Photoacoustic Effect on Liquids Characterized by Transport Phenomena

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For a liquid sample the pressure variation in the gas is generated by a heat wave and an oscillating diffusive and convective flow of mass. It increases strongly with vapor pressure and, therefore, temperature, approaching a finite value the near boiling point. Experimental results confirm the model.

It was found experimentally that the photoacoustic (PA) signal of a wet sample increases strongly with temperature [1]. It was also observed that the presence of a volatile liquid in a gas microphone cell enhances the signal of any sample [2]. We could explain these phenomena fairly well by assuming an oscillating diffusive transport of mass between the sample and the cell gas [3]. The formulas in [3] are only correct if the partial pressure of the vapor is much smaller than the pressure of the cell gas. Now we show that at higher vapor pressures or temperatures a convective motion of the cell gas governs the pressure variation. Approaching the boiling point, the heat generated by the absorption of light in the sample limits the pressure oscillation.

The scheme of the sample cell geometry is shown in Figure 1. For simplicity we assume that light, which is modulated sinusoidally with frequency $\omega/2\pi$ is absorbed at the surface of the liquid at $z=0$ and generates the heat $Q = Q_0(1+e^{i\omega t})$ per unit area. Temperature waves in the form of

$$\Phi_g = \Theta e^{i\omega t - \sigma_g z} \quad \text{and}$$
$$\Phi_s = \Theta e^{i\omega t + \sigma_s z} \tag{1}$$

propagate in the gas (g) and the sample (s), if both media are thermally thick, i.e. $|\sigma_g l_g| \gg 1$ and $|\sigma_s l_s| \gg 1$, with $\sigma_n = (1+i)a_n$. Here, $a_n^{-1} = (2\alpha_n/\omega)^{1/2}$ is the thermal diffusion length with the thermal diffusivity $\alpha_n = \lambda_n/\varrho_n c_{pn}$, where λ_n is the thermal conductivity, ϱ_n the density, and c_{pn} the isobaric specific heat capacity of the medium labelled by n.

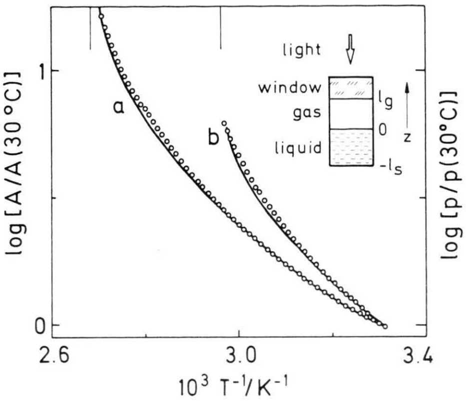

Fig. 1. Calculated pressure amplitude (solid line) and measured amplitude (circles) for water (a) and methanol (b) versus T^{-1}. Boiling temperatures are indicated. Insert: PA-cell, schematic.

A small variation $\Phi_s(0,t)$ in temperature alters the stationary vapor pressure $P_s = C_s RT$ of the sample and, therefore, the average molar concentration C_s at $z=0$ in the gas by the amount [3, 4]

$$\psi(0,t) = \frac{P_s}{RT}\,\frac{\mathrm{d}(\ln P_s)}{\mathrm{d}T}\,\Phi_g(0,t)$$
$$= \frac{P_s L}{R^2 T^3}\,\Theta\, e^{i\omega t}, \tag{2}$$

where L is the heat of vaporization and R the gas constant.

The gas consists of a non-condensable component with the molar concentration C_0 or partial pressure P_0 and a vapor with concentration C_d or partial pressure P_d. The rate of evaporation or condensation per unit area depends on the molar flux J of the vapor at the surface of the sample. If,

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for instance, the concentration $C_d(z, t)$ of the vapor at z is reduced, the concentration $C_0(z, t)$ of gas increases, because at audio frequencies the total pressure $P_t = P_0 + P_d$ and, therefore, the total concentration $C_t = C_0 + C_d$ is constant at each position z. This leads to a convective motion of the whole gas mixture towards the surface. The total molar flux of the vapor passing a plane at $z \geqq 0$ parallel to the surface of the sample is then [5]

$$J = -\frac{C_t D}{C_t - C_d} \frac{\partial C_d}{\partial z} . \tag{3}$$

Using the equation of continuity [6] $-\partial J/\partial z = \partial C_d/\partial t$ we obtain

$$\frac{C_t D}{C_t - C_d}\left[\frac{\partial^2 C_d}{\partial z^2} + \frac{1}{C_t - C_d}\left(\frac{\partial C_d}{\partial z}\right)^2\right] + \frac{\partial C_d}{\partial t} = 0 . \tag{4}$$

The concentration variation in the gas should be expressed by $C_d = C_s + \psi(z, t)$ with a concentration wave

$$\psi = c\, e^{\zeta z + i\omega t} \tag{5}$$

and a complex concentration wave number $\zeta/i = (1-i)/\eta$. Equation (5) is a solution of (4) if the amplitude c of the concentration variation is small compared to the stationary concentration C_s of the vapor, i.e. $c \ll C_s$. Then the non-linear term in (4) can be neglected and it becomes an ordinary diffusion equation with an effective diffusion coefficient D_e defined as

$$D_e = \frac{C_t D}{C_t - C_s} = \frac{P_t D}{P_t - P_s} . \tag{6}$$

In that case $\eta = (2D_e/\omega)^{1/2}$ is an effective concentration diffusion length. The amplitudes Θ and c in (1) and (5) can be determined from the boundary conditions at $z = 0$ for the concentration, (2),

$$c = P_s L \Theta / R^2 T^3 \tag{7}$$

and the heat flow,

$$\lambda_s \operatorname{grad} \Phi_s \Big|_{z=0} - \lambda_g \operatorname{grad} \Phi_g \Big|_{z=0} = Q_0 (1 + e^{i\omega t}) - D_e L \operatorname{grad} \psi \Big|_{z=0} . \tag{8}$$

$D_e L \operatorname{grad} \psi$ is the heat of vaporization necessary to generate the flow of mass $D_e \operatorname{grad} \psi$. With the expressions (1), (5), and (7) the temperature amplitude becomes for $\lambda_s a_s \gg \lambda_g a_g$

$$\Theta = Q_0 e^{-i\pi/4} \left\{ \lambda_s a_s \left[1 + \left(\frac{D_e}{\alpha_s}\right)^{1/2} \times \frac{P_s}{\varrho_s c_{ps} T} \left(\frac{L}{RT}\right)^2 \right] \right\}^{-1} . \tag{9}$$

The temperature variation, (1), averaged along the gas column of length l_g is [7]

$$\langle \Phi_g \rangle = \Theta e^{i(\omega t - \pi/4)} / (a_g l_g) , \tag{10}$$

and the average concentration variation becomes with (5) [3]

$$\langle \psi \rangle = \int_0^{l_g} \psi \, dz / l_g = \left(\frac{D_e}{\alpha_g}\right)^{1/2} L P_s \frac{\langle \Phi_g \rangle}{T} . \tag{11}$$

The total relative pressure oscillation $p(t)$ in the gas is the sum of both averages referred to the mean temperature T and concentration C_t, respectively [4]. For a thermally thick gas one has [8]

$$\frac{p(t)}{P_t} = \gamma \left(\frac{\langle \Phi_g \rangle}{T} + \frac{\langle \psi \rangle}{C_t} \right) \tag{12}$$

with $\gamma = c_{pg}/c_{vg}$, where c_{vg} is the isochoric specific heat capacity of the gas. Approaching to the boiling temperature T_b, i.e. $P_s \rightarrow P_t$, the pressure variation (12) becomes approximately

$$\frac{p(t, P_s \rightarrow P_t)}{P_t} = \frac{Q_0 \gamma R T}{\omega l_g P_t L} . \tag{13}$$

The heat available for evaporation and not the transport of mass in the gas limits the pressure amplitude. It becomes inversely proportional to the heat of vaporization.

Calculated amplitudes p and measured amplitudes A ($A \propto p$) for water and methyl alcohol in air ($P_t = 10^5$ Pa) vs. inverse temperature normalized to that at 30 °C are plotted in Figure 1. To realize optically strong absorption the liquid surface was covered with a thin layer of graphite powder.

In conclusion, we have studied theoretically and experimentally the PAE on liquids. At very low partial pressures of the liquid, the pressure variation is determined by an oscillating flow of heat between liquid and cell gas. With increasing vapor pressure, the signal reflects the diffusive and at still higher pressure the convective oscillatory motion of mass between the liquid surface and the gas. Near the boiling point the heat available for evaporation limits the amplitude.

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