

Research Article

Thermomechanical and Photophysical Properties of Crystal-Violet-Dye/H₂O Based Dissolutions via the Pulsed Laser Photoacoustic Technique

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Different thermoelastic parameters, for example, the acoustic attenuation and the speed of sound, are fundamental for instrumental calibration and quantitative characterization of organic-based dissolutions. In this work, these parameters as functions of the concentration of an organic dye (crystal-violet: CV) in distilled water (H₂O) based dissolutions are investigated. The speed of sound was measured by the pulsed-laser photoacoustic technique (PLPA), which consists in the generation of acoustic-waves by the optical absorption of pulsed light in a given material (in this case a liquid sample). The thermally generated sound-waves traveling through a fluid are detected with two piezoelectric sensors separated by a known distance. An appropriate processing of the photoacoustic signals allows an adequate data analysis of the generated waves within the system, providing an accurate determination of the speed of sound as function of the dye-concentration. The acoustic attenuation was calculated based on the distance of the two PZT-microphones to an acoustic-source point and performing linear-fitting of the experimental data (RMS-amplitudes) as function of the dye-concentration. An important advantage of the PLPA-method is that it can be implemented with poor or null optical transmitting materials permitting the characterization of the mechanical and concentration/aggregate properties of dissolved organic compounds.

1. Introduction

It is well known that conventional UV-Vis-NIR transmission spectroscopies are inconvenient techniques for the characterization of materials with high optical density (opaque samples); indeed, in such cases, Beer-Lambert's law is not applied when the sample presents high scattering and low/poor optical transmission [1]. However, complementary photoacoustic characterization techniques such as the pulsed-laser photoacoustic technique (PLPA) can be used as an adequate alternative to analyze semi- and highly optical absorbent materials in the liquid phase, for instance, organic dyes, paints, liquid crystals, and polymers, among others.

In fact, in recent works, we have successfully implemented the PLPA-technique to study structural anisotropies in different polymeric films (including commercially available organic polarizers and prepared spin-coated and corona-poled push-pull based molecular layers for nonlinear optical NLO-applications) and electrooptical dichroic organic-based dissolutions [2–4]. In this line of research, it is our aim to show in this contribution that the PLPA-technique can also be implemented to further study the material properties of these kinds of organic systems. This can be achieved by performing only small variations on the basic PLPA-experimental setup and adequate numerical data analyses in order to obtain relevant information and physical parameters of the sample

such as the optical molar extinction coefficient, the acoustic attenuation coefficient, and the speed of sound as a function of the organic dye concentration in a liquid phase. This kind of studies can be helpful to further understand important chemical and physical properties of organic compounds in solution such as aggregate and self-assembling molecular properties as function of the concentration. Indeed, our global purpose is to demonstrate that the PLPA-methodology can be used as an overall material characterization technique capable of obtaining standard physical parameters to become a reliable analytical methodology.

2. The PLPA-Technique: Basic Theory and Concepts

The PLPA-technique is based on the detection of acoustic-waves (in general, within the ultrasonic regime) produced by the partial or full absorption of pulsed- laser-light in a semi- or poor-transparent medium. The generated acoustic-waves result from the nonradiative electronic decay and the further fast thermal process induced by the optical absorption of a fraction of the pulsed light energy. According to a phenomenological analysis [5, 6], for homogenous and isotropic media such as an organic-based dissolution, having a dye/chromophore concentration C , an optical path-length L , and an optical extinction coefficient ϵ_λ , which is excited with a single laser wavelength λ and an input pulse intensity I_0 , the amplitude of the photoacoustic signal A is given by the following equation:

$$A(C) = KI_0 \left[1 - 10^{[-\epsilon_\lambda CL]} \right], \quad (1)$$

where K is a term that takes into account the thermoelastic properties of the interacting system, for example, the acoustic attenuation coefficient. If the medium is optically low-loss at the excitation wavelength, that is, $\epsilon_\lambda CL \ll 1$, then (1) can be approximated by a Taylor expansion and rewritten as follows:

$$A(C) = KI_0 \epsilon_\lambda CL. \quad (2)$$

Since the amplitude of the photoacoustic waves is proportional to the laser excitation intensity and to the optical absorptive properties of the sample, the PLPA-technique offers the advantages and simplicity of the UV-Vis-NIR absorbance based spectroscopic detection, with high sensitivity similar to other optical transmission and reemission techniques [7, 8]. In a typical PLPA experiment, the acoustic-waves travel at the characteristic speed of sound of the excited material to reach a coupled piezoelectric detector; this allows the mechanical-electrical experimental interface to collect the PLPA-data from the sample on a digital oscilloscope for subsequent numerical analyses. The experimental simplicity to obtain photoacoustic signals has led to the development of several PLPA-based measurement devices which are commonly used for the accurate evaluation of thermal and optical properties of different materials such as organic and inorganic crystals, semiconductor, and polymer systems [2–9]. In summary, several physical and structural material characteristics can be efficiently studied by means

of diverse PLPA-based techniques and the adequate data analysis thereof.

3. Experimental Details

Figure 1 depicts the implemented experimental set-up for PLPA-measurements. Here, a glass-cell (GC: $\sim 2.3 \times 1.3 \times 0.2 \text{ cm}^3$) is filled with prepared CV/H₂O dissolutions (with increasing CV-concentrations, CV-dye from Aldrich Inc., 90% purity no. C3886). Given that the CV-dye exhibits a high molar extinction coefficient at the implemented laser excitation wavelength ($\epsilon_\lambda \sim 5 \times 10^4 \text{ M}^{-1} \text{ m}^{-1}$, @ $\lambda_{\text{ex}} = 532 \text{ nm}$), this dye can be properly implemented as an adequate absorber compound for photoacoustic experiments. In contrast, the H₂O and GC are highly transparent at λ_{ex} producing negligible PLPA-signals. In this way, the CV/H₂O system was illuminated with a frequency doubled Nd:YAG laser system (from Continuum Co., Minilite II) with light pulses of $\tau \sim 5 \text{ ns}$ (at 10 Hz repetition rate, pulse-energy: $\sim 10.0 \text{ mJ/pulse}$). It is worth noting that the laser beam was not focused into the GC in order to avoid molecular degradation due to strong laser peak intensities. The chemical stability (photodegradation) of the dissolutions was confirmed via UV-Vis-NIR spectroscopic measurements before and after performing the PLPA-measurements.

The generated PLPA-signals were simultaneously monitored by means of two piezoelectric transducer/microphones (M1 and M2, PZT/Lead-Zirconate-Titanate, resonance frequency: $\sim 500 \text{ kHz}$, diameter: 4 mm) attached to the GC along the y -direction and separated by a distance D (see Figure 1). The PLPA-signals were then averaged, visualized, stored, and partially analyzed on a digital oscilloscope. Afterwards, the collected PLPA-signals were ready for numerical processing in a personal computer in order to obtain the representative root mean square (RMS) amplitudes and the corresponding speed of sound as functions of the CV-dye concentration.

4. Results and Discussions

4.1. UV-Vis-NIR Spectroscopic Measurements. Figure 2 shows the comparative absorption spectra of the empty glass-cell (GC), the GC/H₂O reference system, and the studied GC/CV/H₂O sample. It is clearly observed that only the organic CV compound exhibits a strong and characteristic absorbance band within the visible spectral range, with a λ_{max} peak centered at $\sim 590.3 \text{ nm}$. This singular band is associated with a molecular structure rich in π -electrons, which frequently tend to present strong quantum state changes (as observed in fluorescent experiments) and electrostatic bonds with other molecules (as in histological stains). Thus, PLPA-experiments were performed near the CV-chromophore resonance band (with an absorption-emission peak discrepancy of $100 \times |\lambda_{\text{max}} - \lambda_{\text{ex}}| / \lambda_{\text{max}} \sim 11\%$); within this spectral region intense PLPA-signals may be expected from the dissolved CV-dye. In contrast, due to the low optical absorptive properties (at λ_{ex}) of the GC and H₂O, it is assured that these systems are not capable of producing significant PLPA-signals. It is important to point out that during PLPA-experiments neither

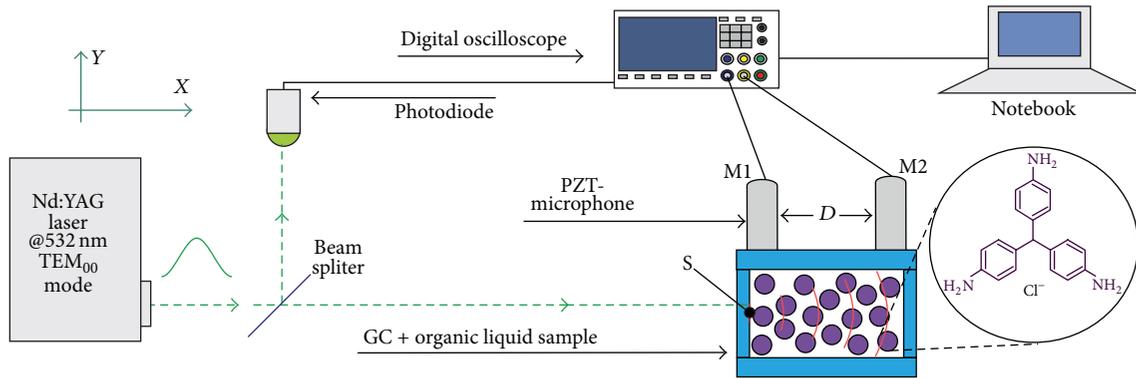


FIGURE 1: Schematic representation of the experimental device implemented to estimate the acoustic attenuation coefficient and the speed of sound in CV/H₂O based dissolutions via the PLPA-technique (molecular structure of the CV-compound).

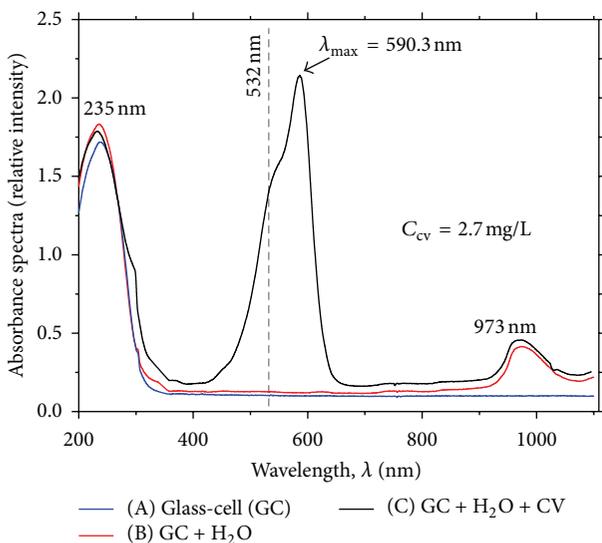


FIGURE 2: Comparative UV-Vis-NIR absorbance spectra obtained from (A) the empty glass-cell (GC), (B) the reference GC/H₂O system, and (C) the studied GC/CV/H₂O dissolution. The CV chromophore exhibits a strong and characteristic absorbance band within the visible spectral range (near the laser excitation wavelength at $\lambda_{ex} = 532$ nm: dashed line).

band phase shifts nor evidence of molecular degradation was induced at the implemented excitation laser power regime and exposure times. In addition, the optical absorption bands observed at 235 and 975 nm represent both the typical UV-absorbance of the common GC and the NIR-absorbance of water molecules at room conditions, respectively [10].

4.2. RMS-Analyses of the PLPA-Measurements and Determination of the CV-Concentration Dependent on Physical Parameters. Figure 3 exhibits four representative examples of unprocessed PLPA-signals directly recorded from the GC/CV/H₂O system. Figure 3(a) corresponds to the PLPA-responses registered (at M1 and M2, separately) for a low CV-concentration sample (at 5.21 ± 0.095 mg/L), whereas Figure 3(b) shows the PLPA-responses measured for a high

CV-concentration (20.68 ± 0.32 mg/L) sample. Qualitatively, it is clear that a high CV-concentration generates larger PLPA-amplitude signals than those generated at lower CV-concentrations. On the other hand, the arrival time difference ($\Delta t = t_f - t_i$) of the PLPA-signals detected by the M1 and M2 transducers is dependent on the CV-concentration $\Delta t(C)$. As the distance D between the two microphones is known ($D = 16.0$ mm), the speed of sound v_s , in the studied liquid phases, as function of the CV dye-concentration, can be given by [11]

$$v_s(C) = D \cdot \Delta t^{-1}(C). \quad (3)$$

In fact, these PLPA-signals are adequate for carrying out numerical processing in order to obtain quantitative and meaningful information concerning the PLPA-amplitude and the characteristic speed of sound as function of the implemented CV dye-concentrations.

The RMS-amplitude analysis performed to the PLPA-signals as function of the CV-dye concentration and detected by the two PZT-detectors is presented in Figure 4. It is observed from this study that the RMS-amplitude analyses precisely fit in a linear progression— $A(C) = mC + b$ —as the CV-dye concentration increases (at least within the implemented 5.21–20.68 mg/L CV-chromophore concentration range). In fact, we observe in this analysis an interesting and similar trend to the well-known Beer-Lambert law (according to (2)) rather than a power-curve (as described by (1)). This linear behaviour has been previously reported in scientific works for semitransparent liquid samples [6, 7]. However, in our case, most of the studied dissolutions are heavily CV-loaded and fully opaque sample systems. Under this framework, the fact that the slope of the fitted line corresponding to the measurements obtained from the M1-detector is larger than the one obtained from the M2-detector evidences the acoustic attenuation of the organic dissolution. Indeed, the M1-detector is closer to the acoustic wave source S (see Figure 1); hence, less attenuated and stronger RMS-amplitude signals can be detected/processed at this point. In other words, since most of the samples are highly opaque, the photoacoustic signals are generated within the first micrometres inside the liquid sample [6]. Then, the

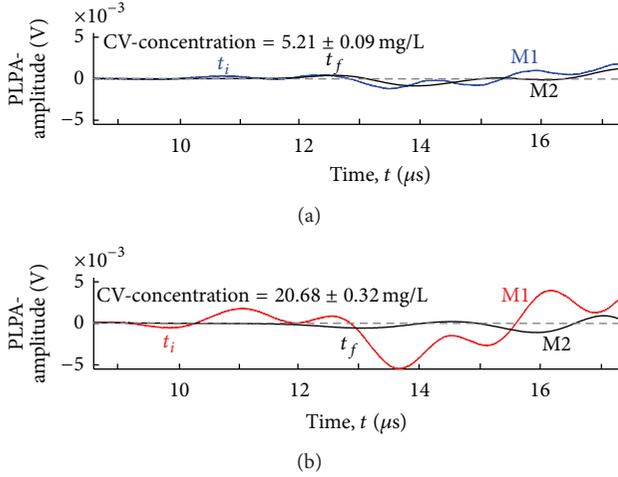


FIGURE 3: Representative averaged (200 data samples) PLPA-signals obtained from the M1 and M2 microphones in the GC/CV/H₂O system at different experimental conditions: (a) PLPA-signals recorded for a low CV-loaded sample and (b) PLPA-signal measured for a highly CV-loaded liquid sample.

acoustic-waves travel a shorter distance through the liquid sample to reach the M1-detector. Moreover, the attenuation of the acoustic-waves is proportional to the acoustical path; thus processed signals from the M1-detector exhibit minor acoustic attenuation than those obtained from the M2-detector. As the acoustic attenuation is a typical material mechanical property, it is part of the K parameter in (2). In this way, from the first linear-fitting (corresponding to the M1-detector), the K_1 parameter was obtained as a reference for further measurements, as follows:

$$K_1 = \frac{m_1}{I_0 \epsilon_\lambda L_1}, \quad (4)$$

where m_1 is the slope in the linear-fitting of the experimental data for the M1-detector. Then, after substitution, we calculated $K_1 = 0.032 \text{ LM/kgC}$ (14% of error). Moreover, in order to calculate K_2 as function of the relative distances (L_1 and L_2) and slopes (m_1 and m_2), the ratio K_2/K_1 —from (2)—leads to the next formula:

$$K_2 = K_1 \cdot \frac{m_2 L_1}{m_1 L_2}. \quad (5)$$

In this case, $K_2 = 0.004 \text{ LM/kgC}$ (16% of error). In this way, the experimental estimation of constants K_2 and K_1 may be important for calibration and reference proposes when measuring other dye-based samples (dissolved in water or other solvents) in order to build an appropriate database of these physical parameters.

On the other hand, according to (2), at zero-concentration, the RMS-amplitude must be null; then, the constant term in the fitted lines may well include an instrumental off-set signal produced by the acoustic impedance; that is, the constant term comprises an instrumental limit for the

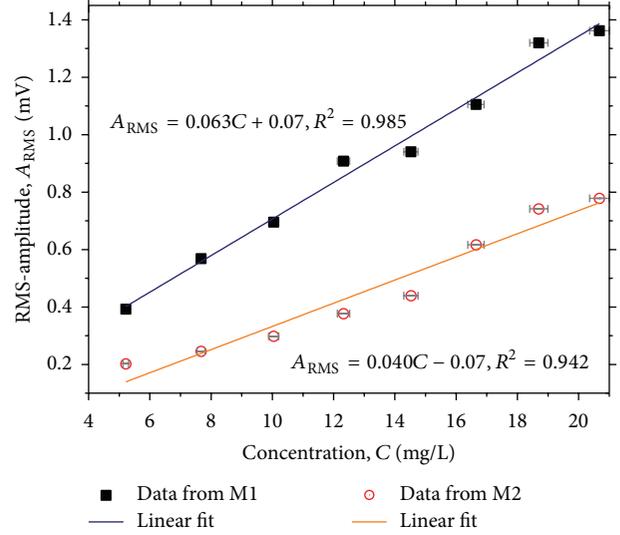


FIGURE 4: RMS-amplitude analyses of the PLPA-signals detected in the M1 and M2 PZT-microphones as functions of the CV-chromophore concentration (H₂O based dissolutions).

instrumented set-up during the measurement procedure for both M1 and M2 detectors.

Finally, the determination of the speed of sound in the implemented CV-based dissolutions as function of the CV-dye concentration by means of the PLPA-signal processing and according to (3) is presented in Figure 5. It is observed that an accurate curve-fitting within the 7.7–20.7 mg/L concentration range can be given by a linear fit. Nevertheless, by including the first point (corresponding to a 5.2 mg/L concentration) to evaluate the complete studied range, it would require an exponential fitting to better describe the physical behaviour of v_s in this particular system. In both cases, it is observed that the low CV-loaded dissolutions exhibit a slow v_s -parameter, tending to the standard H₂O value reported in the literature (1490 m/s @ 20°C [6]). In contrast, for higher CV-loaded dissolutions, the speed of sound reaches extremely high v_s -values up to 2.000 m/s.

As a first and tentative hypothesis we believe that the formation of CV/H₂O-clusters is responsible for the observed increase in the speed of sound. Indeed, in recent literature, it has been reported that octupolar-like compounds such as the implemented CV-molecules can constitute packed clusters at moderate and high concentrations, giving rise to self-assembled staked columnar structures [12, 13]. In fact, X-ray diffraction studies of CV-encapsulated in stable, inert, and bulky SiO₂-matrices evidence the cluster formation as function of the CV-concentration [12]. On the other hand, at nanoscopic level, the water does not constitute homogeneous arrangements [14]. Diverse spectroscopic and X-ray diffraction experiments have demonstrated a variety of H₂O-molecular structures in different phases, including the liquid state [15, 16]; that is, based in Van-der-Walls and hydrogen bonds, water can configure stable clusters. Though these two studies were reported in very different environments as the one implemented in our work, they evidence the possibility to

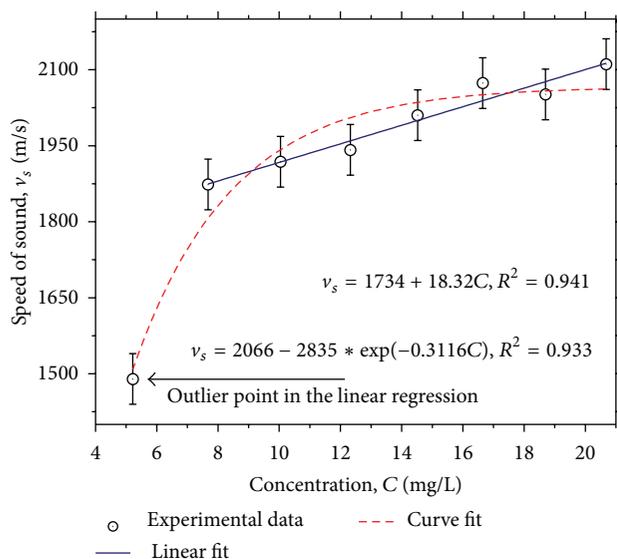


FIGURE 5: Speed of sound evaluated as functions of the CV-dye concentration in H_2O based dissolutions via the PLPA-method.

find CV/ H_2O -clusters at highly loaded samples in the liquid phase. Thus, it is feasible that, at high dye-concentrations dissolved in water, the π -electrons of CV present weak-electrostatic bonds among vicinal water molecules, leading to the conformation of compact structures. As a consequence, we argue that the dramatic increase observed in the speed of sound of our studied systems may provide an evidence of the formation of such aggregates within the liquid phase. However, complementary and conclusive spectroscopic and PLPA-studies in different dye-compounds and other organic materials (including higher concentration) will be necessary in order to confirm this initial conjecture; some of these studies are now underway and will be presented in a future work. In such case, the PLPA-method could also be considered an analytical tool for the study of aggregate formation in organic-based dissolutions or solid-state phases via the measurements of the speed of sound in such opaque media.

5. Conclusions

The PLPA-methodology was implemented as a nondestructive, easy-to-implement, and accurate technique to analyze and quantify the thermoelastic parameter K (as the acoustic coefficient parameter) and the speed of sound in quasi- and fully opaque dye-based liquid samples. This is important since, at the implemented CV-dye concentrations, conventional optical techniques such as the UV-Vis spectroscopy, which is limited by the Beer-Lambert law, are inappropriate to perform precise and trustable data analyses to determine several structural and photophysical material properties in these kinds of samples. In fact, it has been demonstrated that even in opaque dissolutions the RMS-amplitude analysis of the PLPA-signals can be visualized as a linear function of the CV-dye concentration. Moreover, the speed of sound in highly concentrated dissolutions was evaluated showing promising

evidence for the identification of molecular aggregate effects in this kind of compounds. These results represent, from our point of view, a first and important approximation for the future development of PLPA-based measurement-prototypes intended to study. In fact, organic-based dissolutions and their material and structural properties, which are otherwise difficult to quantify in such opaque media, could be easily studied implementing PLPA-based measurement devices.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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