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New approach in determining absorption coefficients of strongly absorbing liquids: optothermal studies on sunflower oil, oleic acid (and its chloroform solutions) at 3.39 microns

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Abstract: Large values (nearly 3000 cm⁻¹) of absorption coefficients β (unaccessible by conventional spectrometric methods), were measured for pure monounsaturated oleic acid (C18:1) at 3.39 μ m (C-H stretch vibration) using He-Ne laser in combination with a novel, compact optothermal sensor. Failure (except in a low concentration range) of C-H stretch vibration to follow Lambert-Beer's law was observed for solutions of C18:1 in chloroform. At 3.39 μ m minimum detectable concentration of C18:1 in chloroform is 0.35 %.

1. INTRODUCTION

In traditional infrared (IR) transmission spectrometry liquids are normally examined either neat (a film (< 10 μ m thick) compressed between two flat windows and held together by the capillarity) or in solution [1]. Thick layers of neat liquids absorb too strongly to produce a satisfactory spectrum. Large (IR) absorption coefficients β of edible oils and triglycerides, as well as inability of experimentalist to exactly specify the effective pathlength are major factors precluding performance of quantitative studies with these samples. Oil chemists and nutritionists prefer therefore new methodologies and a low cost, practical instrument that would not only allow measurements of high β values (approximately 3000 cm⁻¹) of pure compounds in a simple and reproducible fashion, but also enable determination of small amounts of such samples diluted in various solvents without a need to know the sample's thickness.

In this paper results of an experiment carried out with an optothermal window (OW) in IR are presented. Samples (pure and dissolved in chloroform) of monounsaturated oleic (C₁₈H₃₄O₂) acid C18:1, cis (purity larger than 99%) and of sunflower oil were used in this study. All carboxylic acids display broad and intense O-H stretch absorption bands in region of 3300-2500 cm⁻¹ (usually centered near 3000 cm⁻¹; weaker C-H stretching bands are generally superimposed upon O-H band). The measurements were performed using a He-Ne laser (emitting 2 mW) at 3.39 μ m (2949.5 cm⁻¹). Water, for which β value at 3.39 μ m is known was used to calibrate the system. The analytical potential of optothermal window was investigated using solutions of C18:1 in chloroform.

2. EXPERIMENTAL

The recently proposed optothermal window (OW) cell [2] shown in Fig. 1 appears well suited for measuring β of strongly absorbing fluids. Optothermal detection can be performed with arbitrary quantity of sample deposited atop a transparent sapphire window (having large thermal expansion coefficient) that is illuminated (from below) by a chopped radiation (through the very same window) of the IR He-Ne laser. The periodic heat generated in the sample due to absorption of radiation diffuses into the sapphire and leads to a formation of acoustic wave that is sensed by a piezoelectric (PZT) sensor. The lock-in amplifier (EG&G/PAR 5101) amplifies the a.c. signal detected synchronously with the modulated radiation.

Fig. 1 Exploded view of optothermal window (OW) cell and of the experimental set up used in this study.

The amplitude of the signal depends on temperature fluctuations taking place within roughly one thermal diffusion length μ from the sample-sensor interface. It can be shown that when sample (subscript s) is both thermally and optically thick and thermally thick window (subscript w), the amplitude S of optothermal signal is proportional to the expression:

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

while phase ϕ is given by

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

In eqs. (1) and (2) symbols e and μ represent thermal effusivity and thermal diffusion length defined as $e = (k\rho c)^{1/2}$ and $\mu = (k/\pi\rho cf)^{1/2}$ where k , ρ , c and f denote thermal conductivity, density, volume specific heat, and modulation frequency. If $\beta_s \mu_s \gg 1$ and $e_s/e_w \ll 1$, eqs. (1) and (2) give $S=1$ and ϕ takes a zero value (optical saturation). For $\beta_s \mu_s \ll 1$, $S = \beta_s \mu_s / (2)^{1/2}$ and $\phi = -45^\circ$. Such linear regime is however unattainable when investigating strongly absorbing (high β) samples because short μ values are required to match condition $\beta \mu \gg 1$. This in turn implies a need for high modulation frequencies f and hence low level signals will be generated. Experiments described in this paper are performed with product $\beta_s \mu_s$ ranging from 0.7 to 10.

3. RESULTS AND DISCUSSIONS

The specimen of C18:1 acid is a product (purity > 99%) of Merck (art. 471); numerical values of its (and of other samples) thermophysical parameters (specified in Table 1) were taken from the

literature [3,4]. Figure 2 features plots of net optothermal signal S (to compensate for background effects "background" signals obtained with empty OW cell were vectorially subtracted from those measured with actual samples) for oleic acid, sunflower oil, and water within $30 < f < 1000$ Hz range of modulation frequencies.

Fig. 2. The amplitude S of the optothermal signal plotted versus modulation frequency f for three samples.

Fig. 3 Normalized optothermal signal amplitude for various concentrations of oleic acid-chloroform solutions at two modulation frequencies. Broken lines: experiment. Solid lines: theory, i.e. eq. (1).

In order to determine β for C18:1 and sunflower oil, absorption coefficient of some reference sample (at the very same wavelength) is required. The IR spectra of water ($12\mu\text{m}$ thick film) were studied [5] by means of conventional IR spectroscopy yielding $\beta = 806\text{ cm}^{-1}$ at $3.39\mu\text{m}$. Using values for water from Table 1 ($\rho = 1000\text{ kg/m}^3$, $c = 4180\text{ J/kg K}$, $k = 0.595\text{ W/m K}$ and $e = 1577\text{ W s}^{1/2}/\text{m}^2\text{ K}$) with corresponding thermal diffusion lengths ($\mu = 38.3\text{ microns}$ at 30 Hz and 8.60 microns at 600 Hz) one obtains a range of $\beta\mu$ varying from 0.7 at 30 Hz to 3.2 at 600 Hz .

Table 1. Thermophysical data 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
$\rho\text{ (kg/m}^3\text{)}$	1000	≈ 880	3980
$c\text{ (J/kg K)}$	4180	2300	752
$k\text{ (W/m K)}$	0.595	0.230	32.8
$e\text{ (W s}^{1/2}/\text{m}^2\text{ K)}$	1577	682	9900
$\mu\text{ (}\mu\text{m)}\text{ at }30\text{ Hz}$	38.3	34.5	340
$\mu\text{ (}\mu\text{m)}\text{ at }600\text{ Hz}$	8.60	7.76	76

From Fig. 2, maximal value (1.99) for ratio of experimentally measured signals $S_{\text{C18:1}}/S_{\text{water}}$ is found at 600 Hz . Upon substituting this figure and the values for C18:1 from Table 1 into eq.(1) one obtains $\beta\mu = 2.16$ (for C18:1). At 600 Hz thermal diffusion length is $7.76\mu\text{m}$ and hence $\beta = 2782\text{ cm}^{-1}$

for pure C18:1, cis at $3.39\ \mu\text{m}$. A similar computational procedure yields $\beta = 1893\ \text{cm}^{-1}$ for sunflower oil at $3.39\ \mu\text{m}$. Since an overall experimental error is small, the accuracy of obtained absorption coefficients depends in the first place on uncertainty of β for water used here for calibration purposes.

The analytical potential of OW cell was studied next. The results from Fig. 2 were used to calibrate the OW cell (in terms of $\beta\mu$ scale) and another series of measurements performed with solutions of C18:1 in chloroform (no significant absorption at $3.39\ \mu\text{m}$) at two (30 Hz and 600 Hz) modulation frequencies; the results are shown in Fig. 3. Broken lines represent experimental curves obtained with 0%, 1% (by weight), 5%, 10%, 15%, 20%, 25%, 50% and 100% solutions while solid lines illustrate theoretical (eqs. (1) and (2)) variations of signal amplitude. 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) were considered to correspond to a neat oleic acid (100%) as determined above. When inspecting plots in Fig. 3 one is tempted to conclude that, contrary to predicted behaviour, optothermal signal saturates in a 25-100% concentration range. The apparent saturation is presumably due to the fact that even in relatively dilute chloroform solutions bonded O-H...O stretching vibration is not resolved from the C-H stretching vibration at $3.39\ \mu\text{m}$ [6]. Below 10% signal amplitude decreases (according to theoretical curves) down to intercepts with the signal levels corresponding to 0% concentration as seen in Fig. 3. These extrapolated points define detection limits of 0.35% (at 30 Hz) and 0.55% (at 600 Hz) for oleic acid-chloroform solutions.

4. CONCLUSIONS

Unlike traditional infrared spectroscopy where thickness of the sample is a restrictive factor when dealing with strongly absorbing samples, the effective pathlength in OW approach is determined by control of a modulation frequency. Optimization of $\beta\mu$ by controlling modulation frequency is essential for quantitative interpretation of results. The absorption coefficients for oleic acid and sunflower oil at $3.39\ \mu\text{m}$ are $2782\ \text{cm}^{-1}$ and $1893\ \text{cm}^{-1}$, respectively. These values agree well with those obtained with FTIR analysis for same samples but of known thickness ($10\ \mu\text{m}$). Data collected in studies with C18:1/ CH_2Cl solutions suggest 0.35% detection limit (at 30 Hz). Failure of C18:1 to follow Lambert-Beer's law as observed in this study is most likely due to a spectral overlap of C-H and O-H.....O.

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