the amount of heat that passes inside the material when its surface suffers a temperature increment in a certain period of time [5]. The main advantage of this configuration compared to the standard configuration (when the light beam impinges directly to the sample), is that any detection problem related to the optical properties of the sample (transparency, thermal reflectance) is avoided. A simple calculation of the sample thermal effusivity is possible in a frequency range when the sample is thermally thick [15]. The IPPE configuration has been used to measure thermal parameters of some materials such as Cr_2O_3 crystals [15], tomato paste [16], and liquids such as fatty acids and triglycerides [5], among others.

Diglyme is a monomer, in liquid form, that can be polymerized with cold plasma technique and one of its main characteristics is its antibacterial property [17-18]. Therefore one of its main applications is as a coating for contact lenses [19-20]. In this kind of applications the permeability, the optical, mechanical and thermal properties are important [21].

In this work the thermal diffusivity and thermal effusivity of Diglyme were measured, by using the TWRC and IPPE techniques. Water was used for calibration in both techniques. One of the advantages of using these techniques is that there is a best fit between theoretical equations and experimental data, which result in more accuracy of obtained values.

MATERIALS AND METHODS

TWRC

Diethylene glycol dimethyl ether (Dyglime) from Sigma-Aldrich was characterized. Figure 1 shows photopyroelectric scheme used for Diglyme thermal diffusivity (α_s) measurement. In the TWRC configuration the liquid sample is contained in a cavity between a thin metallic light absorbing material and a pyroelectric sensor (PE). In this configuration, a modulated beam with a modulation frequency *f*, hit the frontal surface of an opaque sample (thin metallic light absorbing material makes the transparent liquid sample opaque) and a pyroelectric sensor (polyvinylidene fluoride (PVDF)) located at the back of the sample, with good thermal contact. The sensor detects temperature changes in the simple due to radiation absorption, followed by a non-radiative de-exitation process. The pyroelectric signal as a function of the sample thickness was measured with a step of 10 microns as shown in Figure 1.

It has been shown that photopyroelectric signal for a configuration as showed in Figure 1, at a fixed modulation frequency of incident beam *f*, when the simple is thermally thick, can be calculated using the following equation [10]:

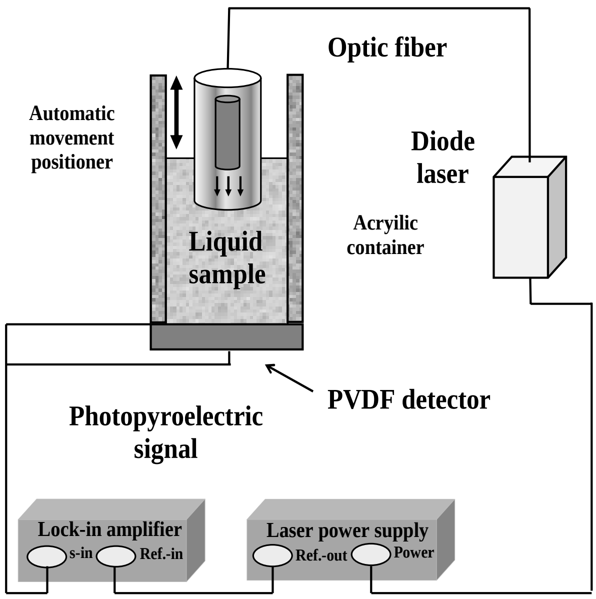

Figure 1. Experimental arrangement used for thermal diffusivity measurement of Dyglime.

$$V(L,\alpha_l,\omega)=C(\omega)\times e^{-\sigma_l L} \tag{1}$$

where: V Output pyroelectric detector signal
L Sample thickness
σ_l Complex thermal diffusivity coefficient

The magnitude of the complex expression can be written:

$$V(L,\alpha_l,\omega)=C(\omega)\times e^{-AL} \tag{2}$$

where: $A=(\pi f/\ \alpha_s)^{1/2}$

The process consists of the measurement of the pyroelectric detector signal as a function of the cavity length and then making a fit of the equation (2) with the experimental data. The equation (2) changes to a lineal expression when the data are in a semi-log scale for the amplitude. Then, the thermal diffusivity is obtained from the slope corresponding to A parameter. Experimental measurements were performed at a fixed frequency of f = 25 Hz.

IPPE configuration

In order to obtain a complete thermal characterization, it is necessary to know other thermal parameter. By using the inverse photopyroelectric configuration (IPPE), it is possible to calculate the thermal effusivity. The IPPE experimental scheme is shown in Figure 2.

In the inverse photopyroelectric technique a modulated light beam impignes the PVDF pyroelectric detector and the sample at the back is in contact with the detector. The photopyroelectric signal is a function of the light modulation frequency and the sample thermal effusivity is obtained by fitting the theoretical expression for this configuration [22] with the experimental data, for a thermally thick sample:

$$\theta(\omega) = [(1 - e^{\sigma plp})(1 + b) + (e^{-\sigma plp} - 1)(1 - b)]/ [(g - 1)e^{-\sigma plp} (1 - b) + (1 + g)e^{\sigma plp} (1 + b)] \tag{3}$$

where: $\theta(\omega)$ is proportional to the output signal of the pyroelectric detector, l_p is the detector thickness, $b = e_s/e_p$, $g = e_g/e_p$, where e_s, e_p and e_g are the thermal effusivities of the sample, the detector and air, respectively, $\sigma_p = (1+j) A_p$, is the complex thermal diffusivity coefficient of the pyroelectric detector, $j = (-1)^{1/2}$ and $A_p = (\pi f/\alpha_p)^{1/2}$, where α_p is the thermal diffusivity of the pyroelectric detector. The output signal was normalized with respect to the detector signal as a function of frequency.

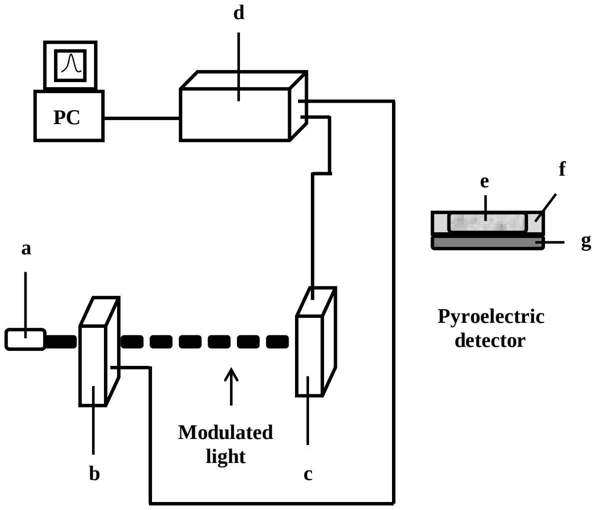

Figure 2. Experimental scheme for the inverse photopyroelectric technique. The elements correspond to: a) He-Ne laser, b) Acousto-optic modulator, c) Photopyroelectric detector (shown in detail in the right figure), d) Lock-in amplifier. Details of the detector: e) Dyglime sample, f) sample container (O-ring), g) PVDF pyroelectric detector.

RESULTS AND DISCUSSION

Figure 3 shows the best fit of Eq. (2) (solid line) with the experimental data (solid squares). From the slope of the linear fit the A value was obtained and by using this value the thermal diffusivity of Diglyme was found.

From the Figure 3, the A value corresponds to the thermal diffusivity of Dyglime with a value of $(24.3 \pm 2.7) \times 10^{-8}$ m^2/s.

Thermal effusivity was obtained by using the IPPE configuration. Figure 4 shows the signal amplitude as a function of the incident beam modulated frequency for the Diglyme sample. The solid line corresponds to the best fit of equation (3) with the normalized amplitude signal.

From the best fitting of the amplitude of equation (3) with the PPE normalized amplitude signal data, thermal efussivity value of e_s = (280 ± 30) W $s^{1/2}/(m^2$ K) was obtained. By using the obtained values of thermal diffusivity (α_s) and thermal effusivity (e_s), the thermal conductivity (k) was

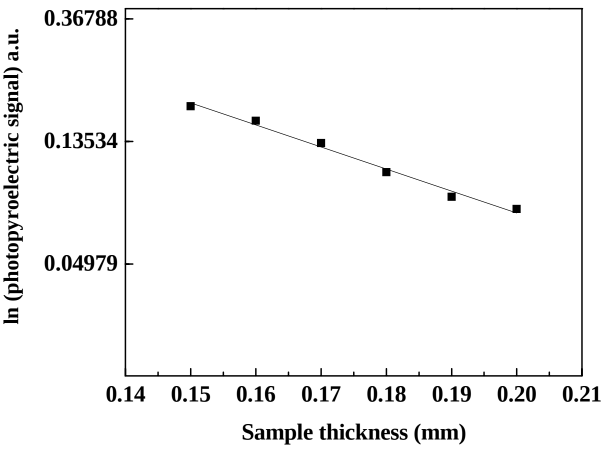

Figure 3. Ln (PPE signal) as a function of sample thickness. The symbols correspond to the experimental data and the solid line is the best fit of the equation (2) with the experimental data.

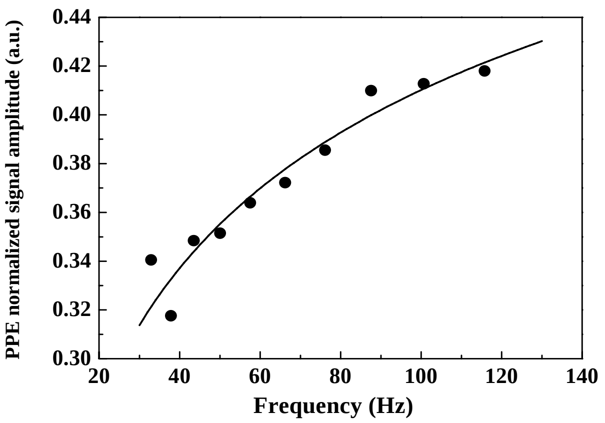

Figure 4. Photopyroelectric amplitude signal as a function of the incident light beam frequency. The solid line corresponds to the best fit of complex equation (3) with the normalized amplitude signal.

calculated from the relationship ($k = e_s\ (\alpha_s)^{1/2}$). The calculated value was $k = (0.14 \pm 0.01)$ W/(m K). Also the specific heat capacity was obtained from equation $\rho c = e_s/(\alpha_s)^{1/2} = (5.68 \pm 0.67) \times 10^5$ J/(m^3 K), that relates experimentally obtained thermal parameters with the sample heat capacity per volume unit.

In order to compare the obtained data with some reported values, thermal properties for a substance similar to Diglyme was found from the literature. It was found that for diethylene glycol diethyl ether (a substance with similar chemical structure of Diglyme) has a reported thermal conductivity of k = 0.15 W/(m K) [23]. This value of conductivity is near to the obtained value for Dyglime ($k = (0.14 \pm 0.01)$ W/(m K)), which supports our results. To our knowledge the thermal characterization of Diglyme has not so far been reported in the literature.

CONCLUSIONS

Photopyroelectric spectroscopy was used for thermal characterization of the diethylene glycol dimethyl ether (Diglyme) solvent. Two configurations of the photopyroelectric technique were used. The thermal diffusivity (α_s) was measured by using the thermal-wave resonator cavity (TWRC) configuration and the thermal effusivity (e_s) was obtained by using the inverse photopyroelectric (IPPE) configuration. The obtained thermal diffusivity value for Diglyme was $(24.3 \pm 2.7) \times 10^{-8}$ m^2/s and the thermal effusivity value was $e_s = (280 \pm 30)$ W $s^{1/2}$/(m^2 K). From the thermal diffusivity and thermal effusivity values obtained, thermal conductivity was calculated, $k = (0.14 \pm 0.01)$ W/(m K). The specific heat capacity per volume unit calculated was $\rho c = (5.68 \pm 0.67) \times 10^5$ J/(m^3 K). The obtained k value was compared with the reported value in the literature for Diethylene glycol diethyl ether (a substance with a chemical structure similar to Dyglime) and the values were found to be very similar. To our knowledge, the thermal characterization of Dyglime was reported for the first time in this study.

REFERENCES

1. Lima, J., Marín, E., Massunaga, M., Correa, O., Cardoso, S., Vargas, H. and Miranda, L. 2001, Appl. Phys. B, 73, 151.
2. Philip, J., Majusha, M. and Soumya, H. 2011, Rev. Sci. Instrum., 82, 104901.
3. Depriester, M., Hus, P., Delenclos, S. and Sahraoui, H. 2005, Rev. Sci. Instrum., 76, 074902.
4. Neamtu, C., Dardalat, D., Chirtoc, M., Sahraoui, H., Longuemart, S. and Bicanic, D. 2006, Instrum. Sci. Technol., 34, 225.
5. Menon, P. C., Rajesh, R. N. and Glorieux, C. 2009, Rev. Sci. Instrum., 80, 054904.

6. Wang, C. and Mandelis, A. 1999, Rev. Sci. Instrum., 70, 2372.
7. Shen, J., Mandelis, A. and Ashe, T. 1998, Int. J. Thermophys., 19, 579.
8. Mandelis, A. 1984, Chem. Phys. Lett., 108, 388.
9. Coufal, H. 1984, Appl. Phys. Lett., 45, 516.
10. Mandelis, A. and Zver, M. 1985, J. Appl. Phys., 57, 4421.
11. Shen, J., Mandelis, A. and Aloysius, D. 1996, Int. J. Thermophys., 17, 1241.
12. Kwan, C., Matvienko, A. and Mandelis, A. 2007, Rev. Sci. Instrum., 78, 104902.
13. Matvienko, A. and Mandelis, A. 2005, Int. J. Thermophys., 26, 837.
14. Delenclos, S., Dardalat, D., Houriez, N., Longuemart, S., Kolinsky, C. and Sahraoui, H. 2007, Rev. Sci. Instrum., 78, 024902.
15. Dadarlat, D. and Frandas, A. 1993, Appl. Phys. A, 56, 235.
16. Bicanic, D., Neamtu, C., Manojlović, M., van der Linden, D., Dardalat, D., Posavec, K., Gijsbertsen, A. and Kurtanjek, Ž. 2004, Acta Chim. Slov., 51, 39.
17. Mar, M. N., Ratner, B. D. and Yee, S. S. 1999, Sensors and Actuators B, 54, 125.
18. Kwok, S., Horbett, T. A. and Ratner, B. D. 1999, J. Control. Release, 62, 301.
19. Paterniani, C. C. and Algatti, M. A. 2003, Proceedings of the 7th Brazilian Congress of Polymers, Brasil, 453.
20. Bruisma, G. M., van der Mei, H. C. and Busscher, H. J. 2001, Biomaterials, 22, 3217.
21. Shimoyama, N., Yokota, M. and Uemura, T. 2008, patent no. US7435452.
22. Caerels, J., Glorieux, C. and Thoen, J. 1998, Rev. Sci. Instrum., 69, 2452.
23. Slawecki, T. and Moldstad, M. 1956, Ind. Eng. Chem., 48, 1100.