

Scientific paper

Photopyroelectric Investigation of Thermal Effusivity of Binary Liquid Mixtures by FPPE-TWRC Method

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Abstract

An alternative front photopyroelectric configuration (FPPE) that uses the thermal wave resonator cavity method (TWRC) is proposed for measuring the thermal effusivity of a liquid, inserted as backing in the detection cell. A theory for a 5 layers (air, sensor, coupling fluid, solid separator layer, and liquid backing) detection cell is developed. The method seems to be particularly suitable when measuring the thermal effusivity of binary liquid mixtures. If the coupling fluid is one component of the binary mixture, the technique acts a “quasi-differential” method and low concentration of the second component of the mixture can be detected. In the paper the method was applied to binary liquid mixtures of water with ethanol, ethylene glycol and DMSO.

Keywords : Liquid mixtures, thermal effusivity, photopyroelectric method, TWRC.

1. Introduction

In the photopyroelectric (PPE) calorimetry one can combine different detection configurations (usually two - “back” or “front”), sources of information (PPE amplitude or phase) and scanning parameters (chopping frequency or sample’s thickness), in order to obtain the dynamic thermal parameters of a condensed matter material.^{1–4}

If we restrict our attention to the front photopyroelectric (FPPE) configuration, it was largely used in the past to obtain thermal parameters of (semi)liquid and solid samples.^{3,5–7} In the FPPE configuration, the radiation impinges on the front surface of the pyroelectric sensor, and the sample, in good thermal contact with its rear side, acts as a heat sink. In principle, a FPPE detection cell contains four layers: air, directly irradiated sensor, solid or liquid sample, and a semi-infinite backing material. The value of the dynamic thermal parameters (thermal diffusivity, effusivity or conductivity) of the layers (sensor, sample or backing) of the detection cell could be obtained by performing frequency or thickness (in the case of liquid

samples) scans of the amplitude or phase of the FPPE signal. The thickness scanning procedure is associated with the so called thermal-wave resonator cavity (TWRC) method, introduced about 10 years ago by Mandelis and co-workers and developed later by others groups.^{9–14} The TWRC method, in the back detection configuration (BPPE), showed to be suitable and very accurate for investigating thermal properties (especially thermal diffusivity) of liquids.^{10,15}

Recently, we proposed a combined FPPE-TWRC method with the purpose of measuring the thermal effusivity of a solid material (inserted as backing in the detection cell).^{16,17} The main advantage of this configuration is connected with the possibility of monitoring the properties (type and thickness) of the coupling fluid, in order to obtain the thermal effusivity of a solid. More specific, the advantages of the TWRC method on frequency scanning procedures are: (i) the absolute value of coupling fluid’s thickness is not always necessary – its thickness variation is sometimes enough; (ii) the method gives the possibility of keeping a thermally thin/thick regime for different layers of the detection cell (sensor, backing, eventually a

separator layer) and, in the mean time, changing the thermal regime of the scanned liquid from thermally thin to thermally thick; (iii) the normalization signal is contained in the same scanning run (thermally very thick regime for the coupling fluid) and consequently, no additional normalization measurement is necessary. Finally, the method proved to be suitable especially in the case when the value of the thermal effusivity of the investigated backing material was close to the thermal effusivity of the coupling fluid.¹⁷

Starting from this last remark, we propose in this paper the use of the very same FPPE-TWRC technique to measure the thermal effusivity of a liquid sample, inserted as a backing in the detection cell.

The value of the thermal effusivity of a liquid was obtained in the past by measuring single values (constant thickness and chopping frequency) of the amplitude of the FPPE signal in the thermally thin and optically opaque or semi-transparent regime for the sensor and thermally thick regime for the liquid sample.^{5,8} Later on, the thermal effusivity of a liquid was measured, in the FPPE configuration, by performing a frequency scan of the phase of the PPE signal, in the thermally thick regime for the sensor and sample and optically opaque sensor.^{18–21} Both methods require calibration procedures involving air, or liquids with known values of thermal parameters, as reference.

The method proposed in this paper makes use of one measurement and involves two liquids: one, acting as coupling fluid and a second one inserted as a backing material. In such a way the method can be a “quasi-differential” one if applied to binary mixtures with one component of the mixture as coupling fluid (acting as reference).

1. 2. Theory

The schematic diagram of the detection cell is a classical one for FPPE configuration (Figure 1). In the case of a liquid backing, it includes 5 layers: semi-infinite air (0), directly irradiated sensor (1), coupling fluid (2), solid separator layer (3) and a semi-infinite liquid backing (4).

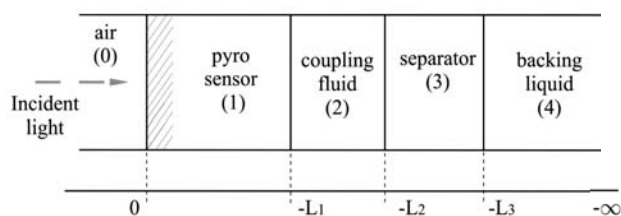


Figure 1. Layout of the 5 layers detection cell in the FPPE-TWRC configuration.

For such a cell, the temperature across the directly irradiated pyroelectric sensor is given by¹⁸:

$$\Theta(x) = \frac{H_0}{4k_1\sigma_1} \frac{(1 + R_{01}) \left[e^{-\sigma_1 x} + \rho_{21} e^{-\sigma_1(2L_1-x)} \right]}{1 - R_{01}\rho_{21} e^{-2\sigma_1 L_1}} \quad (1)$$

where H_0 represents the incident flux and

$$R_{01} = \frac{1 - b_{01}}{1 + b_{01}} = 1$$

$$\rho_{21} = \frac{(1 - b_{21}) + \rho_{32}(1 + b_{21})e^{-2\sigma_2 L_2}}{(1 + b_{21}) + \rho_{32}(1 - b_{21})e^{-2\sigma_2 L_2}} \quad (2)$$

$$\rho_{32} = \frac{(1 - b_{32}) + \rho_{43}(1 + b_{32})e^{-2\sigma_3 L_3}}{(1 + b_{32}) + \rho_{43}(1 - b_{32})e^{-2\sigma_3 L_3}}$$

$$\rho_{43} = \frac{1 - b_{43}}{1 + b_{43}}$$

In order to obtain the photopyroelectric signal, we have to integrate Eq. (1) over the thickness of the pyroelectric sensor.

$$V = \int_0^{-L_1} \Theta(x) dx \quad (3)$$

A similar theoretical procedure can be applied for a 3 layer detection cell (air, sensor and semi-infinite coupling fluid).

If we normalize the signal obtained with a 5 layers cell to the signal obtained with semi-infinite coupling fluid, we obtain for the normalized complex FPPE signal:

$$V_n = \frac{1 - R_{21} e^{-2\sigma_1 L_1}}{1 - \rho_{21} e^{-2\sigma_1 L_1}} * \frac{(e^{-\sigma_1 L_1} - 1) - \rho_{21}(e^{-\sigma_1 L_1} - e^{-2\sigma_1 L_1})}{(e^{-\sigma_1 L_1} - 1) - R_{21}(e^{-\sigma_1 L_1} - e^{-2\sigma_1 L_1})} \quad (4)$$

with

$$R_{21} = \frac{1 - b_{21}}{1 + b_{21}} \quad (5)$$

In Eqs. (1–5) $\sigma_j = (1 + i)a_j$, $\mu = (2\alpha/\omega)^{1/2}$, $b_{ij} = e/e_j$, α and e are the thermal diffusivity and effusivity, ω is the angular chopping frequency of radiation, σ and a are the complex thermal diffusion coefficient and the reciprocal of the thermal diffusion length ($a = 1/\mu$), respectively.

The normalized FPPE signal, described by Eq. (4), contains no approximation concerning the thermal thickness of the layers of the detection cell. It assumes only one-directional propagation of the heat and optical opacity for the sensor. In principle Eq. (4) allows the direct measurement of thermal diffusivity and/or effusivity of the layers 1–3 of the cell, and the thermal effusivity of the backing material.

In the paper we will use as source of information the phase of the PPE signal, which is more convenient from

experimental point of view, and we will focus on the direct measurement of backing's thermal effusivity. As was demonstrated in previous papers,^{16,17} the value of the thermal effusivity of the backing material results from a fit of the phase of the FPPE signal (Eq.(4)) with the sample's absolute thickness and backing's thermal effusivity as fitting parameters.

Figure 2 displays mathematical simulations for the behaviour of the phase of the FPPE signal as a function of coupling fluid's thickness, for a detection cell composed by a 100 μm thick LiTaO_3 sensor, 100 μm thick glass separator, water as coupling fluid and ethylene glycol and ethanol as backing materials, respectively. The shape of the phase is similar with that obtained with a 4-layer cell (separator missing), but the curves are shifted towards lower coupling fluid's absolute thicknesses.

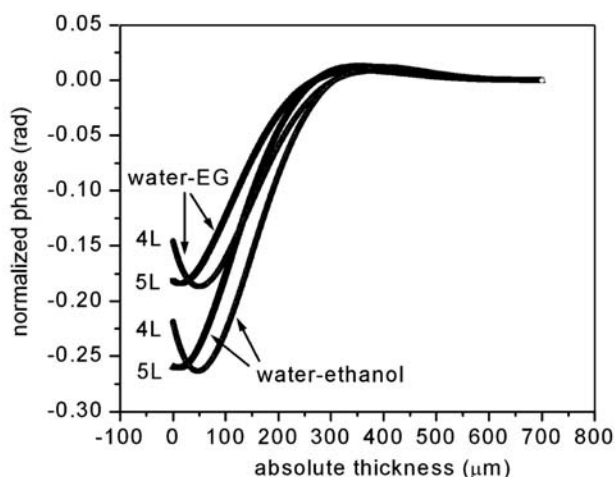


Figure 2. Mathematical simulation of the normalized phase of the FPPE signal as a function of coupling fluid's thickness (Eq. (4)), for a detection cell composed by 100 μm thick LiTaO_3 sensor, water as coupling fluid, 100 μm thick glass separator and ethanol and ethylene glycol backings, respectively. The chopping frequency was 1 Hz. Comparison with a 4-layer cell (separator missing) is also displayed.

2. Experimental set-up

The experimental set-up is classical for FPPE calorimetry, and it was largely described before^{15–17}. Only some details will be presented here.

The pyroelectric sensor, a 100 μm thick LiTaO_3 single crystal ($e_1 = 3.92 \times 10^3 \text{ W s}^{1/2} \text{ m}^{-2} \text{ K}^{-1}$; $\alpha_1 = 1.56 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$), provided with Cr-Au electrodes on both faces, is glued on a rotating stage. The liquid-backing material is accommodated by a 1cm thick and 1cm in diameter glass cylinder, situated on a micrometric stage. The coupling fluid fills the space between the rear side of the sensor and a thin solid foil (separator), glued on the top of the glass cylinder. The coupling fluid's thickness variation is per-

formed with a step of 0.03 μm (9062M-XYZ-PPP Gothic-Arch-Bearing Picomotor) and the data acquisition was taken each 30-th step. The modulated radiation (30 mW He-Ne laser) is partially absorbed by the front electrode of the sensor. The "rough" control of the coupling fluid's thickness and the parallelism between separator and sensor are assured by 3 and 6-axis micrometric stages. During the scanning procedure, the sample's thickness variation is very rigorously controlled, but the absolute sample's thickness is not precisely known. Its correct value is obtained, as explained in the theoretical section, only as a result of a fitting procedure.

All the measurements were performed at room temperature. The FPPE signal was processed with a SR 830 lock-in amplifier. The data acquisition, processing and analysis were performed with adequate software.

In our experiment, the coupling fluid was water ($e_2 = 16.0 \times 10^2 \text{ W s}^{1/2} \text{ m}^{-2} \text{ K}^{-1}$; $\alpha_2 = 14.6 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$) and binary mixtures of water with ethylene glycol, ethanol and DMSO, were inserted as backing materials. Several foils (glass, quartz, mica) were tested as separators between the coupling fluid and liquid backing. Finally we selected a 100 μm thick glass foil ($e_3 = 15.0 \times 10^2 \text{ W s}^{1/2} \text{ m}^{-2} \text{ K}^{-1}$; $\alpha_3 = 8.3 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$).

3. Results

Typical results obtained for the phase of the FPPE signal for a detection cell with water as coupling fluid and water based binary mixtures with ethylene glycol, ethanol and DMSO respectively, are displayed in Figures (3) – (5), and the corresponding dependence of the thermal effusivity as a function of binary mixture composition, in Figures (6) – (8).

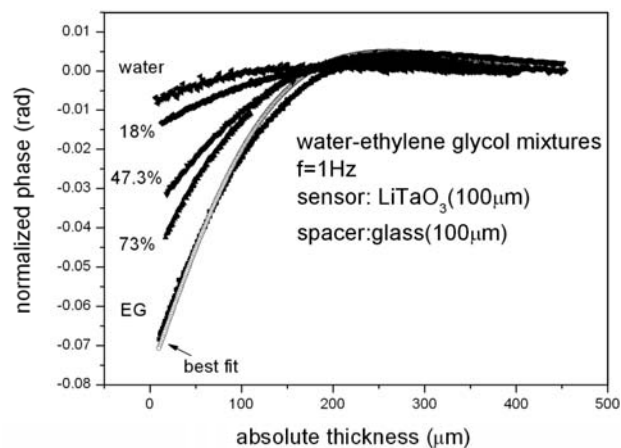


Figure 3. The experimental behaviour of the normalized FPPE phase as a function of coupling fluid's thickness, for water-ethylene glycol binary mixtures, inserted as backing (X % means weight fraction of water in mixture). The best fit for pure ethylene glycol is also displayed (empty circles).

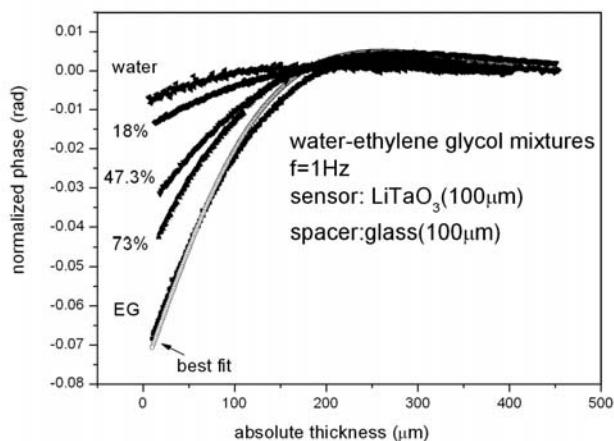


Figure 4. The experimental behaviour of the normalized FPPE phase as a function of coupling fluid's thickness, for water-ethanol binary mixtures, inserted as backing (X % means weight fraction of water in mixture).

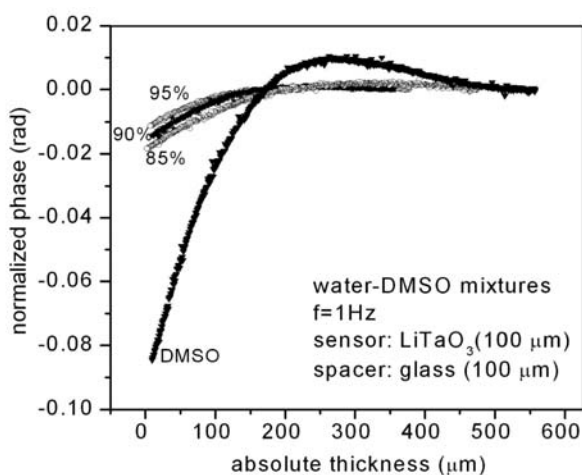


Figure 5. The experimental behaviour of the normalized FPPE phase as a function of coupling fluid's thickness, for diluted water-DMSO binary mixtures, inserted as backing (X % means weight fraction of water in mixture).

The behaviors of the thermal effusivity as a function of the mass composition for the investigated binary liquid mixtures are in good agreement with the results previously obtained with PPE and PA investigations – frequency scanning procedures.^{20–25} As reported before, if in the case of non-associative liquid mixtures (water-ethylene glycol for example) the additivity rule is respected (the thermal effusivity depends linearly on the mass composition of one component), for associative liquid mixtures (water-ethanol and water-DMSO), deviations from this additivity rule are observed.

4. Conclusions

An alternative front photopyroelectric configuration (FPPE) that uses the thermal wave resonator cavity met-

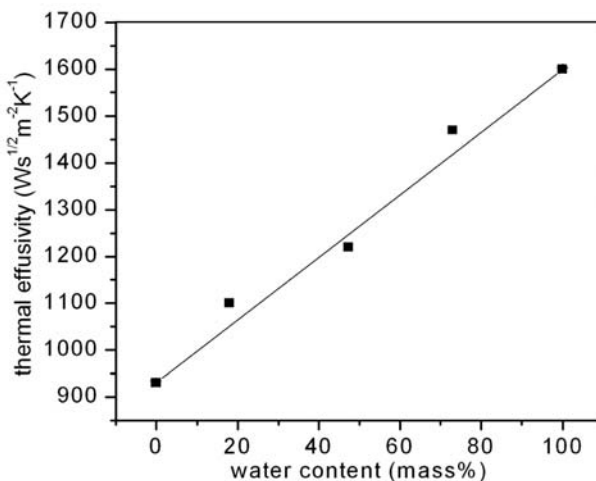


Figure 6. Room temperature values of thermal effusivity for different compositions of water-ethylene glycol mixtures ($f = 1\text{Hz}$).

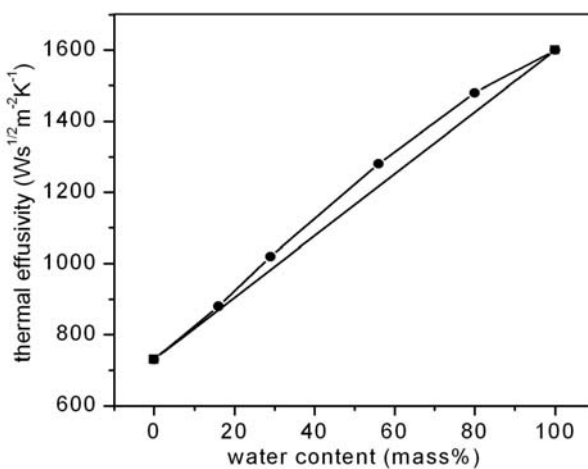


Figure 7. Room temperature values of thermal effusivity for different compositions of water-ethanol mixtures ($f = 1\text{Hz}$).

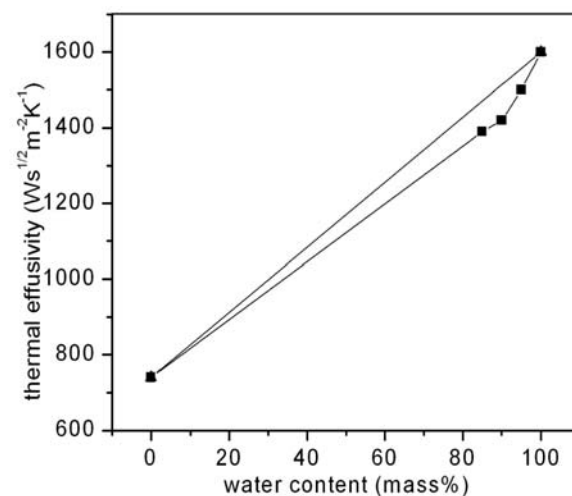


Figure 8. Room temperature values of thermal effusivity for different compositions of water-DMSO mixtures (low DMSO concentrations), $f = 1\text{Hz}$.

hod (TWRC) is proposed for measuring the thermal effusivity of a liquid, inserted as backing in the detection cell. The theory for a 5 layers (semi-infinite air, sensor, coupling fluid, solid separator layer, and semi-infinite liquid backing) detection cell was developed. The method seems to be particularly suitable when measuring the thermal effusivity of binary liquid mixtures. If the coupling fluid is one component of the binary mixture, the technique acts a “quasi-differential” method and low concentration of the second component of the mixture can be detected. In order to support this comment, we investigated only samples with low concentrations of DMSO in water; DMSO is known as a very hygroscopic liquid and consequently, deviations from the additivity rule for the behaviour of the thermal effusivity are expected, even for low DMSO concentrations (see Figure(8)).

Concerning the accuracy of the method, as stated in previous papers,^{14, 16–17} it depends on the relative effusivity ratio of the two liquids of the cell: coupling fluid and backing sample. In the case of close values for the two values of the thermal effusivity (the case of the present investigations) the localization of the position of the backing is not very precise, but the accuracy of the thermal effusivity is rather good.¹⁷

Finally, if we compare the method with the standard frequency scanning procedure, the accuracy of the method described in this paper is not better, but two advantages come out: (i) no additional calibration measurement is necessary (the calibration is contained in the same thickness scanning run – large coupling fluid thickness); (ii) the method is able to offer thermal information about any layer of the detection cell. A possible future application can be the investigation of thermal parameters of thin solid layers (inserted as separators between two identical liquids).

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Povzetek

V tem delu za merjenje termične efusivnosti tekočine, ki je vstavljena kot opora v merilno celico, predlagamo alternativo fotopiroloitično kofiguracijo (FPPE), ki uporablja metodo "votlinskega sozvočja" (cavity resonator method) termičnih valov (TWRC). Razvili smo teorijo za 5 nivojev (zrak, senzor, vezana tekočina, trdna ločilna plast in tekoča opora). Metoda je uporabna zlasti za meritve termičnih efusivnosti binarnih tekočih mešanic. Če je ena izmed komponent vezana tekočina, metoda deluje kot »kvazi-diferencialna« in lahko drugo komponento določimo tudi, če ta prisotna v zelo nizki koncentraciji. Metodo smo uspešno uporabili v binarnih mešanicah vode z etanolom, etilen glikolom in DMSO.