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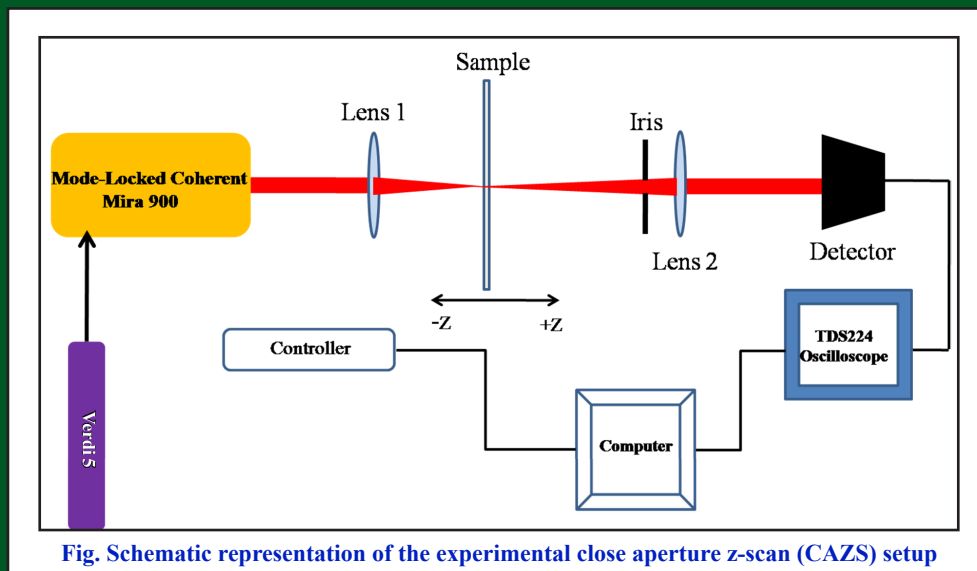


Fig. Schematic representation of the experimental close aperture z-scan (CAZS) setup

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Exploring the effects of intermolecular interactions on the self-defocusing of binary liquid mixtures using single beam z-scan technique

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Self-defocusing (or negative lens effect) study of different sets of binary liquid mixtures having varying polarities has been carried out by employing a high repetition rate (HRR) femtosecond pulsed laser and utilising a single beam close aperture z-scan (CAZS) technique. We determined the change in transmittance values between peak and valley (ΔT_{p-v}) of the CAZS trace for each different binary liquid mixtures at the varying composition of components. We correlated the variation of ΔT_{p-v} values with the composition ratio of components to the change in physical parameters, which in turn affects the intermolecular interactions. Here, the combined effects of polarity differences and different molecular structures having steric hindrance are found to affect intermolecular interactions significantly in binary mixtures which in turn affect the self-defocusing effect. © Anita Publications. All rights reserved.

Keywords: Close aperture z-scan (CAZS), High repetition rate (HRR) femtosecond pulses, Binary liquid mixtures, Intermolecular interactions, Polarity, Steric hindrance.

1 Introduction

Third-order nonlinear optical properties such as nonlinear refraction and nonlinear absorption, which are related to the real and imaginary components of the third-order nonlinear susceptibility χ^3 respectively, have tremendous applications in the field of ultrafast spectroscopy. These nonlinear optical properties can be measured experimentally by applying the z-scan technique, which was first given by Sheik-Bahai *et al* [1-2]. This technique can be used to measure two-photon absorption and nonlinear refraction process occurring in the nonlinear optical materials by irradiating with an intense laser beam. Measurements of two-photon absorption process and nonlinear refraction process are quantified in terms of two-photon absorption cross-sections (σ^2) and nonlinear refractive index (n_2), respectively. So in the basic z-scan experimental setup, the desired sample placed on a motorized stage is scanned along propagation direction (known as z-axis) of the laser beam. The transmitted laser light through the partially closed aperture is detected by a photo-detector placed at the far-field position. This partially closed aperture configuration of the z-scan is known as closed aperture z-scan technique (CAZS) which gives a signal with characteristic curve having peak and valley shapes and subsequently provides us information about the sign and magnitude of the nonlinear refraction. Whereas, when z-scan of the desired sample is carried out in the absence of any aperture than it is known as open aperture z-scan (OAZS) which gives a signal with characteristic curve showing trace of a dip or valley. This dip in the OAZS curve is due to the nonlinear absorption in the materials. Materials that do not show nonlinear absorption can be characterized based on CAZS only. We can characterize a material based on the appearance of peaks in the close-aperture z-scan technique

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and assign whether the material is showing a self-focusing or self-defocusing effect. If the close-aperture z-scan trace is showing a peak followed by a dip, then the given material is showing a self-defocusing effect, whereas for dip followed by peak is assigned a self-focusing effect [3]. These optical effects are influenced by several laser properties viz. polarization [4], pulse width [5], repetition rate [6], and wavelength [7], which indirectly modulate or demodulate the nonlinear optical (NLO) properties of desired materials.

There are various research articles available in literature which dealt with the intermolecular interactions in solvent molecules using non-degenerate dual-beam close-aperture z-scan technique where one laser beam is used as pump beam to create optical effects viz. self-focusing or self-defocusing in the desired sample and other laser beam used to probe the same effect [8-11]. Besides, there are various studies in which high repetition rates (HRR) lasers have been used for such kind of experiments [12]. Since these high repetition rates (HRR) lasers have applications in the field of microscope imaging and biomedical optics, therefore, in the present experiment, we employed the same to carry out the study of intermolecular interactions between different solvent molecules. It has been seen that interest in the binary liquid mixtures is gaining momentum as compared to individual components in the various research fields [13-16]. Intermolecular interactions between the components of the binary liquid mixture are directly related to the nature of the liquids. Chemical and physical properties such as the refractive index (n), heat capacity (C_p), thermo-optic coefficient (dn/dt), coefficient of thermal expansion (β) and the thermal conductivity (k) of these liquid mixtures are greatly influenced by the intermolecular interactions such as hydrogen bonding or non-specific interactions like dipole-dipole, dipole-induced dipole interactions, and self-association. These intermolecular interactions directly affect the spectroscopic properties of the system under consideration. We used the close-aperture z-scan (CAZS) experiment to study the intermolecular interaction between 1,4-dioxane (simply known as dioxane) and isomers of butanol. Binary mixtures of dioxane with isomers of butanol were used because of their high miscibility with each other and with the aim to acquire information about the combined effects of different molecular structures and varying polarities of components on the self-defocusing effect. Dioxane has a similar structure as that of cyclohexane, so it can also adopt various conformations ranging from most stable chair conformation, twist boat conformation and boat conformation. Since, dioxane has two symmetrically placed oxygen atoms, so it becomes highly polar in the boat conformation as compared to twist boat and nonpolar chair conformations. Solvent molecules absorb the pulse energy of the laser and get excited to upper energy states and subsequently relax back to the ground state either radiatively or non-radiatively. The non-radiative relaxation of the excited molecule raises the temperature of the system by creating a temperature gradient, which in turn creates a refractive index gradient within the locally heated area. HRR laser beam produces a cumulative thermal effect due to incomplete decay of the thermal load from the interaction of the single pulse with the desired solvent. This cumulative thermal effect, in turn, produces a negative nonlinear refractive index (n_2) which is related to the change in transmittance between peak and valley (ΔT_{p-v}) in the desired solvent. Since the creation of the negative nonlinear refractive index (n_2) is directly related to the change in the transmittance between the peak and valley (ΔT_{p-v}) in the CAZS experiment so the results can be correlated with the intermolecular interactions within the components of the binary liquid mixtures.

2 Experimental methods

2.1 Materials used

Our experiment focusses on the self-defocusing thermal lens effect in binary liquid mixtures by employing dioxane as a common component with each isomers of butanol viz. *n*-butanol, *sec*-butanol, *iso*-butanol, and *tert*-butanol. All of these organic liquids are of high-performance liquid chromatography (HPLC) grade and were purchased from Spectrochem Pvt Ltd., Mumbai, India. These liquid solvents were used without any further purification.

2.2 Experimental details

To study the self-defocusing effect (also called as negative lens effect), we used the traditional close-aperture (CAZS) z-scan technique for which we employed a high repetition rate (HRR) pulsed femtosecond laser source. The schematic representation of the experimental setup is shown in Fig 1. This experimental z-scan setup consists of femtosecond mode-locked Ti: Sapphire laser (MIRA-900, Coherent Inc. USA), which is powered by a frequency-doubled continuous wave (CW) Nd: Vanadate laser (Verdi-5, Coherent Inc. USA). This laser system has the capability of throwing out pulses with a pulse width ranging from 100 to 200 fs, and wavelength can be tuned from 730 nm to 900 nm with a fixed repetition rate of 76 MHz.

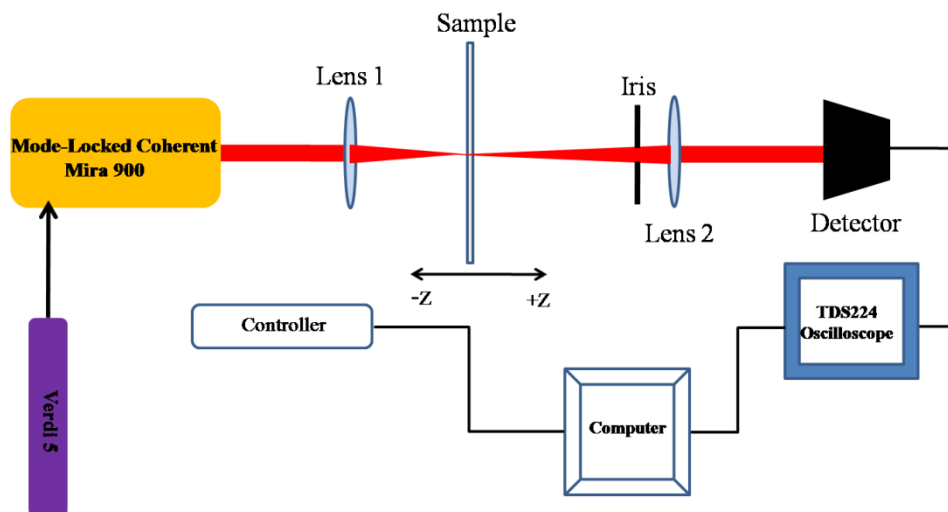


Fig 1. Schematic representation of the experimental close aperture z-scan (CAZS) setup.

Femtosecond pulses thrown out by the laser system were focused with a converging lens (L1) having a focal length of 20 cm into a sample cuvette of 1 mm path length containing the liquid binary mixture. In this experiment, the average power recorded before the sample cuvette was 250 mW. First of all, we calculated the beam waist (w_0) at the focal point of the converging lens by using the relation: $w_0 = 2\lambda f/\pi d$, where f = focal length of the lens, d = beam diameter and λ = Excitation wavelength. We used the knife-edge technique to measure the beam diameter just before the focusing lens (L1), and the value calculated using the technique was found to be 0.5 cm at 780 nm. Therefore, beam waist (w_0) at the focus was calculated to be 20 μm at 780 nm. Further, The Rayleigh range was calculated using the equation, $z_0 = \pi w_0^2/\lambda$ and was found to be 1.6 mm at the 780 nm wavelength. In the experiment, the sample path length has adhered to the condition that it should be less than the Rayleigh range of the laser beam [2]. So, according to the z-scan technique (CAZS), sample cuvette was scanned along the focal plane of the converging lens using a motorized translation stage (Newport Inc. model ESP 300), which has the minimum step size of 0.1 μm . This whole process results in a smooth intensity scan of the laser beam throughout the sample positions on the translational stage which gives CAZS signal showing a curve having peak and valley. Further, the transmitted laser beam after being passed through the sample was collected into a detector (UV-enhanced amplified silicon photodiode, Thorlabs PDA100A-EC) through an iris of 20% transmittance which was kept before the collecting lens (L2) of 7.5 cm focal length. We measured the peak- to- peak values of the photodiode voltage using an oscilloscope (Tektronix TDS Model 224, real-time digital oscilloscope), which was self-triggered. Oscilloscope and the translation stage were interfaced with the computer using a GPIB card (National Instruments Inc.). We used LabVIEW programming for all data acquisition.

3 Results and Discussion

In this experiment, we used the 780 nm wavelength light with a 76 MHz repetition rate from the laser source, which is transparent to all the liquids used as samples. We used the close aperture z-scan (CAZS) experimental technique to study the intermolecular interactions in binary mixtures. We prepared different sets of binary mixtures of dioxane with isomers of butanol with varying volume fractions of components, and measured the change in transmittance between peak and valley (ΔT_{p-v}) in the curve of the acquired signal for all sets of binary mixtures by using CAZS technique. This change in transmittance (ΔT_{p-v}) is related to nonlinear refractive index (n_2) through the relation [2], $\Delta T_{p-v} \approx 0.406 kn_2 I_0 L_{eff}$, where k is the wave vector, n_2 is nonlinear refractive index, I_0 is the incident laser intensity and L_{eff} is the effective sample path length. In addition, all these organic solvents did not show any nonlinear absorption when irradiated with 780 nm light.

Isomers of butanol were chosen as one of the binary components with dioxane in binary mixtures for investigating the effects of the polarity and steric hindrance due to molecular structures on the intermolecular interactions between the binary mixture components as their volume fractions are varied. CAZS traces for all pure organic liquids are shown in Fig 2 in which there is a peak followed by a dip in each of them. Since, isomers of butanol are protic solvents whereas 1,4-dioxane is an aprotic solvent, so we can expect some weak intermolecular interactions in their binary mixtures of the type dipole-induced dipole at various volume fractions of components. Variations of ΔT_{p-v} with the volume fractions of isomers of butanol in binary mixtures with dioxane can be seen in Fig 2 (a) to (d).

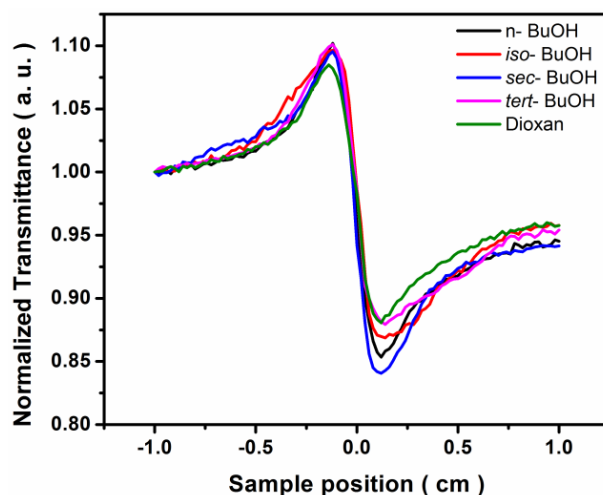


Fig 2. CAZS traces of pure *n*-butanol, *sec*-butanol, *iso*-butanol, *tert*-butanol and dioxane at a constant incident laser power.

Since the polarity of a liquid can be signified by the dielectric constant values (Table 1), so on this basis, *n*-butanol has the highest polarity followed by *iso*-butanol and *sec*-butanol, whereas *tert*-butanol has the least polarity. Further, physical parameters such as dielectric constant, density, and dipole moment have direct relationship with the thermo-optical properties of the liquids under study [17-18]. Therefore, we can expect to observe intermolecular interactions when individual butanol isomers are mixed one at a time with nonpolar dioxane for binary mixtures at various volume fractions through thermal self-defocusing effect in CAZS experimental regime. Dioxane is a highly flexible six-membered heterocyclic molecule, so it can adopt various different conformations viz. stable chair conformation and unstable boat conformation. Chair form having two symmetrically placed oxygen atoms, has a nonpolar character, whereas, in boat form, it

has very high polarity. In the present study, our experiments indicate that dioxane is assuming stable chair conformation as signified by the least ΔT_{p-v} value (Table 1) and hence the binary mixtures show more nonpolar character.

Table 1. Summary of ΔT_{p-v} values (measured from the normalized CAZS curve) and corresponding few known physical properties of pure organic liquids used in the experiments.

Organic liquid	ΔT_{p-v}	Dipole moment (Debye)	Density (gm-l^{-1})	Dielectric constant
1,4-Dioxane	0.204	0.45	1.033	2.25
<i>n</i> -Butanol	0.248	1.75	0.810	17.7
<i>sec</i> -Butanol	0.255	1.41	0.807	15.8
<i>iso</i> -Butanol	0.228	1.79	0.802	16.68
<i>tert</i> -Butanol	0.222	1.31	0.781	10.9

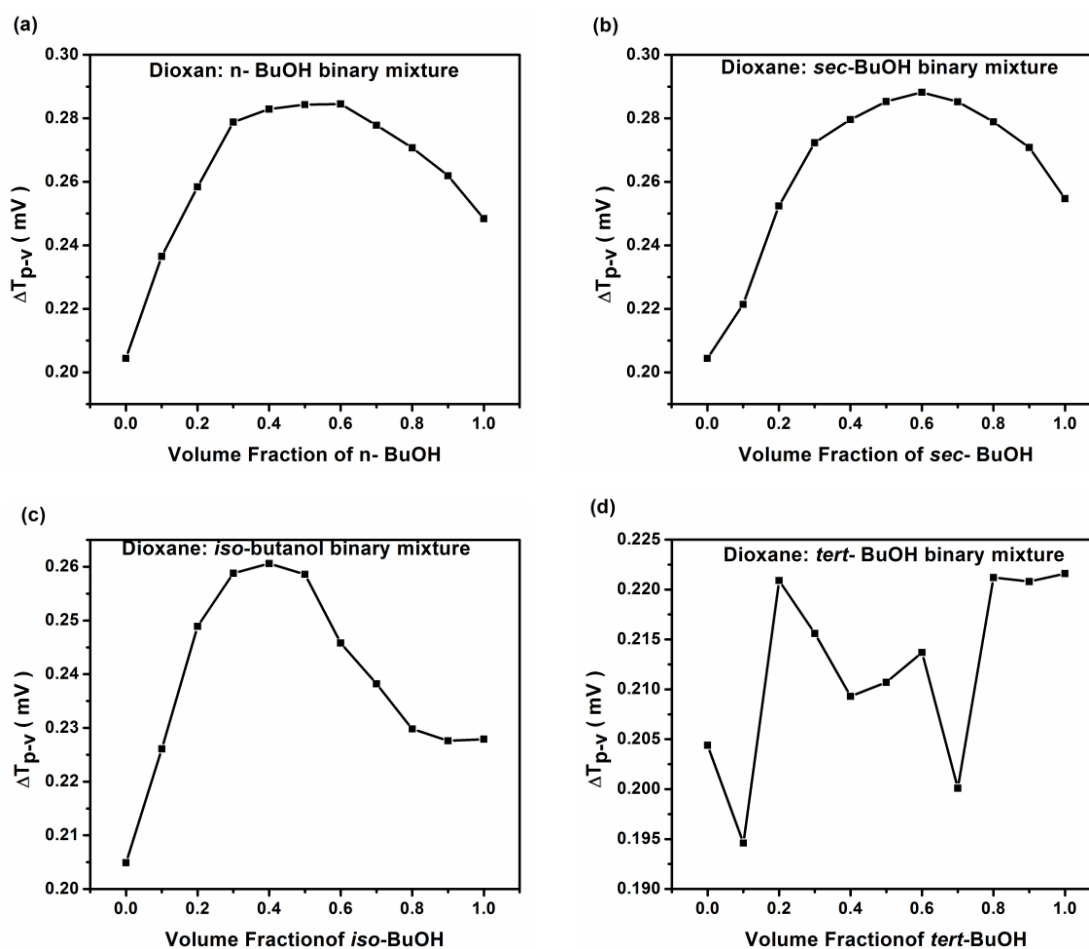


Fig 3. Variation of ΔT_{p-v} with the volume fractions of isomers of butanol in the binary mixtures with dioxane (a) *n*-Butanol-Dioxane, (b) *sec*-Butanol-Dioxane, (c) *iso*-Butanol-Dioxane and (d) *tert*-Butanol-Dioxane.

This conclusion can also be verified from increasing ΔT_{p-v} values (Fig 3) with increasing volume fractions as the polarity of the isomers of butanol in their binary liquid mixtures with dioxane, namely: *n*-butanol, dioxane: *sec*-butanol and dioxane: *iso*-butanol binary liquid mixtures (i.e. ΔT_{p-v} value is increasing with the polarity). However, the expected linear behavior, in the variation of ΔT_{p-v} value with increasing polarity, gets affected with the huge deviations at higher volume fractions of butanol isomers in each of these mentioned binary mixtures. The reason for this behavior can be associated with the nonpolar character of dioxane as compared to polar butanol isomers, which in turn gives rise to significant molecular property mismatch. Further, these observations can be correlated with the excess thermodynamic properties such as volume, viscosity, diffusion, and refractive index, etc. of the binary liquid mixtures [19-24]. These properties are directly related to intermolecular interactions of the respective binary liquid systems [25]. Variation in the ΔT_{p-v} values has the origin concerning the change in molecular properties for each of the three mentioned binary mixtures under the given experimental conditions. Apart from the above-mentioned factors, structural characteristics have a very important role to play in the excess volume measurements that correspond to geometrical fitting [19,20] of the structure of one of the components with that of other in the binary mixtures studied. So, we can correlate the observed random variation in the ΔT_{p-v} values (Fig 3 (d)) with the volume fractions of *tert*-butanol in the dioxane:*tert*-butanol binary mixture to the polarity difference and the geometrical fitting of the components. Thus, this observation of *tert*-butanol showing random ΔT_{p-v} values in the binary mixture with dioxane can be correlated to the least polarity and the highest branched structure among all isomers of butanol.

4 Conclusion

The study on the self-defocusing effect of a laser propagating in binary liquid mixtures of organic liquids using the close-aperture *z*-scan (CAZS) technique with pulsed HRR femtosecond laser reveals the effects of polarity and steric hindrance in molecular structures on the intermolecular interactions between components of the binary liquid mixtures. In this study, dioxane: *n*-butanol, dioxane: *sec*-butanol and dioxane:*iso*-butanol show huge deviations from the linear behaviour in the ΔT_{p-v} values at higher volume fractions of butanol isomers. This can be directly correlated with the polarity difference between the components of the binary mixtures that results from the weak intermolecular interactions such as dipole and induced dipole. Last but not the least, *tert*-butanol having the least polarity and a highly branched structure (maximum steric hindrance among all isomers of butanol) showed random ΔT_{p-v} values in its binary mixtures with dioxane at different compositions.

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