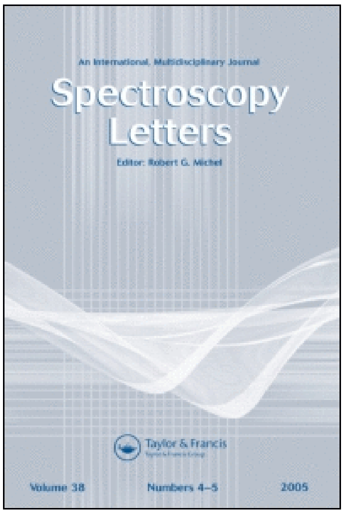

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New Technique for Measuring Absorption Coefficients of Strongly Absorbing Liquids: Optothermal Study of Sunflower Oil, Oleic Acid and Its Chloroform Solutions at 3.39 Microns

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NEW TECHNIQUE FOR MEASURING ABSORPTION COEFFICIENTS OF STRONGLY ABSORBING LIQUIDS: OPTOTHERMAL STUDY OF SUNFLOWER OIL, OLEIC ACID AND ITS CHLOROFORM SOLUTIONS AT 3.39 MICRONS

Key words: optothermal spectroscopy, oleic acid, sunflower oil, absorption coefficients, infrared laser spectroscopy

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ABSTRACT

Optothermal window (OW) cell and a low power infrared (IR) laser (He-Ne) were used to measure absorption coefficient β of sunflower oil, oleic acid (C18:1) and its solutions in chloroform at 3.39 μm. Values of β as high as 2782 cm^{-1} (for C18:1) were measured in a simple and reproducible fashion without the need to know actual sampling pathlength. Failure of C-H stretch vibration to follow Bouger-Beer's law was observed and 0.35 % detection limit of C18:1 in CH$_3$Cl at 30 Hz determined.

INTRODUCTION

Application of infrared (IR) spectroscopy to analysis of fatty acids (FA) and vegetable oils requires spectral data of a large number of pure reference compounds [1]. In the IR region, liquid specimens are generally investigated in transmission either neat [liquid film of a pure compound less than 10 μm thick (thicker samples absorb too strongly to produce a satisfactory spectrum) compressed between flat windows and held together by capillarity] or in a solution [2]. High IR absorption coefficients β of edible oils necessitate the use of very short and difficult to reproduce pathlengths affecting accurate quantitative studies. In addition as constants obtained from pure liquids are not always strictly applicable for quantitative purposes to measurements on solutions (potential effect of solvent on IR spectral properties); it is useful to record IR spectra of such compounds in solvents at a concentration level employed for actual analytical purposes [3]. Development of novel methodologies and a low cost, practical instrumentation that would allow both, direct measurement of β for pure, strongly absorbing samples, as well as determination of small amounts of these specimens dilluted in specific solvent, is desired.

In this paper results of an experiment carried out with a newly developed optothermal sensor are being presented. Absorption coefficients were determined for undilluted sunflower (SF) oil and oleic acid C18:1 ($C_{18}H_{34}O_2$), as well as for chloroform mixtures of varying C18:1 content. All carboxylic acids display a weaker C-H stretch band superimposed upon the broad and intense O-H band that usually centers near 3000 cm^{-1} in 3300 to 2500 cm^{-1} region [4]. Measurements were performed at 2967 cm^{-1} (3.39 μm) using only few milliwatts of power emitted by a home made IR He-Ne laser. The major advantage of a newly proposed approach is its simplicity, ease of sampling and a good reproducibility in measurement of high β values without a need to know exact sample's thickness.

EXPERIMENTAL

Specimens of SF oil and C18:1 were placed on a thin, 14 mm diameter sapphire (having high transmission from 0.25 to 6 μm and a large thermal expansion coefficient) optothermal window OW (diameter of sensitive area 4 mm) manufactured by AB Varilab, as it is being shown in Fig. 1. Samples were irradiated from below (through the very same OW window) by a mechanically (chopper EG&G 192) interupted (modulation

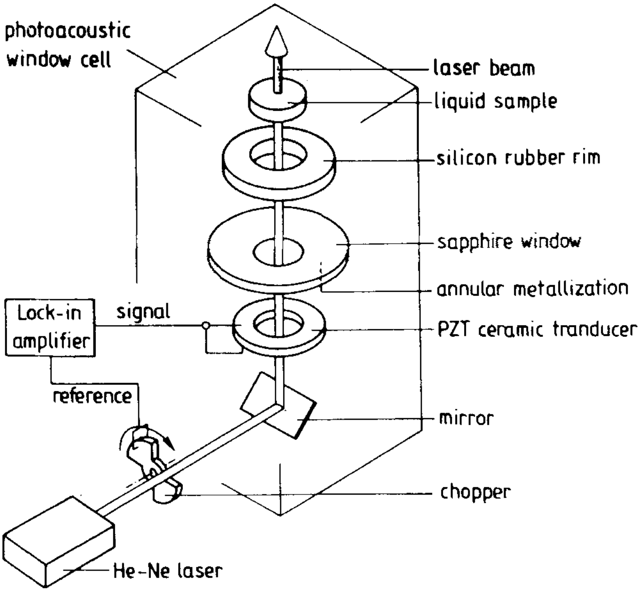

Fig. 1. Exploded view of optothermal window (OW) cell and the experimental set up with infrared He-Ne laser used in this study.

frequency f) beam of He-Ne laser (5.2 mW at $\lambda = 3.39$ μm). For unobstructed passage through the OW window, diameter of modulated laser beam may not exceed 4 mm; stray radiation gives rise to a false signal. Periodic heat (generated in sample due to absorption of radiation) diffuses into sapphire window that expands and exerts pressure on a piezoelectric (PZT) sensor (low noise and susceptible to mechanical vibrations) producing voltage as an output signal. The output impedance of detector (typically 3 Mohms at 100 Hz) depends on the modulation frequency as f^{-1}. The output signal, the magnitude of which strength also varies as f^{-1} was processed (EG&G/PAR 5101 lock-in amplifier) at modulation frequency. In order to compensate for background effects, signals obtained from an empty cell were consistently subtracted (vectorially) from those measured with actual samples.

The amplitude S of optothermal signal depends on temperature fluctuations taking place within approximately one thermal diffusion length from the sample-sensor interface. It can be shown[4] that for a thermally and optically thick sample (subscript s) (which implies that thermal diffusion length μ_s and the inverse $1/\beta_s$ of optical absorption coefficient, are both shorter than the actual sample's physical actual thickness d_s) and a thermally thick window (subscript w), the normalized amplitude and the phase ϕ are given by:

$$S = \beta_s \mu_s [(1 + \beta_s \mu_s)^2 + 1]^{-1/2} (1 + e_s / e_w)^{-1} \tag{1}$$

and

$$\phi = - \arctan (1 + \beta_s \mu_s)^{-1} \tag{2}$$

Symbol e in eq. (1) represents thermal effusivity defined in general as:

$$e = (k\rho c)^{1/2} \tag{3}$$

where k, ρ and c are thermal conductivity, density and volume specific heat, respectively. Thermal diffusion length μ and the modulation frequency f are related through:

$$\mu = (k/\pi\rho cf)^{1/2} \tag{4}$$

Theoretical signal amplitude S and phase ϕ are normalized in a sense that if $\beta_s \mu_s \gg 1$ and $e_s / e_w \ll 1$ eqs. (1) and (2) give $S = 1$ and $\phi = 0$ i.e. optical saturation. In the opposite case $\beta_s \mu_s \ll 1$, $S = \beta_s \mu_s/(2)^{1/2}$ and $\phi = -45°$. For strongly (high β) absorbing samples, short μ_s values are required to satisfy the condition $\beta_s \mu_s \ll 1$ implying a need for high modulation frequencies which results in a low level of generated signals. Experiments described in this paper were performed with a product $\beta_s \mu_s$ taking values from 0.7 to 10.

RESULTS AND DISCUSSION

The samples of SF oil and C18:1 were kindly provided by Unilever Research Laboratory, Vlaardingen, The Netherlands. The fatty acid composition of SF oil: C14:0 (at a trace level), C16:0 (5.7%), C18:0 (7.4%), C18:1, cis (18.5 %) and C18:2 (68.1) was determined by means of chromatographic analysis (FAME). Oleic acid used in this experiment is a product of Merck (art. 471); its purity excedeed 99 %. The measurements were performed in a laboratory maintained at 293 K and 60% relative humidity.

Figure 2 represents strength S of the measured optothermal signal for C18:1, SF oil and water, plotted versus modulation frequency in a 30 Hz to 600 Hz range. With the literature value[6] for β of water (806 cm^{-1} at 3.39 μm), product $\beta_s\, \mu_s$ (with μ taken from Table 1) for this substance ranges from 0.70 at 600 Hz to 3.2 at 30 Hz. The signals from SF oil and C18:1 were larger than those for water and, as expected from the theory, resolution was better for lower $\beta_s\, \mu_s$ values (higher modulation frequency f). The ratio S(C18:1)/S(H_2O) of measured optothermal signals for C18:1 and water (Fig. 2) has a maximal value (1.99) at 600 Hz. Substituting numerical values of parameters for C18:1 and water (from Table 1) in eq. (1) for S, and computing S(C18:1)/S(H_2O) ratio using experimentally obtained signals (Fig. 2), one obtains $\beta_s\, \mu_s = 2.16$ for C18:1 from which $\beta = 2782$ cm^{-1} for C18:1; the same procedure yields $\beta = 1893$ cm^{-1} for SF oil.

At 30 Hz $\beta_s\, \mu_s$ for C18:1 is 9.6 resulting in optical saturation which explains comparable signal strengths for C18:1 and SF oil. The S(C18:1)/S(H_2O) ratio is 1.35 (and not unity) which is due to differences in thermal properties of two substances rather than due to the optical ones. It should be noted that at 30 Hz sapphire window (thickness $d \approx 0.3$ mm) is no longer thermally thick, so that the term e_s/e_w in eq. (1) must be multiplied by μ_w/d_w.

The slope of curves (Fig. 2) in vicinity of f=600 Hz is close to -9 dB/octave. From this, -3 dB/octave is due to the frequency dependence of signal S ($S \sim f^{-1/2}$ via the quantity $\beta_s\, \mu_s$) while the remaining -6 dB/octave is a result of decreasing amplitude in sapphire window at higher frequencies (as f^{-1}). This effect, not included in eq. (1), is due to the fact that at higher frequencies (shorter irradiation periods) less energy is being deposited during each pulse. It is less pronounced in thermally thin window ($f^{-1/2}$ dependence) and consequently at 30 Hz the slope is less steep. Another reason for observed tendency of the curves to flatten off at lower frequency, is the fact that there the input resistance of preamplifier loads (discharges) the sensor (500 pF); the cut-off frequency of this high pass filter is 32 Hz.

Results from Fig. 2 were then used to calibrate OW cell in terms of $\beta\, \mu$ scale. Another series of measurements with solutions of C18:1 in chemically pure chloroform (no significant absorption at 3.39 μm) at two (30 Hz and 600 Hz) modulation frequencies was performed; the results of the study are shown in Figs. 3 and 4. Broken lines represent the experimental curves obtained with 0%, 1%, 5%, 10%, 15%, 20%,

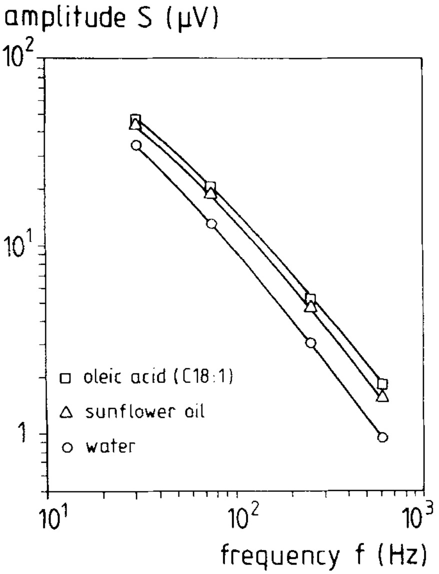

Fig. 2. The amplitude S of the optothermal signal plotted versus modulation frequency f for water, sunflower oil and oleic acid; the reason for decreasing slope is explained in the text.

Table 1. Thermophysical data [6] for water, oleic acid and sapphire: density ρ, specific heat c, thermal conductivity k, thermal effusivity e and thermal diffusion length μ (at two modulation frequencies).

	water	oleic acid	sapphire
ρ (kg/m^3)	1000	≈ 880	3980
c (J/kg K)	4180	2300	752
k (W/m K)	0.595	0.230	32.8
e (Ws$^{1/2}$/m^2 K)	1577	682	9900
μ (μm) at 30 Hz	38.3	34.5	340
μ (μm) at 600 Hz	8.60	7.76	76

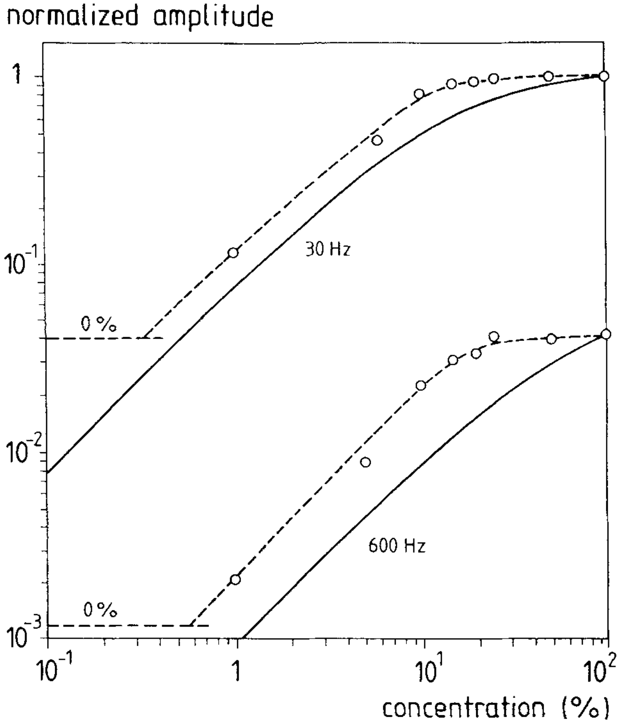

Fig. 3. Normalized optothermal signal amplitude at two modulation frequencies for varying concentration of oleic acid in chloroform. Broken lines: experiment. Solid lines are obtained from the theory using eq. (1) assuming that 100% corresponds to $\beta_s \mu_s$ = 9.6 and 2.16 at 30 Hz and 600 Hz respectively. The 0% (pure chloroform) signal levels determine the detection limit for oleic acid; for explanation of saturation behaviour refer to the text.

25%, 50% solutions and pure (100%) sample. The solid lines illustrate variations of normalized signal amplitude S and of phase ϕ calculated from eqs. (1) and (2). A linear variation of $\beta\mu$ with concentration of C18:1 was assumed and values $\beta\mu$ = 9.6 (at 30 Hz) and $\beta\mu$ = 2.16 at (600 Hz) taken to correspond to undiluted sample of C18:1. Although such modelling approach is not strictly valid for similar class of substances (as shown[1] with C18:0/CH_3 mixtures) in low concentration range, it enables one to estimate the signal behavior for samples used in this study.

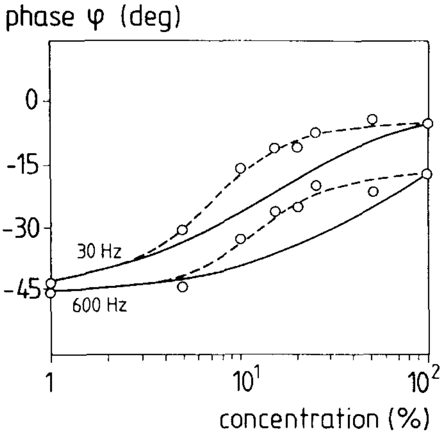

Fig. 4. The phase φ of optothermal signal for varying concentration of oleic acid in chloroform at two modulation frequencies. Broken lines: experiment. Solid lines are theoretical curves obtained with eq. (2) by assuming that a 100% solution corresponds to $\beta_s \mu_s$ = 9.6 at 30 Hz and $\beta_s \mu_s$ = 2.16 at 600 Hz.

When inspecting the experimental results in Fig. 3 one is tempted to conclude that optothermal signal optically saturates in the 25-100% concentration range. However, theoretical predictions (solid lines) in Fig. 3, especially at 600 Hz cannot explain such effects. The apparent saturation is presumably due to hydrogen bonding and the solute-solvent interaction. Failure of a C18:0/CH_3Cl mixture to follow Bouger-Beer law (range from 5 g/lit to 40 g/lit i.e 0.34% to 2.7%) in above mentioned study (IR transmission cell length 400 μm) was attributed to a shift of absorption maximum (expected between 2.75 and 2.8 μm) characteristic for free O-H stretching vibration toward longer wavelengths. Apparently, this latter is large enough (0.4 μm to 0.6 μm) and causes bonded O-H...O stretching vibration to become unresolvable from the C-H stretch vibration at 3.39 μm.

For concentration below 10%, calculated amplitude of signal (Fig. 3) decreases down to intercepts with signal levels corresponding to 0% concentration. These extrapolated points define detection limits 0.35% (at 30 Hz) and 0.55% (at 600 Hz) for C18:1/CH_3 solution. Curves for experimentally measured phase (Fig. 4) also display an anomaly, but in a broader concentration range. The limiting values for phase are those expected from the theory (eq. (2)); i.e. approximately 0° (optical saturation) and -45° (weak absorption).

In order to check the validity of gathered data, results obtained by optothermal window technique were compared to those of conventional transmission IR spectroscopy (using the cell consisting of two parallel KBr windows and a spacer). The actual distance ($L = 11.2\ \mu m$) between windows was determined by scanning the empty cell while at the same time observing wavenumber positions corresponding to the first and N^{th} fringe maxima [3]. The cell was then loaded with pure C18:1 (or SF) oil, and absorbance A in the region of interest measured with Biorad BST-7 IR FRT spectrometer. At 3.39 μm the values for A are 1.209 (for C18:1) and 0.847 (for SF oil) from which absorption coefficients $\beta = 2531\ cm^{-1}$ (for C18:1) and $\beta = 1757\ cm^{-1}$ (for SF oil) were calculated using $\beta = 2.303\ A/L$. These values are in a good agreement with 2782 cm^{-1} and 1893 cm^{-1} obtained via optothermal measurements on same samples. The reader is reminded that the accuracy of latter figures depends in a first place on β of water used here for calibration purposes.

CONCLUSION

This paper is concerned with application of optothermal window method, a variant of photoacoustic spectroscopy, for determination of IR absorption coefficients β of SF oil and C18:1, and for analytic studies of C18:1/chloroform mixtures. The radiation source was a fixed (3.39 μm) wavelength He-Ne laser. Before measurements, the cell was calibrated using water as a reference sample. Unlike traditional IR transmission spectrometry where thickness is a restrictive factor when dealing with strongly absorbing samples, effective optical pathlength $\beta_s\ \mu_s$ in optothermal approach is determined by the control of modulation frequency ($\mu = (k/\pi\rho c f)^{1/2}$) allowing also for more flexibility.

Experimentally found values of β for C18:1 and sunflower oil at 3.39 μm are 2782 cm^{-1} and $\beta = 1893\ cm^{-1}$ respectively. Values for β agree well with results obtained with cell of precisely known length using conventional transmission IR spectroscopy. Data collected in studies on C18:1/CH_3Cl solutions suggest 0.35% detection limit at 30 Hz; at higher modulation frequencies linearity is better but the signals were lower. Finally, it should be noted that optimization of $\beta_s\ \mu_s$ product by controlling modulation frequency f is of essential importance for quantitative interpretation of results. The method can easily be extended to other samples and wavelengths as well, provided that excitation of sample can be achieved and transparency of the OW in a spectral region of interest guaranteed.

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