

Scientific paper

Accurate Photopyroelectric Calorimetry Applied to Isotopic Liquid Mixtures

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Abstract

The suitability of the photopyroelectric (PPE) calorimetry for detection of molecular associations in binary liquid mixtures was investigated. Accurate PPE measurements in two detection configurations (using the information contained only in the phase of the PPE signal) were performed to obtain the values of thermal diffusivity and effusivity. The limits of the method were tested by detecting isotopic effects in H₂O–D₂O and DMSO(6H)–DMSO(6D) mixtures. The composition behaviour of the above mentioned thermal parameters for DMSO(6H)–H₂O mixtures was presented for comparison. Small isotopic effects in thermal diffusivity were observed for H₂O–D₂O and DMSO(6H)–DMSO(6D) mixtures (about 4% and 8%, respectively).

Keywords: photopyroelectric calorimetry, thermal diffusivity, thermal effusivity, molecular associations, isotopic mixtures

1. Introduction

In the photopyroelectric (PPE) technique, the temperature variation of a sample, exposed to a modulated radiation, is measured with a pyroelectric sensor. In the last years, the two PPE calorimetric configurations (i.e. “back” and “front”, respectively) have been applied for investigating the behaviour of static (specific heat) and dynamic (thermal conductivity, diffusivity, effusivity) thermal parameters of condensed matter samples.^{1–3}

In the most general case, the complex PPE signal depends on all optical and thermal parameters of the layers of the detection cell. After some mathematical approximations, one can obtain results in which the amplitude or the phase of the signal depend on one or, in a simple way, on two of the sample’s related thermal parameters.^{1,3} In these special cases of experimental interest, the information is usually contained in the amplitude of the signal, the phase being often constant.² However, sometimes, the phase of the PPE signal also contains information, and it refers either to thermal diffusivity or effusivity of the sample.^{2,4,5}

It is very convenient to measure the phase of the signal, because the phase represents only a time delay of the signal, as compared to a reference one, and it is not dependent on the power fluctuations of the incident radiation and on the quality of the incident surface (as is the case of the amplitude).

In the *back* (standard) *configuration*, the most convenient PPE particular case, largely used in order to find

the values of the *thermal diffusivity*, requests thermally thick sample and sensor and optically opaque sample. In this configuration, a modulated light impinges on the front surface of a sample, and a pyroelectric sensor, situated in good thermal contact with the sample’s rear side, measures the heat developed in the sample due to the absorption of radiation. In order to find the thermal diffusivity of a given sample, the phase of the PPE signal can be measured, by performing either a frequency or a thickness scan.⁴

Recently, it has been demonstrated that the methodology based on sample’s thickness scan leads to very accurate and reproducible values for the thermal diffusivity, due to the possibility of precisely controlling the sample’s thickness variation.^{4,6}

Concerning the *front* (inverse) *configuration* (the radiation impinges on the front surface of the sensor, and the sample, in good thermal contact with its rear side, acts as a heat sink), two main detection schemes were proposed until now: (i) with thermally thin and optically opaque sensor, and (ii) with thermally thick and semitransparent sensor.^{7, 8} In both cases, the sample must be thermally thick, and the information is contained in the amplitude of the signal.

Recently, this front configuration, but with opaque sensor and thermally thick sensor and sample, was used to measure the *thermal effusivity* of some (semi)liquids. The experimental conditions (chopping frequency, number and geometrical thickness of the layers of the detection cell) were set up in such a way that the information (the

value of the thermal effusivity) is contained in the phase of the signal.^{9,10}

Both back and front configurations were independently used by the authors in order to detect molecular associations in some water-based binary mixtures (as water-ethanol, methanol, ethylene glycol, acetic acid, glycerol).^{4,11} It has been demonstrated that both thermal diffusivity and effusivity are thermal parameters suitable for molecular association studies, the expected excess value¹¹ being larger for the thermal diffusivity.

In principle, concerning molecular association processes in binary mixtures, the liquids were divided in two classes: “interacting” and “non-interacting” liquids.^{4,11} When interacting liquids are involved in a binary mixture (water-ethanol, for example), large deviations from additivity for thermal parameters (thermal diffusivity and effusivity) were found. In the case of non-interacting liquids (water-ethylene glycol, for example), the excess values (deviation from linearity) of thermal parameters are small (few percents), or zero. In such a context, a PPE calorimetry applied to isotopic liquid mixtures represents a challenge; small deviations from linearity of the thermal parameters as a function of composition is expected and, consequently, accurate investigations are necessary.

In this paper we intend to test the limits of the two particular PPE detection cases mentioned above and, using the information contained only in the phase of the PPE signal, to detect isotopic effects in H₂O – D₂O and DM-SO(6H) – DMSO(6D) liquid mixtures. Due to the fact that thermal effusivity is less sensitive to association processes (than thermal diffusivity), a special attention was paid to mathematical fits of the measured data for this parameter.

2. Theory

The theory of the two configurations (including the approximations for each particular case), together with the schematic diagrams of the detection cells, were largely presented elsewhere.^{1,3,5,7,12} We will present here only the results.

Back Configuration

In the particular case when the sample and the sensor are thermally thick and, additionally, the sample is optically opaque, the phase θ of the PPE signal is given by:²

$$\theta = \theta_0 - L_s (\omega/2\alpha_s)^{1/2}, \quad (1)$$

where θ_0 is an instrumental, frequency independent, phase offset, L_s and α_s are the sample's thickness and thermal diffusivity, respectively, and ω is the angular modulation frequency of the incident radiation.

As mentioned before, an inspection of Eq.1 leads to the conclusion that, in order to find the thermal diffusivity, one can perform either a frequency or a thickness scan of

the phase.

Front Configuration

In the front configuration, with opaque sensor and thermally thick sensor and sample, the phase of the PPE signal is given by^{9,10}:

$$\tan \theta = \frac{(1 + R_{sp}) \exp(-L_p/\mu_p) \sin(L_p/\mu_p)}{1 - (1 + R_{sp}) \exp(-L_p/\mu_p) \cos(L_p/\mu_p)}. \quad (2)$$

From Eq.2, for a given frequency, one can calculate R_{sp} and then derive the sample's effusivity e_s , according to the following relationship:

$$\frac{e_s}{e_p} = \frac{1 + R_{sp}}{1 - R_{sp}}. \quad (3)$$

In Eqs.2 and 3,

$$R_{ij} = (b_{ij} - 1) / (b_{ij} + 1) \quad (4)$$

represents the reflection coefficient of the thermal waves at the interface of two media, where $b_{ij} = e_i/e_j$. The symbols “p” and “s” refer to the pyroelectric sensor and substrate (sample), respectively. The thermal diffusion length is:

$$\mu = \left(\frac{\alpha}{\pi f} \right)^{1/2}. \quad (5)$$

where f is the modulation chopping frequency and α is the thermal diffusivity, related to the other thermal parameters (the volume specific heat C , thermal conductivity k and thermal effusivity e) by:

$$k = C \alpha; \quad e = (Ck)^{1/2}, \quad (6)$$

3. Experimental

A standard PPE calorimetric line was used for investigations.² The radiation source was a 30 mW HeNe laser, chopped by an acousto-optical modulator. The signal from a 500 μm thick LiTaO₃ pyroelectric sensor was processed with a SR 830 lock-in amplifier.

The detection cell in the front configuration was presented elsewhere.¹² The liquid sample accommodates the space between the sensor and a glass window, its thickness (5 mm) being delimited by two glass spacers. It is to point out that the cell can be filled and the sample removed without moving the sensor. The frequency scan was performed in the 1 – 46 Hz frequency range, with a step of 0.75 Hz. In this frequency range, both the sensor and the sample are thermally thick. The optical opacity of

the sensor was ensured by its front (Cr–Au) electrode. In order to eliminate parameters difficult to be estimated experimentally (e.g. incident radiation power density, radiation to heat conversion efficiency, thermal and electrical time constants of the electrical circuit), the PPE phase was normalized to the one obtained with air instead of sample;¹⁰ the obtained normalized phase satisfies Eq.2.

The detection cell, in the back configuration, was largely described before.⁴ The radiation source was modulated at 1 Hz by an acousto-optical modulator, driven from the internal oscillator of the lock-in amplifier, used also for signal processing. The value of the frequency was kept constant with a precision better than 0.1 mHz. The thickness scan was performed between 600 and 1100 μm (incremental step 50 μm) with a precision of 1 μm .

In both configurations, a computer was used for data acquisitions. The signal/noise ratio was better than 1000.

For each investigated concentration, 10 mL solution was prepared starting from 99% pure solvents, by adding x volume parts of solute (s) to $(1-x)$ parts of solvent (w). Since such a binary mixture does not obey the simple volume additivity law, the mass concentration c_s (% mass) = $100 \times (\rho_s \times V_s) / (\rho_s \times V_s + \rho_w \times V_w)$ was used for the graphical representation of the obtained results. The necessary sample quantity was 200–300 μL . The two isotopic dimethylsulfoxid species $\text{C}_2\text{H}_6\text{OS}$ and $\text{C}_2\text{D}_6\text{OS}$ (denoted in the paper DMSO(6H) and DMSO(6D)) were selected for investigations due to their large use in drugs industry.

4. Results and Discussion

Typical thickness scans of the phase of the PPE signal, in the back configuration, for pure H_2O , D_2O , DMSO(6H) and DMSO(6D) are presented in Figure 1, and the corresponding frequency scans of the normalized phase, in the front configuration, are displayed in Figure 2.

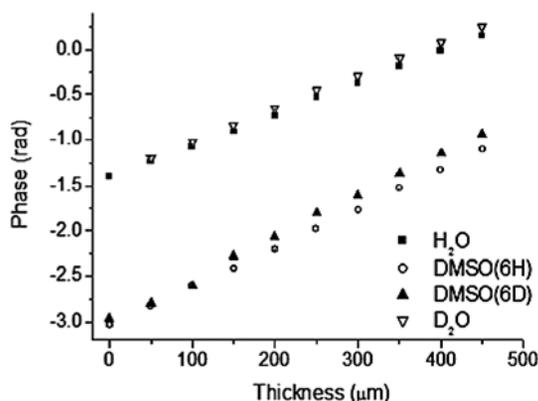


Figure 1. Typical thickness scans of the phase of the PPE signal, in the “back” configuration, for the pure components of the investigated mixtures.

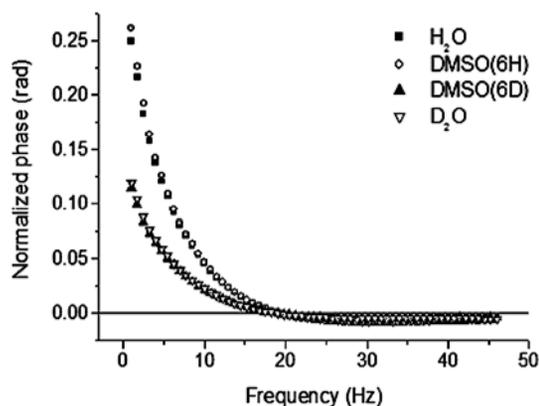


Figure 2. Typical frequency scans of the phase of the PPE signal, in the “front” configuration, for the pure components of the investigated mixtures. The frequency for which all curves cross the zero value is used for the calculation of the sensor’s thermal diffusivity.¹⁰

In the back configuration, the precision of the fits performed with Eq.1, and expressed by percent of residuals about mean explained, is 100%.

A special attention was paid to the fits of the experimental data obtained in the front configuration. The parameters of the LiTaO_3 sensor were: $\alpha_p = 1.56 \times 10^{-6} \text{ m}^2/\text{s}$ and $e_p = 3823 \text{ W s}^{1/2}/\text{m}^2\text{K}$. The sample’s thermal effusivity was considered as a parameter, and the best fit was selected by minimizing the root mean square. An example is presented in Figure 3.

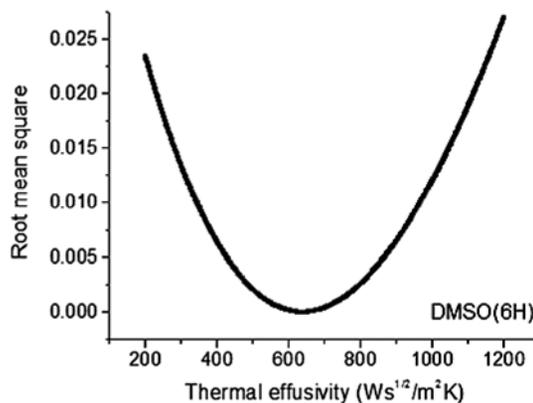


Figure 3. The root mean square obtained with experimental points and different fits, having as fitting parameter the sample’s effusivity. DMSO(6H) was selected as an example.

The obtained relative deviations from additivity for the thermal diffusivity and effusivity for H_2O – D_2O , DMSO(6H)–DMSO(6D) and H_2O –DMSO(6H) are presented in Figure 4 and Figure 5, respectively.

The maximum relative deviation from additivity of the thermal diffusivity for H_2O –DMSO(6H) mixtures is about –18% and indicates association processes taking place in this system. In fact, DMSO is well known for its

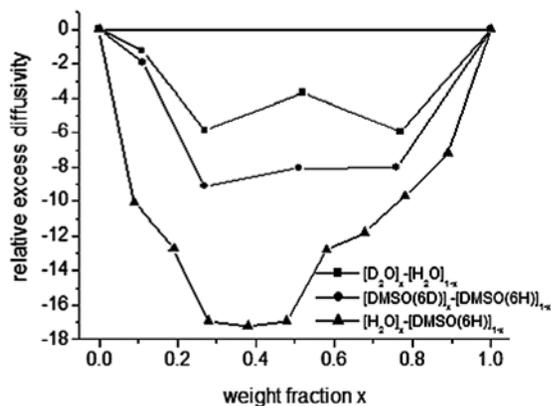


Figure 4. Relative deviations from additivity of the thermal diffusivity for $\text{H}_2\text{O}-\text{D}_2\text{O}$ and $\text{DMSO}(6\text{H})-\text{DMSO}(6\text{D})$, together with a mixture ($\text{H}_2\text{O}-\text{DMSO}(6\text{H})$) known for its “aggressivity” in forming molecular associations.

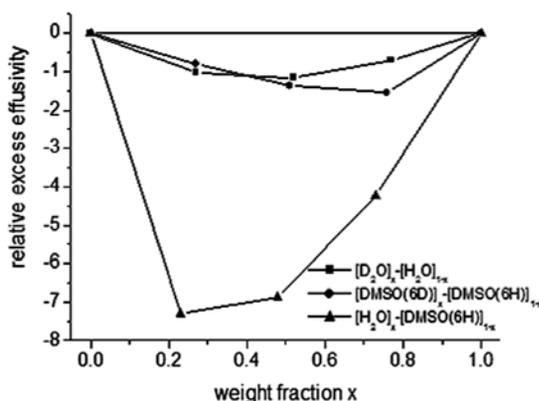


Figure 5. Relative deviations from additivity of the thermal effusivity for $\text{H}_2\text{O}-\text{D}_2\text{O}$ and $\text{DMSO}(6\text{H})-\text{DMSO}(6\text{D})$, together with a mixture ($\text{H}_2\text{O}-\text{DMSO}(6\text{H})$) known for its “aggressivity” in forming molecular associations.

hygroscopicity; this is the reason why this mixture was selected as comparison system. On the other hand, the maximum relative deviations from additivity of the thermal diffusivity for $\text{H}_2\text{O}-\text{D}_2\text{O}$ and $\text{DMSO}(6\text{H})-\text{DMSO}(6\text{D})$ are about -4% and -8% , respectively. This fact can be explained only as an isotopic effect because, from chemical point of view, H_2O and D_2O , and $\text{DMSO}(6\text{H})$ and $\text{DMSO}(6\text{D})$ molecules, respectively, are almost equivalent. The larger effect observed in the case of DMSO mixtures is due to an increased number of possibilities of interchanging H–D ions and creating $\text{DMSO}(1\text{D}) \dots \text{DMSO}(5\text{D})$ species. In the case of $\text{H}_2\text{O}-\text{D}_2\text{O}$ mixtures, there is only one possibility of creating a HDO intermediate molecule. We want to stress also on the fact that, in the case of DMSO mixtures, the (accidental) presence of OH^- radicals accelerates the H–D change.

Concerning the relative deviations of the thermal effusivity (Figure 5) for $\text{H}_2\text{O}-\text{D}_2\text{O}$ and $\text{DMSO}(6\text{H})-\text{DMSO}(6\text{D})$ mixtures, they are about -1% – -2% , at the reso-

lution limit of our method. The same deviation for $\text{H}_2\text{O}-\text{DMSO}(6\text{H})$ mixtures is about -7% – -8% , respecting the (about)3 reduction factor for the sensitivity (in detecting molecular associations) of thermal effusivity, as compared to thermal diffusivity, observed for water-ethanol mixtures.¹¹

5. Conclusions

Two PPE detection configurations, (i) the back one, with thermally thick sample and sensor, and optically opaque sample (for thermal diffusivity measurements), and (ii) the front configuration, with opaque sensor and thermally thick sensor and sample (for thermal effusivity measurements), were used to detect isotopic effects in $\text{H}_2\text{O}-\text{D}_2\text{O}$ and $\text{DMSO}(6\text{H})-\text{DMSO}(6\text{D})$ binary liquid mixtures. In both cases the information was contained in the phase of the PPE signal, and was obtained via a sample thickness and frequency scan, respectively. High accurate investigations were necessary in order to detect isotopic effects; the sensitivity of both methods is about 1%, and, consequently, small isotopic effects were observed in the behaviour of the thermal diffusivity of the two isotopic mixtures. No clear isotopic effects were detected in the composition behaviour of the thermal effusivity.

Work is in progress with increasing the accuracy of thermal diffusivity measurements, by increasing the quality of thickness variation control.

6. Acknowledgement

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Povzetek

Proučevali smo primernost uporabe fotopiroelektrične kalorimetrije za raziskave asociativnih procesov v binarnih tekočih mešanicah. Z natančnimi meritvami z dvema možnostima detekcije smo dobili vrednosti termične difuzivnosti in efuzivnosti. Omejitve metode smo testirali z detekcijo izotopskega efekta v mešanicah $\text{H}_2\text{O}-\text{D}_2\text{O}$ in $\text{DMSO}(6\text{H})-\text{DMSO}(6\text{D})$. Opazili smo relativno majhne izotopske efekte in termično difuzivnost: približno 4 % za mešanico $\text{H}_2\text{O}-\text{D}_2\text{O}$ in 8 % za $\text{DMSO}(6\text{H})-\text{DMSO}(6\text{D})$.