Measurements of the Thermal Diffusivity of Liquids with a Thermal-Wave Resonator Cavity

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High precision measurements of Thermal Diffusivity of liquids, using a liquid-compatible Thermal Wave Resonant Cavity (TWRC), are presented. The analytical procedure involved linear fittings to the photothermal signal’s amplitude as function of the cavity length. The thermal-diffusivities of distilled water, glycerol, olive oil and ethylene glycol were determined at room temperature (25 oC), with four-significant-figure precision. The liquid-state TWRC was applied to the measurements of Thermal Diffusivity of various mixtures of methanol and salt in distilled water. The sensitivity limits were found to be 0.5 % (v/v) and 0.03 % (w/v), respectively. The use of the TWRC to measure gas evolution from liquids was explored by recording the sensor’s signal amplitude for carbonated water as CO2 was evolving. The obtained results show the TWRC potential for environmental applications.

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The liquid state plays an important role in science and technology. Therefore the design of experimental techniques to measure properties of substances in the liquid state becomes relevant. Especially important are the measurements of thermal properties of substances in the liquid state because of their widespread use as refrigerants, lubricants and heat exchangers. The utility of the photothermal techniques for measuring thermal properties of materials has been well documented in the literature.1-7 The basic principle of these techniques consists of measuring the temperature fluctuations in a sample as a result of the nonradiative deexcitation process that takes place following the absorption of intensity-modulated radiation. The development of the Thermal Wave Resonant Cavity (TWRC)8-10 has introduced the possibility of measuring thermal properties by monitoring the spatial behavior of the thermal wave through cavity-length scans, instead of scanning the modulation frequency, common to various photothermal techniques. The major advantages of cavity-length scans are the fixed noise bandwidth of the system, which improves the signal-to-noise ratio (SNR), as well as disposing with the requirement for instrumental transfer-function normalization. This kind of device has been successfully utilized to measure the thermal diffusivity of gases, particularly air8,9, and vapors10 to a high degree of precision. Although it is possible to carry out thermal diffusivity measurements in the frequency domain with the TWRC, cavity scans on this device have shown further advantages in terms of precision and stability.11 This paper reports the application of a liquid-state compatible design of the TWRC to the measurement of the thermal-diffusivity of liquids. The sensitivity of this technique is also evaluated by measuring the thermal diffusivity of various mixtures (salt in distilled water and methanol in distilled water). The potential of the TWRC as an environmental sensor is demonstrated in detecting dissolved gases in liquids and liquid mixtures.

Experimental

The experimental set-up used for the thermal diffusivity measurements of liquids (For details see Ref. 12), consisted of an IR (806 µm) semiconductor laser (Opto Power Corporation), operating at powers up to 200 mW. The intensity-modulated laser light was incident on an aluminum foil (80 µm thick and 1 cm in diameter). Thermal waves were generated in this foil which was mounted on a micrometer stage. This stage allowed the cavity length, L, to vary with 10-µm step resolution. The thermal wave generator head (cross-sectional design shown in Fig. 2, Ref. 12) was dipped in the various liquids under study. Thermal waves conducted across the liquid interface (“intracavity region”), reached the pyroelectric sensor, which consisted of a polyvinylidene fluoride (PVDF) pyroelectric film (25-µm thickness and 1.5-cm diameter) with metal electrodes (Ni-AI) on both sides. To avoid vibrations and possible contributions of the piezoelectric response of the PVDF sensor, its bottom rear face was attached with conductive epoxy to a metal (copper) electrode. The pyroelectric voltage signal generated in the sensor was pre-amplified (ITHACO

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For sensitivity analysis of the liquid-state TWRC sensor, time scans were used to observe the changes in the pyroelectric signal when small amounts of various substances were added to distilled water. The signal output with the sensor immersed in distilled water was used as the baseline. The sensitivity analysis procedure was as follows: The container with the TWRC was filled with 10-13 ml of distilled water. By maintaining the cavity length constant (about 200 microns), the PVDF signal was recorded as a function of time. As soon as a steady-state signal was obtained (about 600 seconds), the solute substance (methanol or a saturated solution of sodium chloride in distilled water) was added. The experiments were performed at a modulation frequency of 4.35 Hz. This frequency was chosen because it combined a good SNR and satisfactory signal amplitude in our system. The test consisted in establishing the minimum volume necessary to obtain a change in the signal baseline. This procedure helped to determine the sensitivity limit of the TWRC device.

The next step was to measure the thermal diffusivity of various liquid mixtures obtained by scanning cavity length on the TWRC. For comparison purposes, the thermal diffusivity of some pure substances (glycerol and ethylene glycol), thermal diffusivity values have been reported in the literature, were also measured. The thermal diffusivity values were obtained by fitting the experimental data to the model described in the theory (see ref. 12). Fitting was done by the least-squares minimization method.

![Figure 1. PVDF signals recorded vs. time for the mixtures of methanol and salt dissolved in distilled water used in this work. The correspondence between different lines and substances is as follows: (1) Distilled water in distilled water, (2) one drop of saturated solution of salt in 13 ml of distilled water, (3) five drops of methanol in 10 ml of distilled water, (4) three drops of saturated solution of salt in 10 ml of distilled water (5) ten drops of methanol in 10 ml of distilled water. The arrow indicates, approximately, the time at which the various substances were added to the water.](image)

**Results and Discussion**

In order to ensure that baseline changes were only due to the addition of a different substance to distilled water, the following experiment was conducted. Once a baseline time scan for the given volume of distilled water was obtained, ten drops of the same distilled water were added. Following this experiment the container was emptied and filled again with the 10 ml of reference sample for the next scan. This time five drops of methanol were added to the distilled water. The procedure was repeated with ten drops of methanol and three drops of a saturated solution of sodium chloride in distilled water. In order to determine the sensitivity of the sensor to smaller concentrations of salt solutions, the experiment was carried out with a single drop of saturated solution of salt in 13 ml of distilled water. All solutes were added, drop by drop, by means of a high precision syringe.

The variation on the baseline signal due to various concentrations of methanol and salt in distilled water is shown in Figure 1. In this Figure the line-symbol trace 1 corresponds to the baseline for distilled water and the line-symbol trace 2 to the mixture obtained by the dilution of one drop of salt solution in 13 ml of distilled water (0.03 % w/v). It is clear that this concentration is close to the sensitivity limit of the sensor. It was verified that there was no significant variation on the pyroelectric signal following the addition of distilled water in distilled water.

![Figure 2. Typical results of the pyroelectric signal amplitude vs. relative cavity length for two liquid substances: glycerol (1) and distilled water (2). The continuous lines correspond to best fits to the linear model proposed.](image)

Considering that the volume of ten drops of methanol (and the same number of drops of the saturated solution of salt) were approximately 0.1 ml, it was concluded that the sensor has enough sensitivity to detect at least 0.5 % (v/v) of methanol, or as low as 0.03 % (m/v) of salt in distilled water. To obtain a saturated solution of salt in distilled water about 35 g of salt in 100 ml of distilled water are required.  

To complete the analysis, the thermal diffusivities of the mixtures described previously and of some other homogeneous liquid substances (distilled water, glycerol, ethylene glycol and olive oil) were measured by performing a cavity-length scan of the TWRC device. This cavity-length scan was carried out in 10-µm steps and at a modulation frequency of 4.35 Hz. All the measurements were made at room temperature (25 °C). In figure 2 a typical behavior of the amplitude of the pyroelectric signal is shown vs. the cavity length for two substances. The continuous lines are the best fits to the linear model proposed in Ref. 12.
The resulting thermal diffusivity values measured with this technique are summarized in Table I. The thermal diffusivities reported in this table are averages over, at least, 5 measurements. The reported uncertainties therefore constitute the standard deviation. By comparing the thermal diffusivity values measured for one drop of saturated solution of sodium chloride in 13 ml of distilled water (0.03% w/v) with that of pure distilled water (0.001442 cm²/s and 0.001445 cm²/s, respectively), the high precision of the present device is evident. Variations up to the fourth significant figure are meaningful.

Finally, in order to evaluate the potential of TWRC sensor for monitoring gases in liquids and possible applications in environmental analysis, the time evolution of the pyroelectric signal was monitored as a function of the evolution of CO₂ in carbonated water. To do this a can of commercial carbonated water was opened and some of the liquid poured in a beaker flask. The liquid was left to rest for 5 minutes in order to allow for the initial profuse evolution of gas bubbles. After this, the container was filled with this liquid and the PVDF signal recorded as a function of time; the result is shown in Fig. 3. In this figure the initial flat line corresponds to the distilled water baseline (reference). Upon exposure to the carbonated water, a rapid signal decrease followed by an approximately linear increase due to the evolution of the gas was observed. At the end of the gas evolution a flat baseline at the distilled-water level was followed by an approximately linear increase due to the corresponding change on carbonated water is a measure of the kinetics of gas evolution and the PVDF signal recorded as a function of time; the result is shown in Fig. 3. In this figure the initial flat line corresponds to the distilled water baseline (reference). Upon exposure to the carbonated water, a rapid signal decrease followed by an approximately linear increase due to the evolution of the gas was observed. At the end of the gas evolution a flat baseline at the distilled-water level was obtained again. The increase of the signal with time for the carbonated water is a measure of the kinetics of gas occlusion from the liquid and the corresponding change on its thermal properties. These results suggest the possibility of using the TWRC in assessing content and evolution of gases (methane, CO₂, O₂, etc.) from water resources, or other biological systems, with important applications to environmental science.

**Figure 3.** Evolution of the PVDF signal vs. time for carbonated water from a commercial can. The distilled water baseline and the transient due to carbon dioxide occlusion are shown.

In conclusion, a novel thermal-wave resonant cavity design for thermophysical measurements in the liquid state has been demonstrated. The device was shown to be capable of measuring thermal diffusivities of liquids, including mixtures and solutions, with fourth-significant-figure precision. The high sensitivity of the liquid-state TWRC raises the possibility of monitoring the quality of a large range of liquids and liquid compounds, carrying out water pollution assessments based on thermophysical property dependence on gas concentrations (oxygen, methane) or solid-matter content, as well as measuring transient responses due to gaseous occlusions or possibly solid-matter dissolution. The limitations on the current design of this device are associated with the PVDF detector itself, specifically the temperature range of operation (−20°C to 80°C) and the exclusion of aggressive liquids that could be harmful to the sensor material.

<table>
<thead>
<tr>
<th>Liquid Sample</th>
<th>TWRC Technique αₜ(x 10⁻² cm²/s)</th>
<th>Literature αₜ(x 10⁻² cm²/s)</th>
<th>Ref.</th>
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</thead>
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<tr>
<td>Distilled Water</td>
<td>0.1445±0.0002</td>
<td>0.1456 (24°C)</td>
<td>15</td>
</tr>
<tr>
<td>Glycol</td>
<td>0.0922±0.0002</td>
<td>0.0929 (30°C)</td>
<td>15</td>
</tr>
<tr>
<td>Olive oil</td>
<td>0.0881±0.0004</td>
<td>0.0799</td>
<td>3,14</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>0.0918±0.0002</td>
<td>0.0939 (20°C)</td>
<td>16</td>
</tr>
<tr>
<td>Salt in Distilled Water (0.03%)</td>
<td>0.1442±0.0003</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Salt in Distilled Water (0.1 %)</td>
<td>0.139±0.0004</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methanol in dist. Water (0.5%)</td>
<td>0.1438±0.0002</td>
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<td></td>
</tr>
<tr>
<td>Methanol in dist. Water (1%)</td>
<td>0.1425±0.0004</td>
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**Table I.** Thermal Diffusivities obtained using the TWRC technique and comparison with (some) known literature values.

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References