**2037-8**

## Introduction to Optofluidics

*1 - 5 June 2009*

**A thermal lens model including the Soret effec**

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# A THERMAL LENS MODEL INCLUDING THE SORET EFFECT

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## Outline

1. Introduction.

2. Theoretical considerations.

3. Experimental setup.

4. Results and discussions.

5. Conclusions.

# Introduction

The are very few experiments which uses the thermal lens effect to measure the Soret coefficient, and they only permit the qualitative understanding of the Soret effect. In this work we present an accurate thermal lens model that allows a qualitative and quantitative description of the Soret effect.

# *Introduction*

## Soret effect

**The r component of the mass flux of the reference chemical compound in a binary mixture can be expressed as:**

$$J_r = -\rho D \nabla c - \rho D_T c_0 (1 - c_0) \nabla T$$

**The first term is the Fick´s law of diffussion, with c the mass fraction of the reference compound and d the molecular diffusion coeficient, the second term describes the Soret effect (or thermodiffusion effect), proportional to temperature gradient, with $D_T$ thermodiffusion coefficient. Since the effect does not exist in pure fluids one usually writes $c_0(1-c_0)$ factor of $D_T$. Thus the second term describes mass separation due to a temperature gradient, whereas the first describes homogenization by normal diffusion.**

**The two terms are thus of opposite sign, and when they are of equal intensity, we are in steady-state conditions $J_r=0$ implying**

$$\nabla c = -\frac{D_T}{D} c_0 (1 - c_0) \nabla T \qquad\qquad S_T = \frac{D_T}{D}$$

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*1. H. Tyrell, Diffusion and Heat Flow in Liquids (Butterworths, London, 1961).*

# Theoretical considerations

## Thermal and concentration lenses

**Probe beam**

**Sample**

**Chopper or Shutter**

**Excitation beam**

Filter

TL signal (a.u)

2000

0

-2000

Time t (s)

0.00    0.25    0.50
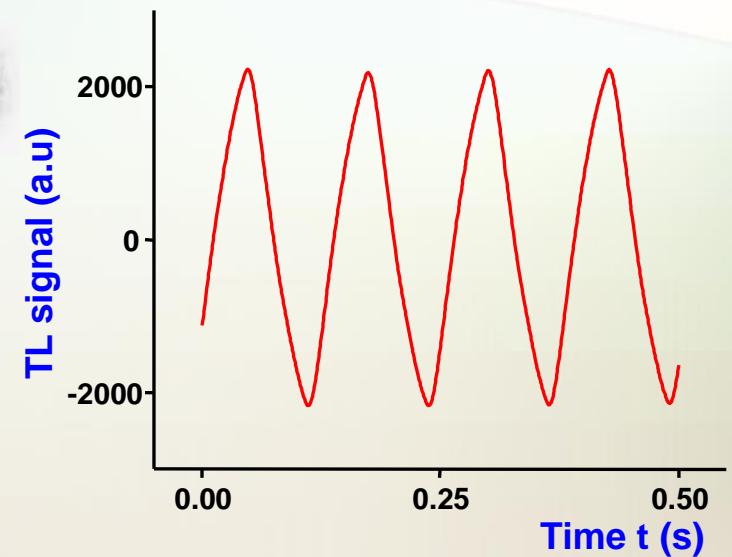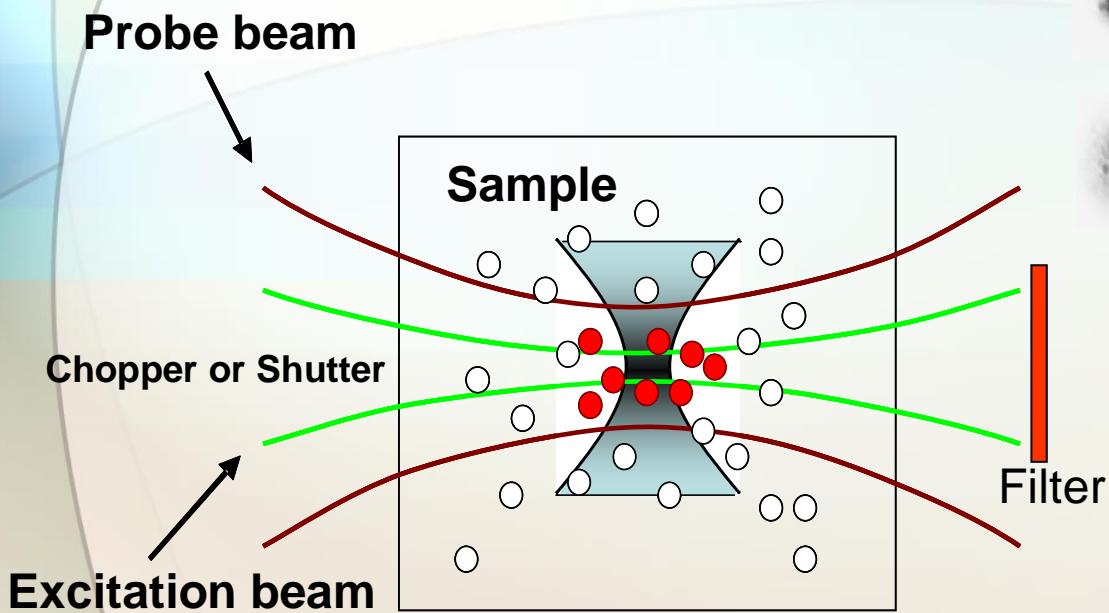
$$I(r,z) = \frac{2P_e}{\pi w_e^2} e^{-2r^2/w_{e(z)}^2}$$

## Temperature distribution

$$C_p\rho\frac{\partial[\Delta T(r,z,t)]}{\partial t} - \kappa\nabla^2[\Delta T(r,t)] = \dot{Q}(r,z) = 2\pi\frac{2P_e\alpha}{\pi w_e^2(z)}\exp\left\{-\frac{2r^2}{w_e^2(z)}\right\}$$
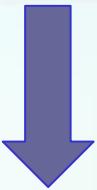
$$\Delta T(r,z,t) = \frac{2P_e\alpha}{\pi\rho C_p\omega_e^2(z)}\int_0^t\frac{1}{1+2t'/t_c(z)}\exp\left(-\frac{2r^2}{\omega_e^2(z)(1+2t'/t_c(z))}\right)dt'$$

$$I(r,z) = \frac{2P_e}{\pi w_e^2}e^{-2r^2/w_e^2}$$

$$D_{th} = \kappa/\rho C_p$$

$$t_c(z) = \omega_e^2(z)/4D_{th}$$

1. Caslaw et al., Conduction of head in solids, 2 ed. (Clarendon Press, Oxford, 1959)

2. Dennemeyer et al., Introduction to diff. partial equations (McGraw-Hill, N. York, 1968), p. 294.

## Refractive index gradient and induced phase shift

**The refraction index is temperature and concentration dependent:**

$$\Delta n(r,z,t) = \left(\frac{\partial n}{\partial T}\right)\Delta T(r,z,t) + \left(\frac{\partial n}{\partial c}\right)\Delta c(r,z,t)$$

**But the concentration change can be given as**

$$\Delta c(r,z,t) = -S_T c_0(1-c_0)\Delta T(r,z,t)\Gamma(z,t)$$

**With**

$$\Gamma(z,t) = 1 - \sum_{i=1}^{\infty}\frac{4}{(2i-1)\pi}\sin\left[\frac{(2i-1)\pi}{2}\right]\exp\left[-(2i-1)^2\frac{t}{t_D(z)}\right] \qquad t_D(z) = \frac{\omega_e^2(z)}{4D}$$

**The phase difference $\Delta\Phi(r,t)$ is due to no uniform increase of the temperature:**

$$\Delta\Phi(r,t) = \frac{2\pi}{\lambda_p}l\left[\Delta n(r,z,t) - \Delta n(0,z,t)\right]$$

$$\Delta\Phi(r,z,t) = \frac{2\pi}{\lambda_p}l\left[\frac{\partial n}{\partial T} - \frac{\partial n}{\partial c}S_T c_0(1-c_0)\Gamma(z,t)\right]\left[\Delta T(r,z,t) - \Delta T(0,z,t)\right]$$

1. H. Cabrera, E. Sira, K.Rahn, and M. García-Sucre, Appl. Phys. Lett., **94**, 051103 (2009).

2. Marcano et al., J. Opt. Soc. Am. B 19, 119 (2002)

3. Giglio et al., Phys. Rev. Lett. 38, 26 (1977).

$$\Delta\Phi(r,z,t) = (\phi_s \Gamma(z,t) - \phi_{th}) \int_{1/(1+2t'/t_c(z))}^{1} \frac{1 - \exp[-2t'r^2/\omega_p^2(z)]}{\tau} d\tau$$

$$\phi_{th} = \frac{P_e \alpha l}{\lambda_p k} \frac{\partial n}{\partial T}$$

$$\phi_s = \frac{P_e \alpha l}{\lambda_p k} \frac{\partial n}{\partial c} S_T c_0 (1 - c_0)$$

1. H. Cabrera, E. Sira, K.Rahn, and M. García-Sucre, Appl. Phys. Lett., **94**, 051103 (2009).

2. Marcano et al., J. Opt. Soc. Am. B 19, 119 (2002).

**Thermal lens induces additional phase in the probe field:**

r

$$\vec{E}_0 \exp i(\omega t - kz)$$

$$\vec{E}_0 \exp i(\omega t - kz - \Delta\Phi(r,t))$$

$$\exp(-i\Delta\Phi(r,t))$$

1. H. Cabrera, E. Sira, K.Rahn, and M. García-Sucre, *Appl. Phys. Lett.,* **94**, 051103 (2009).
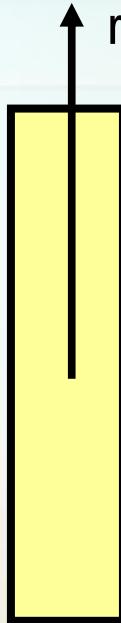
**Thermal lens signal**

$$T(z,t,\Delta\Phi)=2\pi\int_0^{r_0}|E(r,z,t)|^2\,r\,dr$$

**Following the same lines of Ref.1**

$$S_{total}(z,t)=\frac{T(z,t,\Delta\Phi)-T(z,t,0)}{T(z,t,0)}$$
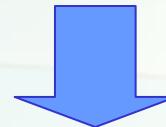
$$S_{total}(z,t)=S_{th}-S_s=\phi_{th}K(z,t)-\phi_s K(z,t)\Gamma(z,t)$$

$$K(z,t)=\arctan\left\{\frac{4m(z)\upsilon(z)t/t_c(z)}{\upsilon^2(z)+[1+2m(z)]^2+\left[1+2m(z)+\upsilon^2(z)\right]2t/t_c(z)}\right\}$$
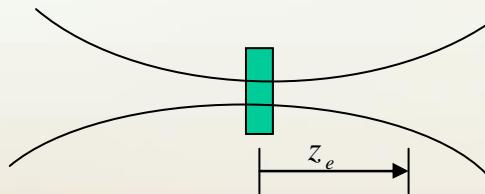
$$z_e=\frac{\pi w_{0e}^2}{\lambda_e}$$

$$\phi_{th}=\frac{P_e\alpha l}{\lambda_p k}\frac{\partial n}{\partial T}\quad;\quad m(z)\equiv\left(\frac{\omega_p(z)}{\omega_e(z)}\right)^2\quad;\quad z_p=\frac{\pi w_{0p}^2}{\lambda_p}\quad;\quad \upsilon(z)\equiv\frac{z-a_p}{z_p}+\frac{z_p}{L-z}\left[1+\frac{(z-a_p)^2}{z_p^2}\right]$$

1. Marcano et al., J. Opt. Soc. Am. B **19**, 119 (2002).

2. *H. Cabrera, E. Sira, K.Rahn, and M. García-Sucre, Appl. Phys. Lett., **94**, 051103 (2009).*

$$K(z,t) = arctg\left(4m(z)v(z)t/t_c(z)/\left\{\left[1+2m(z)+v(z)^2\right]2t/t_c(z)+\left[1+2m(z)\right]^2+v(z)^2\right\}\right)$$

**If** $t \to \infty$ **y** $z_p \to \infty$ **for** $z = 0$

$$K(0,t \to \infty) = arctg\left\{2(\lambda_p/\lambda_e)(L/z_e)\right\}$$

**As** $L \gg z_e$ → $K = \pi/2$

$$\Gamma = 1$$

$$S_{total}(z,t) = S_{th} - S_s = \phi_{th}K(z,t) - \phi_s K(z,t)\Gamma(z,t)$$

$$\phi_{th} = \frac{P_e\alpha l}{\lambda_p k}\frac{\partial n}{\partial T}$$

$$S_{total}(z,t) = S_{th} - S_s = \phi_{th}\frac{\pi}{2} - \phi_s\frac{\pi}{2}$$

$$\phi_s = \frac{P_e\alpha l}{\lambda_p k}\frac{\partial n}{\partial c}S_T c_0(1-c_0)$$

$$S_{total}(z,t) = \frac{P_e\alpha l\pi}{k\lambda_p 2}\left[\frac{\partial n}{\partial T}-\frac{\partial n}{\partial c}S_T c_0(1-c_0)\right]$$

1 . A. Marcano, and H. Cabrera, J. Opt. Soc. Am. B, 23, 1408 (2006).

2. H. Cabrera, E. Sira, K.Rahn, and M. García-Sucre, Appl. Phys. Lett., **94**, 051103 (2009).

# Experimental setup
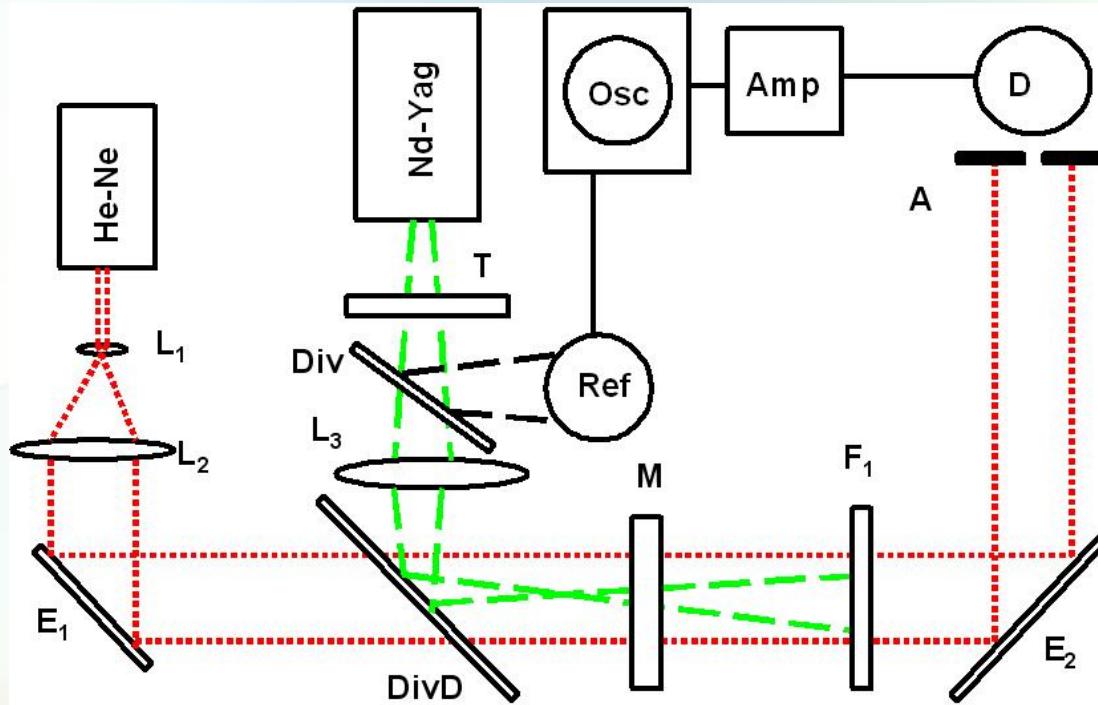


$$S_{total}(z,t) = \frac{T(z,t,\Delta\Phi) - T(z,t,0)}{T(z,t,0)}$$

*The sample consists of cobalt nitrate as a solute disolved in ethanol/water solvent. A cobalt nitrate was chosen beacuse it does not changes the thermo-optical properties of the solvent, it is not fluorescent, and the absorption at the probe wavelength is lower than the absorption at the excitation wavelength. The abs. was measured with an Ocean Optics spectrometer.*

*1. H. Cabrera, E. Sira, K.Rahn, and M. García-Sucre, Appl. Phys. Lett., **94**, 051103 (2009).*

# Results and discussions

## Calculation of the Soret coefficient

**(P=0.54 mW, cell 1 cm)**



$$\lambda_e = 532nm$$

$$\lambda_p = 632.8nm$$

$$L = 140cm$$

$$\phi_{th} = -0.0278$$

$$\phi_s = -0.00305$$

$$D = 1.19 \times 10^{-3} cm^2 / s$$

$$z_e = 1cm$$

$$z_p = 10000cm$$

$$t_D = 1.6s$$

$$S_{total}(z,t) = S_{th} - S_s = \phi_{th}K(z,t) - \phi_s K(z,t)\Gamma(z,t)$$

$$S_{total}(z,t) = \frac{P_e \alpha l \pi}{k \lambda_p 2}\left[\frac{\partial n}{\partial T} - \frac{\partial n}{\partial c} S_T c_0 (1 - c_0)\right]$$

$$\frac{\partial n}{\partial T} = 2.58 \times 10^{-4} K^{-1} \qquad \frac{\partial n}{\partial c} = 3.72 \times 10^{-2}$$

$$c_0 = 0.3912$$

$$S_T = (-3.19 \pm 0.08) \times 10^{-3} K^{-1}$$

$$c_0 = 0.3912$$

$$S_{total} = -0.0388$$
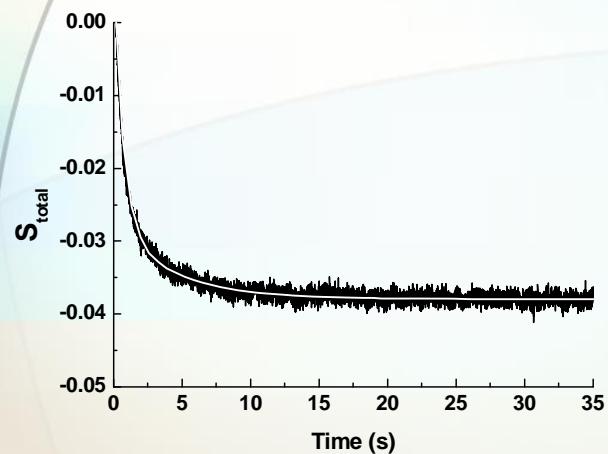
$$k = 3.80 \times 10^{-3} W cm^{-1} K^{-1}$$

$$D = \frac{\omega_e^2}{4t_D} = (4.60 \pm 0.2) \times 10^{-6} cm^2 s^{-1}$$

$$S_T = (-3.21 \pm 0.07) \times 10^{-3} K^{-1}$$

$$\alpha = (4.80 \pm 0.06) \times 10^{-2} cm^{-1}$$

1. H. Cabrera, E. Sira, K.Rahn, and M. García-Sucre, *Appl. Phys. Lett.*, **94**, 051103 (2009).

# Results and discussions

TABLE I: Soret coefficient ($S_T$) and diffusion coefficient ($D$) of mixtures of ethanol and water in mass fraction of ethanol at $T = 298$ K. The errors for $S_T$ corresponding to the five cases illustrated are from left to right 0.15, 0.05, 0.07, 0.25, and 0.3, respectively.

| $c_0$ | 0.166 | 0.350 | 0.3912 | 0.540 | 0.760 |
|---|---|---|---|---|---|
| $S_T$ ($10^{-3}$ K$^{-1}$)[a] | 4.60 | -2.20 | $-3.21$ | -4.60 | -3.90 |
| $D$ ($10^{-6}$ cm$^2$s$^{-1}$)[a] | 7.30 | 4.80 | 4.60 | 4.20 | 4.50 |
| $S_T$ ($10^{-3}$ K$^{-1}$) | 4.70 [c] | -2.16 [c] | -3.21[b] | -4.80 [d] | -4.30 [d] |
| $D$ ($10^{-6}$ cm$^2$s$^{-1}$) | 7.60 [c] | 4.70 [c] | 4.55[b] | 4.30 [d] | 4.60 [d] |

[a] from this work.
[b] from Ref.[8].
[c] from Ref.[11]
[d] from Ref.[12]

1. This work, Cabrera et al., Appl. Phys. Lett., **94**, 051103 (2009).

[8] K. J. Zhang, M. E. Briggs, R. W. Gammon, and J. V. Sengers, J. Chem. Phys. **104**, 6881 (1996).

[11] P. Kolodner, H. Williams, and C. Moe, J. Chem. Phys. **88**, 6512 (1988).

[12] R. Kita, S. Wiegand, and J. L. Strathmann, J. Chem. Phys. **121**, 3874 (2004).

[4] C. Nieto-Draghi, J. B. Avalos, and B. Rousseau, J. Chem. Phys. **122**, 114503 (2005).

# Results and discussions
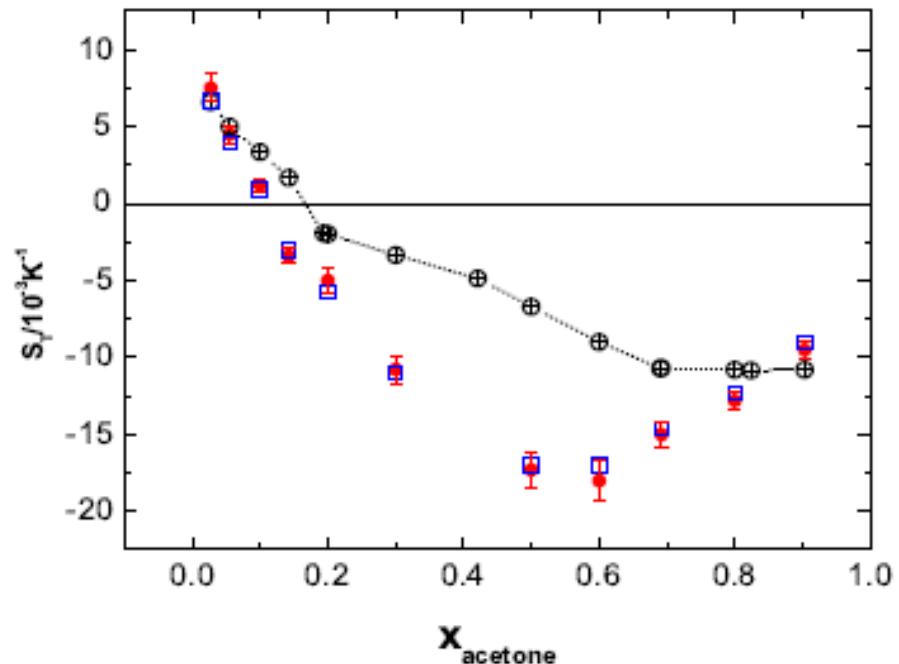


FIG. 3: (Color online) Soret coefficient of acetone as a function of the molar fraction of organic solvent. The solid red circles refer to the experimental data measured in this work and the corresponding open blue squares represent the results reported by Ning *et al.* [3]. The cross black circles represent simulation results [4]. The dashed line is a guide for the eyes.

*1. This work, Cabrera et al., J. Chem. Phys. , submitted (2009).*

[3] H. Ning, and S. Wiegand, J. Chem. Phys. **125**, 221102 (2006).

[4] C. Nieto-Draghi, J. B. Avalos, and B. Rousseau, J. Chem. Phys. **122**, 114503 (2005).

## Conclusions

- **A generalized thermal lens model, including the Soret effect, have been developed.**

- **The model allows the precise determination of the Soret coefficient.**

- **The mass-diffusion coefficient was also determined.**

- **Good agreement was achieved between the experimental results and the existing data in the literature.**

- **Our results also suggest a failure of the simulation procedure, around equimolar concentrations, for acetone/water mixtures.**

# *Thanks*