Solvent isomers effect on thermal lens signals and diffraction ring patterns of the acid blue 29 dye

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The CW laser dual-beam z-scan technique was used to investigate the influence of solvent isomers on thermal lens signals of acid blue 29 dyes. The acid blue 29 dye were separately dissolved in the following solvents: 1-propanol, 2- propanol, 1-butanol and 2-butanol, in order to study the effect of solvent isomers on the thermal lens signal. The thermal lens signals of the acid blue 29 / 1- butanol were found to be the highest among the others used samples; this can be explained on the basis of the transfer heat by convection processes. Also, the self-diffraction rings were observed for the studied samples in order to investigate the influence of solvent isomers on the generating of the diffraction ring pattern. Then, we were able to extract all the thermal lens parameters of the acid blue 29/solvents from the experimental measurements for emphasizing the most effective isomer of the used solvents. The reported work has shown that the molecular heat convection is crucial on the formation of thermal lens signals.

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Keywords: Thermal lens effect, Acid blue 29, Thermo-optic coefficient, Diffraction ring pattern

1. Introduction

The thermal lens (TL) spectrometry is considered to be sensitive technique for the determination of thermo-optical properties of very low absorption optical materials [1-4]. The formation of TL effect rises when the Gaussian laser beam interacts with the nonlinear optical (NLO) materials until the sample molecules get the thermal equilibrium state through the heating transfer processes [4, 5]. Two similar techniques were exploited to probe the TL effect, namely, the mode-matched and the mode-mismatched dual beam techniques. However, it was mentioned that the second technique is useful and more sensitive[6].

The TL technique was employed for investigating the thermo-optical properties of macromolecules and complexes, such as: liquid resin [7], Fluorescein–Rhodamine B dye mixtures [8], Tris(2,2′-bipyridyl)iron(II) tetrafluoroborate [9], sodium carbide nanoparticle [10], liquid ethanol [11], Sudan IV [12], series of liquid aliphatic alkanes [13], the structural isomers of butanol, [4], and series of primary alcohols [14, 15]. The NLO properties of dye molecules can be changed due to the environmental effects such as solvent polarity [16, 17]. Also, the NLO properties of Azophloxine dye mixed with a surfactant were investigated using z-scan technique [18]. Recent studies have been reported about the optical limiting behavior of acid blue 29 [19, 20] and the effect of solvents on the NLO properties of acid blue 29 using single z-scan technique [21, 22].

This work reports, a dual-beam z-scan technique for utilizing and investigating the influence of the molecular structure isomers of alcohols on TL effect and diffraction ring pattern of the acid blue 29 dye (AB29).

2. Experimental techniques

The TL data was acquired using similar experimental setup mentioned in our recent published work [5]. Here, we will give a short brief about the experimental setup (Fig. 1). It depends on the mode-mismatched pump-probe beams technique, the chosen angle between the incident pump laser and the probe beam was $\Phi \approx 1.4^0$. A diode pump solid state laser (DPSS) was used as pump laser with $\lambda = 532$nm, and low power (1mW) stabilize TEM_{00} Gaussian He-Ne laser with $\lambda = 632.8$nm used as probe beam. The transmitted beam signals were forward to the silico photo-detectors, which connected to digital oscilloscope in order to trace the thermal lens effect in the sample. The studied sample cell was 2 mm thick. A pulse generator was used to modulate the CW laser excitation source in order to have long period of time (2s), as on/off exposure time as seen in left-hand side in Fig.1.

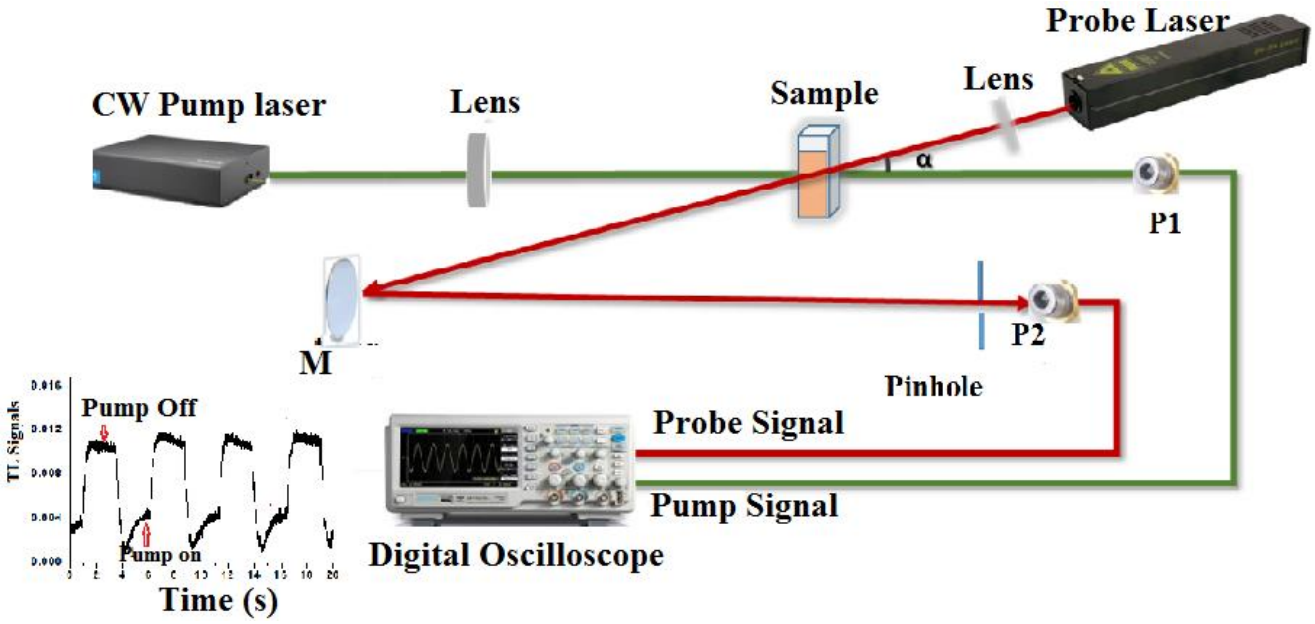

Fig. 1. The experimental setup of CW laser dual beam z-scan thermal lens measurements (color online)

3. Results and discussion

The AB29 dye was dissolved in different solvents, such as: 1-propanol, 2-propanol, 1-butanol, and 2-butanol with concentration of 0.01m*M*. Then, the UV-Vis absorption spectra were taken using UV-1601PC Shimadzu spectrophotometer (Fig. 2). The observed strong absorptions band is located in the visible region nearby λ=600 nm and the intensities of the AB29 dye dissolved in the following isomer solvents are: 1-propanol> 1-butanol> 2-propanol> 2-butanol.

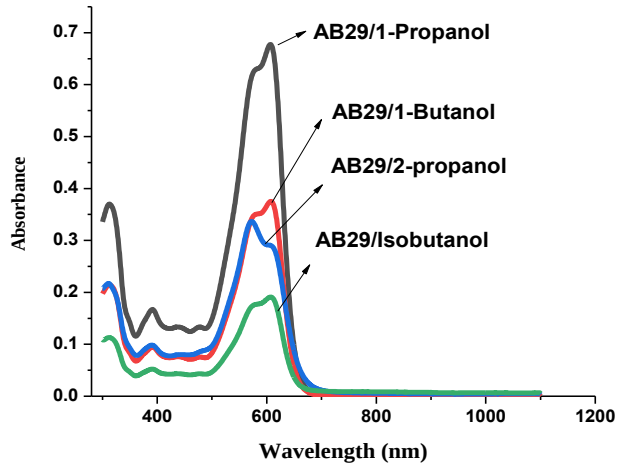

Fig. 2. UV-Vis absorption spectra of AB29 dye in 1-propanol, 2-propanol, 1-butanol, and 2-butanol (color online)

Closed-aperture z-scan measurements were performed using a CW laser with a wavelength of λ=532 nm for AB29 dye in 1-propanol, 2-propanol, 1-butanol, and 2-butanol with concentration of 10^{-3} *M*. Fig. 3 shows the transmitted intensity of the AB29 dye in different solvent isomers. The feature of the each recorded curve is a peak / valley configuration, which is considered the sample as self-defocusing materials or negative lens. Fig. 3 indicates that the value of the peak-to- valley (ΔT_{p-v}) is larger than $1.7\times Z_R$, where is Z_R=4.176 mm. The ΔT_{p-v} of each curves were calculated using the experimental data in Fig. 3 (a, b). Then, using the following relations of 1, 2, 3, 4 and 5, we were able to calculate the phase shift ($\Delta\phi_0$), n_2, Δn and dn/dT and listed in Table 1.

$$S= 1-\exp(-2r_a^2/\omega_a^2) \quad (1)$$

$$\Delta T_{p-v}=0.406(1-S)^{0.25}|\Delta\phi_0| \quad (2)$$

$$n_2 =\lambda\,\Delta\phi_0 /2\pi\, I_0\, L_{eff} \quad (3)$$

$$\Delta n = n_2\, I \quad (4)$$

$$\Delta n = \frac{dn}{dT}\frac{I\,\alpha_0\,\omega_o^2}{4\,k} \quad (5)$$

All quantities of S, r_a, ω_a, $\Delta\phi_0$, n_2, Δn, I_0 , dn/dT, ω_0, α_0, k, and L_{eff} used in the above equation are defined in ref. [21].

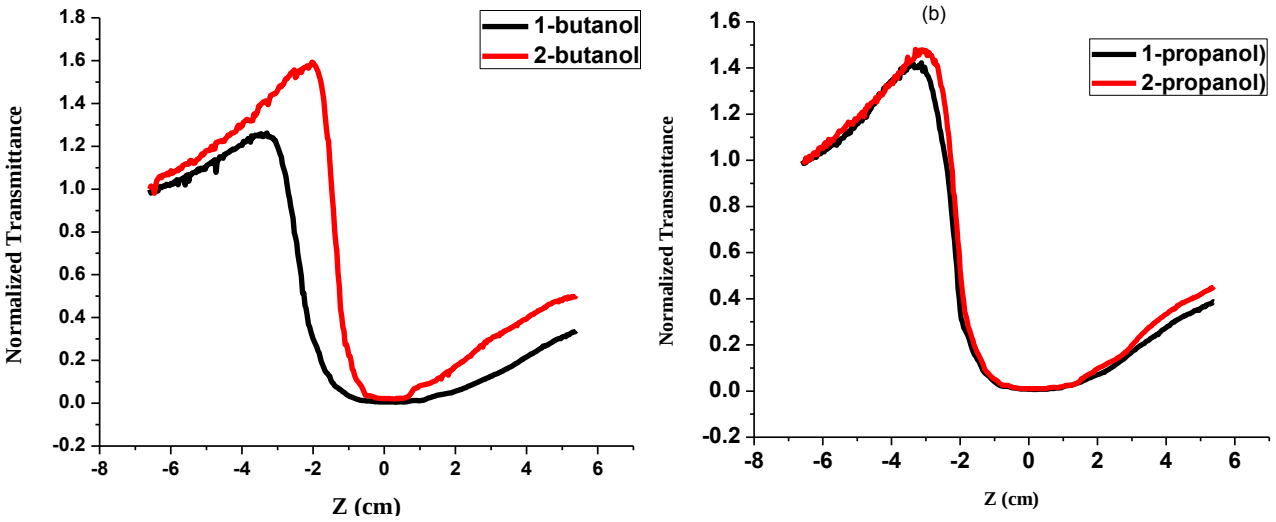

Fig. 3. Closed-aperture z-scan measurement of AB29 dye: (a) in 1-butanol, and 2-butanol, (b) in 1-propanol, 2-propanol with concentration of 10^{-3} M (color online)

In order to study the influence of the isomers molecular structure of the solvents on the TL signals, we have recorded the TL signals of the AB29/1-butanol and the AB29/2-butanol (Fig. 4). Also, Fig. 5 presents TL signals of the AB29/1-propanol and the AB29/2- propanol. In both Figs. 4 and 5, there are some differences regarding to the TL signals. However, the observed TL signals of AB29/2-butanol are stronger than the AB29/1-butanol, the same features are observed on using the AB29/2-propanol and the AB29/1-propanol. The recorded data have confirmed the presence of the molecular structure influence of the solvent isomers on the TL signals. This can be explained on the bases of the molecular size of the isomers, the 1-butanol has longer chain than the 2-butanol, but, there is branching effect in the 2-butanol. Both effects have an important role on the molecular heat convection [15]. Our results show that the TL signals change with changes of the two isomers, 1-butanol (or the 2-butanol) and1-propanol (or the 2-propanol). In both, Figs. 4 and 5, the TL signals of the 2-butanol and the 2-propanol are higher than other isomers (1-butanol and1-propanol). Usually, the TL signals of the studied sample depend on a number of factors, such as, absorption coefficient (α_0), thermal conductivity (k), thermal expansion coefficient (β), thermo-optic coefficient (dn/dT), and heat capacity (C_p). Also, it was found that the NLO properties (NLA coefficients) of materials like dyes molecules can change with the solvent polarity [16, 23, 24]. It is well known that the absorption of the pump laser beam changes very little with changes in the isomer structure. The heat generated in the isomers molecules is transferred by conduction mode. But, there is strong absorption of the laser beam, so, there will be heat convection mode. The other mentioned parameters may vary at high level with isomer structures[4]. The useful model for TL study is the model developed by Goswami et al.[15]. It was based on the heat conduction and heat convection. So, the important TL parameters were obtained using the model developed by Goswami, which can be represented with equation 6[15]:

$$\frac{I(t)}{I(0)} = [1 - \frac{\theta_1 + \theta_2}{2} \tan^{-1}\left(\frac{2mV}{[(1+2m)^2+V^2](\frac{t_c}{2t})+1+2m+V^2}\right)]^2 + F[\frac{\theta_1+\theta_2}{4} \ln\{\frac{[1+2m/(1+\frac{2t}{t_c})]^2+V^2}{(1+2m)^2+V^2}\}]^2 \quad (6)$$

$$\text{Where, } \theta_1 = -[\frac{A\,l\,(\frac{dn}{dT})}{\lambda_p\, k}],$$

$$\theta_2 = -[\frac{(\alpha P - A)\,l\,(\frac{dn}{dT})}{\lambda_p h}] \exp(-t/t_d)$$

All quantities of m, V, θ_1, θ_2, A, λ_p, dn/dT, α, P_e, F, k, h, t_c and t_d used in the above equation are defined in ref.[15].

All the new TL parameters were obtained by fitting the experimental data into equation 6, and they are tabulated in Table 2.

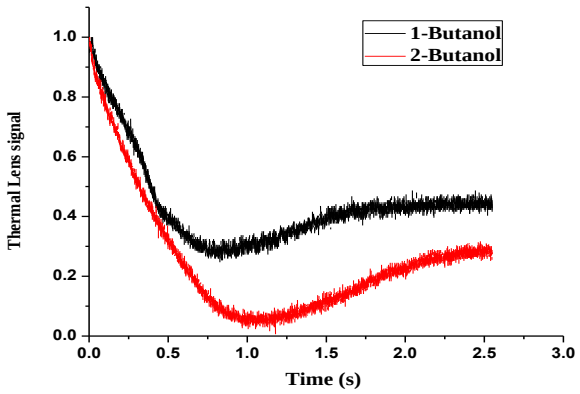

Fig. 4. Thermal lens signal for AB29/ 1-Butanol, 2-Butanol at I = 60 mW (color online)

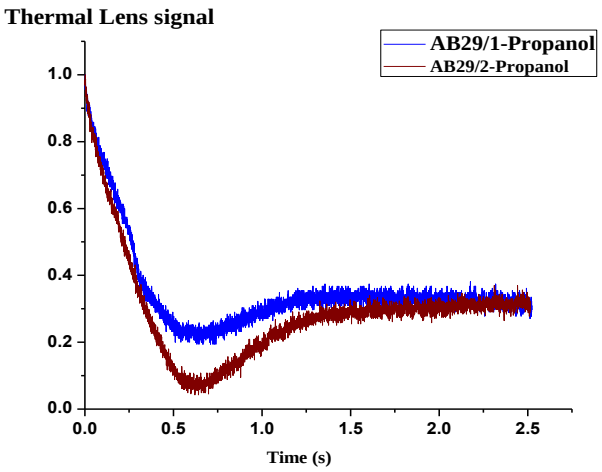

Fig. 5. Thermal lens signal for AB29/ 1-propanol, 2-propanol at I = 60 mW (color online)

Also, the thermal diffusivity "D" of the medium was calculated from the relation $[t_c = (\frac{\omega_e^{\ 2}}{4D})]$, where ω_e the beam radius of the laser beam.

It was reported by Goswami [4], there were two important factors can influence on the molecular heat convection in the solvents isomers (the same molecular formula): (1) molecular surface area, which would decrease with increased branching, and (2) steric hindrance, which increases with molecular branching. However, these two factors oppose each other; so, it would be interesting to see how they affect the molecular heat convection. Our results in Table 2 indicate that the value of 'h' is higher for 1-butanol than 2-butanol as well as 1-Propanol and 2-Propanol, and t_c is smaller for 2-butanol than 1-butanol (the same behavior for 1-Propanol and 2-Propanol). However, we found that the values of h, t_c and t_d depend on the molecular structure, our results agreed with reported results of ref.[4].

A digital camera used to captured the generated DR`s during passing the Gaussian laser beam (CW laser with λ=532 nm) through the AB29/ solution. Full details of the experimental set were mentioned in ref. [25]

To study the influence of isomers structure of the solvents on the DR's pattern, we have recorded the DR's pattern of the AB29/1-butanol/2-butanol and AB29/1-propanol and the AB29/2- propanol. As seen in Fig. 6 there are some differences between the observed DR's, where the number of rings decreased markedly when using the 2-butanol as solvent with AB29 dye, this can be understood on the basis of the 1-butanol has the highest capability to transfer heat by convection [4]. The number of DR`s, NL phase shift ($\Delta\phi_0$), NL refractive index (n_2), Δn, and thermo – optic coefficient (dn/dT) were calculated using the following equations 3, 7, 8 and 9 [25, 26]:

$$\Delta n = n_2 I \tag{7}$$

$$\Delta\phi_0 = 2\pi N \tag{8}$$

$$\frac{dn}{dT} = \frac{\Delta n \times 4k}{I\ \alpha_0\ \omega_o^2} \tag{9}$$

where "k" is the thermal conductivity of used solvent, α_0 is the linear absorption coefficient and ω_0 is the radial of beam waist. All the previous quantities are listed in Table 3.

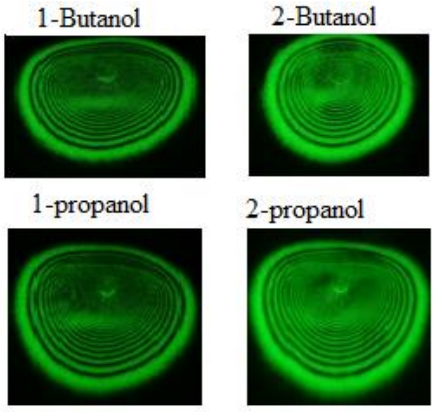

Fig. 6. Image of DR`s of AB29 dye dissolved in different solvents (1-butano,2-butanol1-propanol,2-propanol) at I = 60 mW (color online)

Table 1. The calculated quantities of ΔT, $\Delta\phi_0$, n_2, Δn, dn/dT, K and α_0.

Acid blue 29 /Solvents	**ΔT**	**phase shift $\Delta\phi_0$**	**n_2 $\times10^{-7}$**	**Δn $\times10^{-4}$**	**dn/dT(K^{-1}) $\times10^{-5}$**	**K (W/mk)**	**α_0 (cm^{-1}) Absorption coefficient**
1-butanol	1.25	-3.188	-1.35	1.82	3.51	0.146	3.17
2-butanol	1.57	-3.991	-1.47	1.98	6.74	0.133	1.64
1-propanol	1.41	-3.590	-1.89	2.55	2.80	0.149	5.68
2-propanol	1.47	-3.730	-1.61	2.17	3.55	0.132	3.39

Table 2. The TL parameters tc (conduction time constant), td (convection time constant), D (the thermal diffusivity), dn/dT (thermo-optic coefficient) and h (convective heat transfer factor)

AB29 / solvent	t_c (s)	t_d (s)	D(cm^2/s) $\times10^{-6}$	dn/dT(K^{-1}) $\times10^{-5}$	h(W/cmK) $\times10^{-2}$
1-butanol	**1.23×10^{-2}**	**0.29**	**13.82**	**- 8.26**	**4.07**
2-butanol	**1.06×10^{-2}**	**0.20**	**20.28**	**- 3.55**	**1.17**
1-Propanol	**3.99×10^{-4}**	**0.35**	**11.35**	**- 5.77**	**3.22**
2-Propanol	**2.83×10^{-3}**	**0.57**	**6.97**	**- 0.38**	**0.06**

Table 3. The calculated quantities of N, $\Delta\phi_0$, n_2, Δn and dn/dT

Acid blue 29 /Solvents	Number of rings (N)	phase shift ($\Delta\phi_0$)	$n_2(cm^2/W)$ $\times10^{-6}$	Δn $\times10^{-3}$	dn/dT(K^{-1}) $\times10^{-4}$
1-butanol	20	-125. 6	-1.33	7.19	- 3.47
2-butanol	10	-62.8	-0.58	3.13	- 2.65
1-propanol	21	-131.88	-1.73	9.39	- 2.57
2-propanol	18	-113.04	-1.22	6.60	- 2.96

4. Conclusion

We were able to show that the thermal lens signals depend on the molecular structure isomers. The AB29 dye was dissolved in two structure isomers of 1-propanol, 2-propanol and 1-butanol,2-butanol, the results have shown that the 2-Butanol has better effect on the thermal lens signal than 1-Butanol, the same feature is applied to the 2-propanol. Also, we have studied the influence of structure isomers of the solvents on the generated DR's pattern using the AB29/1-butanol/2-butanol and AB29/1-propanol/2- propanol.

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