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Measurement of mass diffusivity in air using thermal wave interference detection

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A discussion on the use of the thermal wave interference (TWI) for the monitoring of the transient of hydrocarbon in air is presented. The thermal wave signal was modeled using the logarithm-mixing model for the thermal diffusivity of a two-phase gas system in which the hydrocarbon vapor concentration in the air-filled TWI cell is a varying function of time. The time varying hydrocarbon vapor concentration was described assuming the simple Fick's model for mass diffusion of the hydrocarbon vapor in the stagnant air column of the TWI cell. The transient TWI signal amplitude data fitting yielded two parameters, namely, the saturation concentration and the characteristic diffusion time. From the corresponding values of the diffusion time the hydrocarbon mass diffusivities were straightforwardly obtained. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1520331]

I. INTRODUCTION

The concept of thermal wave interference introduced by Bennett and Patty[1] in the early 1980s has gained considerable interest in recent years after Shen and Mandelis[2] have demonstrated feasibility of the pyroelectric detection of a thermal wave propagating across the air gap formed between a pyroelectric sensor and a thin aluminum-film wall acting as the source of thermal waves. As a consequence, a growing number of papers have recently applied this technique to the investigation of the thermal properties of gases[3–6] and liquids.[7] The thermal wave interference (TWI) method consists essentially of recording the temperature fluctuation of the pyroelectric sensor as a function of the cavity gap length. This fact renders this technique as a well-suited method for gas and liquid samples analysis. One of the immediate applications of the TWI technique aimed at the evaluation of the thermal diffusivity of air:hydrocarbon vapor mixtures.[4–6] In these experiments, a liquid portion of the hydrocarbon under investigation is placed inside the cell in which the initially air-filled TWI cavity is assembled. The hydrocarbon vapor resulting from the evaporation process diffuses into the air inside the TWI cavity. As a result, the thermal properties of the resulting gas mixture change with time, following the changes of the vapor concentration in the air. This process evolves with time until the hydrocarbon vapor inside the cell reaches saturation. Once saturation is reached, the TWI signal is recorded as a function of the cavity length in order to measure the thermal diffusivity of the resulting air:hydrocarbon vapor mixture. In this article, we address ourselves to the quantitative understanding of the transient TWI data of air:hydrocarbon vapor mixtures.

II. METHODOLOGY

The TWI experimental setup has been discussed in detail elsewhere and it is schematically shown in Fig. 1. It consists of a temperature-controlled closed glass cell in which the TWI is enclosed. At the bottom of the glass cell there is a screwed reservoir of 30-mm diameter on which 18 ml of the liquid hydrocarbon is poured. The vapors resulting from the hydrocarbon evaporation at ambient temperature diffuses into the air cell, filling the TWI cavity with the resulting air:hydrocarbon vapor mixture. The TWI cavity of variable length is formed between a 15-μm-thick Al foil and a pyroelectric sensor consisting of a 25-μm-thick polyvinyledene difluoride film with Al metalized surfaces. The surface of this Al foil facing the inner glass tube space is painted with black ink so that it acts as a light absorber. The second glass tube attached to the right glass cell end guides a nylon cylinder on top of which the pyroelectric sensor is assembled. This nylon cylinder is coupled to a translational stage so that the distance L between the Al foil and the pyroelectric sensor can be varied. The vertical distance between the center of the resulting TWI cavity and the liquid hydrocarbon level at the bottom reservoir is equal to 7 cm, whereas the vertical air column extending from the liquid level to the top of the glass cell is equal to 10 cm. The light beam from a 20 mW He-Ne laser (Meredith Instruments), modulated at 10 Hz by means
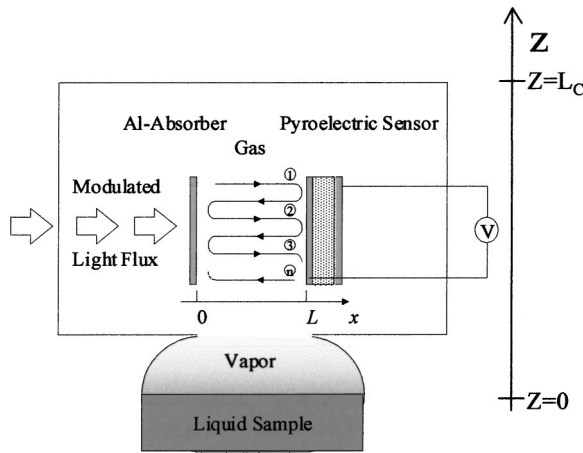
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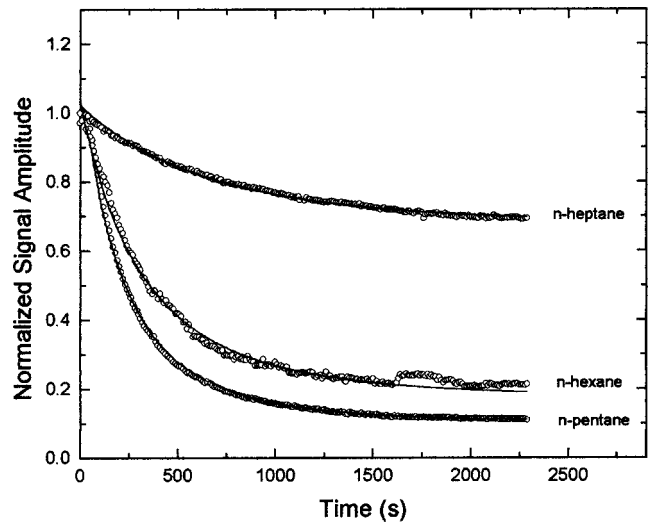FIG. 1. Schematic view of the experimental TWI setup.

FIG. 2. Time evolution of the room-temperature TWI signal amplitude, normalized to its initial $t=0$ value, of the different hydrocarbon samples. The solid curves in this plot correspond to the experimental data fitting to the expression the following expression: $V_N = \exp\{-L(\pi f/\alpha_{air})^{1/2}[(\alpha/\alpha_{air})^{1/2} - 1]\}$.

of a mechanical chopper (Model 650 EG&G), impinges on the black-painted outer surface of the Al foil. The thermal waves thus generated propagate back and forth between the Al foil and the pyroelectric sensor. The temperature rises at the pyroelectric surface, is probed using a lock-in amplifier (Model 5210 EG&G). The resulting voltage V is proportional to the average temperature rise in the pyroelectric sensor. This, in turn, is proportional to $T(L)$, so that the resulting measurable voltage may be written as (Refs. 5–9)

$$V = V_0 \frac{e^{-L\sigma}}{1-\gamma e^{-2L\sigma}}, \tag{1}$$

where V_0 is a complex function containing the frequency response of the pyroelectric sensor signal and geometrical parameters. Here, we note that the pyroelectric sensor output voltage depends explicitly on the modulation frequency and the cavity length L. The basic idea of the steady-state TWI technique consists of using a lock-in detection technique to recording the real (in-phase) and imaginary (quadrature) parts of V, or, equivalently, its amplitude and phase, as a function of the cavity length L. From the resulting dependence of the pyroelectric signal voltage on the cavity length, the thermal diffusivity is obtained from two different methods. One of them is based upon the fact that the L dependence of Eq. (1) is such that their in-phase and quadrature signals exhibit maxima and minima according to Refs. 3 and 4.

III. RESULTS AND DISCUSSION

In Fig. 2, we show a typical time evolution of the TWI signal amplitude for different air:hydrocarbon mixtures recorded for a fixed cavity length of $L=2$ mm. These measurements were carried out at ambient temperature (23 °C) and pressure (760 mm Hg) with the laboratory relative humidity at 60%. The signal decay as a function of time is reflecting the changes of the gas thermal diffusivity with time as a result of the changes of the hydrocarbon vapor concentration in the air until a saturated mixture is formed. For the present experimental situation, the gas layer in our TWI cavity may be considered as thermally thick so that Eq. (1) reduces to

$$V = V_0 \times e^{-L/\mu} = V_0 \times e^{-L(\pi f/\alpha)^{1/2}}. \tag{2}$$

To quantitatively describe the behavior of the experimental data shown in Fig. 2 we assume that the TWI is adequately described by Eq. (2) in which the thermal diffusivity is a time-dependent function of the hydrocarbon concentration in the air. To model the time dependence of the thermal diffusivity, we resort to the kinetic theory of gas mixtures.[10,11] Due to the complexity of the theoretical expression for the thermal conductivity predicted by the kinetic theory, empirical expressions are often used to analyze the experimental data. Among these, the most widely used is the so-called logarithm mixing[12] for the thermal conductivity. In this model, the thermal conductivity for the binary mixture of components 1 and 2 is written as

$$\kappa = \kappa_1^{(1-\eta)} \times \kappa_2^{\eta}, \tag{3}$$

where η denotes the concentration of Gas 2 (hydrocarbon vapor) in the reference Gas 1 (air). As discussed in Ref. 12, the logarithm-mixing model for the thermal conductivity is quite adequate for the case of a random distribution of a two-phase system. Combining the effective thermal conductivity with the expression for the heat capacity per unit volume for the binary mixture, namely,

$$\rho c = (\rho c)_1 (1-\eta) + (\rho c)_2 \eta \tag{4}$$

we can readily express the thermal diffusivity of the binary gas mixture in terms of the thermal properties of the constituents gases. One gets

$$\alpha = \alpha_1 \frac{\lambda^n}{(1+(\zeta-1) \cdot \eta)}, \tag{5}$$

where we have introduced the parameters λ and ζ defined as

$$\lambda = \frac{\kappa_2}{\kappa_1}, \quad \zeta = \frac{(\rho c)_2}{(\rho c)_1}. \tag{6}$$

Equation (5) is the basic equation we assume to describe the transient behavior of our air:hydrocarbon mixtures. The ther-

TABLE I. Values of the fitting parameters η_0 and τ as obtained from the room-temperature TWI signal amplitude data fitting. The values of the hydrocarbons diffusion coefficients in air D were calculated from $D = L_c^2/2\tau$, where L_c was taken to be equal to the length of the gas column above the liquid reservoir, namely, $L_c = 10$ cm.

Hydrocarbon	η_0	$\tau(s)$	D (cm^2/s)	$D_{literature}$ (cm^2/s)
n-Penthane	0.534 ± 0.002	580.8187 ± 2.5061	0.0861 ± 0.0004	0.0842
n-Hexane	0.349 ± 0.001	701.5513 ± 5.3165	0.0713 ± 0.0006	0.0732
n-Heptane	0.062 ± 0.0001	793.0834 ± 3.54688	0.0630 ± 0.0002	0.0674

mal diffusivity time dependence comes from the fact that the hydrocarbon concentration in the air-filled TWI cell varies with time until saturation is reached. To model the time evolution of the hydrocarbon concentration in the TWI cell, we assume the simple Fick's model for mass diffusion of hydrocarbon vapor in the stagnant air of the TWI cell. For the sake of simplicity, we assume that the relevant part of the diffusion process sensed by the TWI cavity corresponds to the hydrocarbon diffusion along the air column above the liquid reservoir shown in Fig. 1. Denoting by z the coordinate along the gas column, and assuming a Fickian diffusion, the equation describing the hydrocarbon vapor diffusion in the TWI cell may be written as

$$\frac{\partial \eta}{\partial t} = D \frac{\partial^2 \eta}{\partial z^2}, \tag{7}$$

where D is the mass diffusion coefficient (mass diffusivity) of the hydrocarbon in air. The solution to the mass diffusion equation is discussed in several texts.[13–15] Solving Eq. (7) for the gas column above the liquid reservoir of Fig. 1, with the boundary condition that the particle flux $-D\partial\eta/\partial z$ at the bottom of the gas column is proportional to the concentration difference $\eta_0 - \eta$, where η_0 is the hydrocarbon vapor saturation concentration, we may write the spatially averaged hydrocarbon concentration as

$$\eta(t) = \eta_0(1 - e^{-t/\tau}), \tag{8}$$

where τ is the hydrocarbon vapor diffusion time in our system, defined as $\tau = L_c^2/2D$, in which L_c is the characteristic length of our gas column. To test the above model for the description of the transient TWI behavior, we have applied it to the different set of measurements. The solid curves in Fig. 2 represent the results of the normalized (to its initial $t = 0$ value) TWI signal amplitude data fitting to the theoretical expression,

$$V_N = e^{-L(\pi f/\alpha_{air})^{1/2}[(\alpha_{air}/\alpha)^{1/2} - 1]} \tag{9}$$

in which the time-dependent thermal diffusivity α is given by Eq. (5) with η given by Eq. (8). Here, we note that at $t = 0$, the TWI signal is simply that of an air-filled cavity. In carrying out the data fitting to Eq. (9), the only parameters left as adjustable parameters in the data fitting procedure were η_0 and τ. All the other physical properties values involved in Eq. (5), namely, thermal conductivity and heat capacity per unit volume for the hydrocarbon and air, were taken from the literature (see Ref. 16). The values we got for

the diffusion time τ from the data fitting were 581 ± 3 s, 702 ± 5 s, and 793 ± 4 s, for n-pentane, n-hexane, and n-heptane, respectively. From these values of τ, we can estimate the corresponding hydrocarbon diffusion coefficient in air from $D = L_c^2/2\tau$. For instance, for n-pentane, the value we got for D was 0.0861 ± 0.0004 cm^2/s. This value is in good agreement with the ones reported in the literature,[17,18] for n-pentane, namely, $D = 0.0842$ cm^2/s. The same procedure was adopted with the other two hydrocarbons investigated. In Table I, we summarize the results of our TWI signal amplitude data fitting. Also included in this table are the values of the mass diffusion coefficient for the different hydrocarbons reported in the literature. These results indicate that the above model provides an adequate description of the transient TWI signal behavior.

IV. CONCLUSIONS

In this article, we have addressed the quantitative description of the TWI monitoring of the transients of hydrocarbon the evaporation kinetics in air. The TWI signal was modeled assuming the logarithm-mixing model for the hydrocarbon vapor:air mixture in which the hydrocarbon vapor concentration is a function of time. The time evolution of the hydrocarbon vapor concentration in the air-filled TWI cell was described assuming the simple Fick's model for mass diffusion of the hydrocarbon vapor in the stagnant air column of the TWI cell. The transient TWI signal amplitude data fitting yielded two parameters, namely, the saturation concentration η_0, and the characteristic diffusion time τ. From the corresponding values of τ, the hydrocarbon mass diffusivities were straightforwardly obtained. We believe the results presented in this article not only fill the lack of discussion on the transient TWI signal description but also suggest a framework for investigating a wide range of applications involving transient diffusion, such as the monitoring of soil and plants respiration kinetics, and pollutant diffusion in ambient air.

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