

Solvent Effect on the Third Order nonlinearity of Oxazine Dye Doped PMMA Films by Using Z-Scan Techniques

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ABSTRACT

This experimental work is a study for solvents effect on the nonlinear optical properties of oxazine dyes doped films in PMMA at concentration of 10^{-5} M in three solvents (Trichloroethan, Chloroform, THF) by using a high sensitive method known as Z-Scan technique. Z-scan experiment was performed using CW diode laser at 650 nm in two parts. The first part was done using a closed-aperture placed in front of the detector to measure the nonlinear refractive index and in the second part; the aperture in front the detector was removed (open aperture) to measure the nonlinear absorption coefficient and then to measure third order susceptibility. The nonlinear refractive index is found to be of the order of 10^{-6} cm²/W. The magnitude of third order susceptibility is of the order of 10^{-9} cm/watt. The nonlinear absorption coefficient has also been determined.

The results suggest that among the three organic solvents, chloroform is a promising class of organic solvent for such nonlinear optical studies due to its relatively higher polarity when compared with other solvent. The value of the third-order susceptibilities is dramatically influenced by the used solvent polarity index, dielectric constant, dipole kind of solvent polar or not polar with limiting decreasing in the order chloroform > THF > Trichloroethan.

The interest of these materials arises from the high sensitivity of their nonlinearity (nonlinear refraction, nonlinear absorption, third order susceptibility) to the nature of the solvent. The latter property provides the possibility of adjusting the optical windows by changing the solvents, which may offer the potential of tuning an optical limiter to a desired spectral range.

Keyword: Z-scan technique, nonlinear refraction and nonlinear absorption, dye doped polymer films, solvent effect.

1 Introduction:

With growing advancement in the technological field of photonics and bio-photonics, the search for organic materials exhibiting large nonlinear optical (NLO) properties and having applications in low power nonlinear optical devices has picked-up. Organic dyes are the most attractive optical materials for studying nonlinear optical properties for the point of view of understanding their photo-physics and impending applications [1]. The use of a synthetic polymer host presents advantages as these materials show much better compatibility with organic laser dyes and are amenable to inexpensive fabrication techniques. These polymers provide an opportunity for the production of active elements that can effectively control the characteristics of laser radiation. [2].

A nonlinear absorber of light has the unique property that its optical absorption can be altered by introducing changes in the intensity of radiation incident upon it. [3] Embedding it in solid matrices can modify the nonlinear

optical properties of the dye. The basic absorption processes in dyes can be divided into linear and nonlinear absorption. Nonlinear optics is a material phenomenon in which intense light induces a nonlinear response in the medium, and in return the medium modifies the optical fields in a nonlinear way. In fact, all media are nonlinear to a certain degree [4, 5]. The interest of these materials arises from the high sensitivity of their linear absorption spectra to the nature of the solvent. The latter property provides the possibility of adjusting the optical windows by changing the solvents, which may offer the potential of tuning an optical limiter to a desired spectral range [6]. It is found that the polar solvent strongly influences the more polar state of the molecule. Since molecular electronic transitions lead to redistribution of charge, the dipole moment of the ground state and an excited state of a molecule will, in

general, be different.[7]. The organization of solvent molecules about a solute molecule alters the electronic and vibration energies of the solute's ground and excited states, and more generally the potential surfaces,

intersections, and barriers that separate different molecular states and structures. As a consequence of these perturbations, the nonradiative energy relaxation processes in a solute molecule can be strongly affected by the solvent polarity. [8]. Studies about the optical properties of solvents- cast films showed that the casting process induces distinct molecular order in the solid films. The optical films properties depends on the general mode and conditions of the casting procedure, on the optical properties and the molecule weight of the polymer, the solvent type ,the casting temperature, and the surface energy of the substrate[8,9] .

Z scan technique is a simple, sensitive and popular experimental method to measure nonlinear optical properties (NLO) of materials. There were two parts of the Z-scan: closed aperture and open aperture. Closed aperture Z-scan helps to measure the sign and magnitude of ,both real & imaginary part of third order (NLO) and nonlinear refractive index (n₂) .Open aperture Z-scan either two types: saturable absorption (SA) and reverse saturable absorption (RSA) depending on the pump intensity and on the absorption cross section at the excitation wavelength [5]. Open aperture Z-scan helps to measure the nonlinear absorption coefficient β₂.

In this paper, we report the results of our investigations of the third-order susceptibility characteristics of a laser dyes oxazine at concentration of 10⁻⁵ M in three solvents: Trichloroethan (polar), Chloroform (nonpolar), THF (apricot polar) doped films in PMMA by using CW diode laser at 650 nm.

The nonlinear refractive indices and nonlinear absorption coefficient and third order susceptibility were measured by using Z-scan techniques. As will be shown in this paper, changing the solvent not only affects the linear absorption spectra, but also has a dramatic influence on the nonlinearity and optical limiting characteristics of the compound.

2 Theory

When the applied electric fields are sufficiently small, the electric polarization (p) is approximately linearly proportional with the applied electric field E:

$$\vec{P} = \chi \cdot \vec{E} \tag{1}$$

Where (χ) is the electric susceptibility, it is a property of matter that describes the interaction of matter with the electric field of light [10].

This is the case of linear optics. However, when the applied electric fields are high enough, the induced polarization has a nonlinear dependence on these electric fields and can be expressed as a power series with respect to the electric field

$$P = \chi^{(1)} \cdot E + \chi^{(2)} \cdot EE + \chi^{(3)} \cdot EEE + .. \tag{2}$$

$$p = P^{(1)} + P^{(2)} + P^{(3)} + \tag{3}$$

Where χ⁽¹⁾ is the linear susceptibility, χ⁽²⁾ is the second order nonlinear susceptibility and χ⁽³⁾ is the third order nonlinear susceptibility. Third-order nonlinear optical interactions, which are described by the term χ⁽³⁾ can take place in any material, it is related to the nonlinear index of refraction and, implicitly, optical limiting phenomenon [11].

The third order nonlinear susceptibility is considered to be a complex quantity:

$$\chi^{(3)} = R \chi^{(3)} + \text{Im} \chi^{(3)} I \tag{4}$$

The real part is related to nonlinear refractive index n₂ through:

$$R \chi^{(3)} = 10^{-4} \epsilon_0 n_0^2 c^2 n_2 / \pi \tag{5}$$

$$\text{Im} \chi^{(3)} (\text{esu}) = 10^{-2} \epsilon_0 c^2 n_0^2 \lambda \beta / 4\pi^2 (\text{cm/W}) \tag{6}$$

Where n₀ is the linear refractive index, ε₀ is the permittivity of free space, c is the speed of light in vacuum, n₂ is the nonlinear refractive index [12] .

2.1 Closed – Aperture Z- Scan:

The standard “closed aperture” Z-scan (i.e. aperture is placed in the far field) for determining nonlinear refraction is shown in Fig. (1), where the sample is moved along the propagation direction z while keeping the power is fixed. The normalized transmittance of the sample through the aperture is monitored in the far field as a function of the position Z. The normalization is performed in such a way that the transmittance is unity for the sample far from focus where the nonlinearity is negligible [10]. An intensity dependent on the refractive index causes the beam radius of the transmitted beam to change while retaining the Gaussian profile.

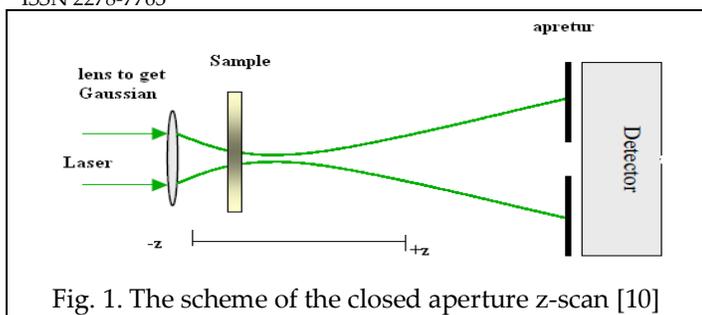


Fig. 1. The scheme of the closed aperture z-scan [10]

The size of the aperture is signified by its transmittance (S), in the linear regime. In most reported experiments, $0.1 < S < 0.5$ has been used for determining nonlinear refraction. [13].

The Z-scan technique is based on the transformation of phase distortions to amplitude distortions during beam propagation. A qualitative physical argument that explains the transmittance variations in the Z-scan experiment can be given as follows: Starting the scan from a distance far away from the focus (negative z), the beam irradiance is low and negligible nonlinear refraction occurs leading to linear transmittance. As the sample is brought closer to the focus, the beam irradiance increases leading to self-lensing in the sample. A negative self-lensing (self-defocusing) prior to focus tends to collimate the beam and reduce the diffraction leading to a smaller beam at the aperture and an increased transmittance. As the scan continues and the sample crosses the focal plane to the right (positive z), the same self-defocusing effect will tend to augment diffraction and reduce the aperture transmittance. A prefocal transmittance maximum (peak) and a post focal transmittance minimum (valley) will be, the z-scan signature of a negative nonlinearity as shown by the dotted line figure. (2), while a positive one, following the same analogy, will give rise to an opposite valley-peak configuration, as shown by Solid line fig. (2). [13]

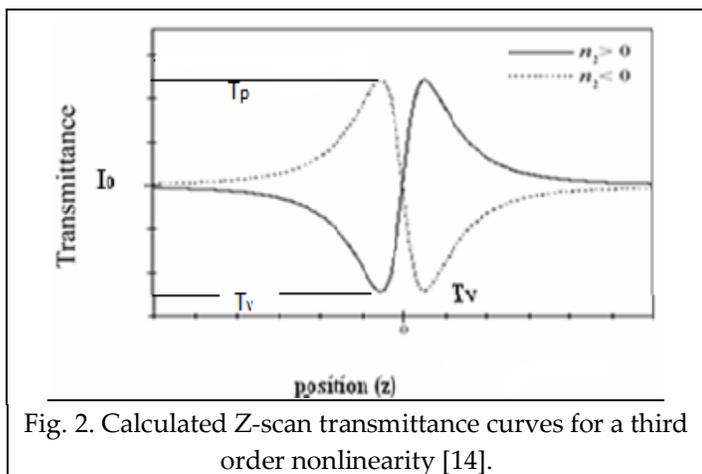


Fig. 2. Calculated Z-scan transmittance curves for a third order nonlinearity [14].

2.2 Open Aperture Z-Scan

An open-aperture Z-scan measures the change in intensity of a beam, focused by lens *l* in Fig. (3), in the far field at detector PD, which captures the entire beam, and gives the estimate of the absorptive nonlinearity of a sample.

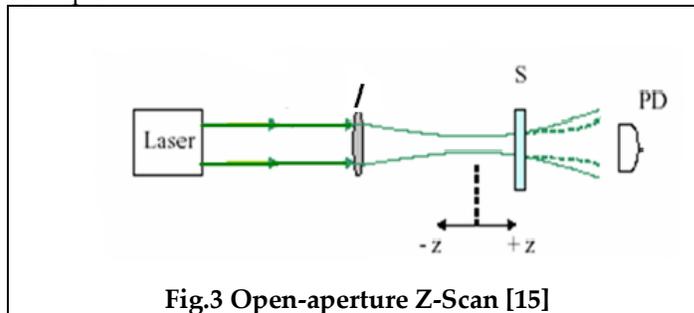


Fig.3 Open-aperture Z-Scan [15]

The absorptive nonlinearity can be due to either (i) saturable absorption (SA), in which the absorption coefficient decreases resulting in the transmittance increase with increase in the input laser intensity, and (ii) reverse saturable absorption (RSA), in which the absorption coefficient increases resulting in the transmittance decrease with increase in the input laser intensity.

2.3 self Focusing and Defocusing

Self-focusing (or Kerr-Lensing) is a consequence of the non-uniform spatial profile of the laser Gaussian beam. If the intensity of a transmitted light beam is sufficiently high, the refractive index change will modify the light propagation not only with respect to the polarization but in its geometrical properties too [3].

For a Gaussian beam of radius ω_0 (beam waist) the Kerr-lens focal length is:

$$F = a \omega_0^2 / 4Ln_2I \quad (7)$$

Where *L* is the thickness of the nonlinear medium (sample), *I* is the irradiance and *a* is a correction term.

When n_2 is negative, the above equation shows there will be a negative focal length and thus self de-focusing of the incident beam [14].

3- Experimental Section

Oxazine is from xanthene family with fluorescence emission in the yellow-red region of the electromagnetic spectrum are well known for their excellent laser performance in liquid solutions as well as in solid matrices [16], fig. (3) shows its molecular structure. Oxazine dyes are planer and are rigid like xanthene dyes. All oxazine dyes are photochemically more stable than xanthenes.[17]

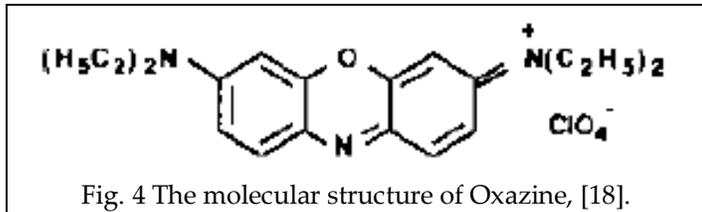


Fig.4 shows The oxazine doped film with PMMA in three different solvents

Polymethylmethacrylate (PMMA) is from ICI Company. All the solvents were spectroscopic grade and were used without further purification. These solvents are: Chloroform is from Lab-Scan LTd., Analytical Science HPLC Ireland-Dublin. , Tetrahydrofloran (THF): from (BDH) laboratory reagents (BDH Chemicals Ltd Poole England, Trichloroethan: From Merck-Schuchardt.

Table (1) shows some physical properties of the solvents which used in the study.

Table 1: Some physical properties of the solvents which used in the study

Solvents	type	Molecular formula	Solubility parameter	Polarity (water 100)	Dipole (D)	Dielectric constant (20°C)
THF	apricot polar	(CH ₂) ₄ O	9.1	21	1.75	7.6
Trichloroethan	polar	CH ₃ CHCl ₂	7.7	17.0	1.7	7.25
Chlorofom	nonpolar	CHCl ₃	9.3	25.9	1.1	4.8

CW diode laser system from at 650nm, max.Power is 50 mwatt, beam diameter: (1.5 mm), Beam Divergent (1.5) mrad, Ac: 220-240 volt, Frequency: 50-60 Hz 250mA.

Solution of concentrations (10⁻⁵) M in three solvents (THF, Trichloroethan ,and Chloroform) where prepared by weighting amount of the material by using a matter balance having a sensitivity of 10⁻⁴ gm. Dye doped polymer films were fabricated by the free casting technique(FC). Polymer solution was prepared by dissolving the required amount of polymer (7 gm. in 100ml of the used solvents.

The free casting (FC), involves casting a polymer solution in a flat bottomed glass cup (Petri dish) without imposing hydrodynamic stress on the liquid . Solvent is allowed to evaporate under ambient conditions until the films harden fig. (4).

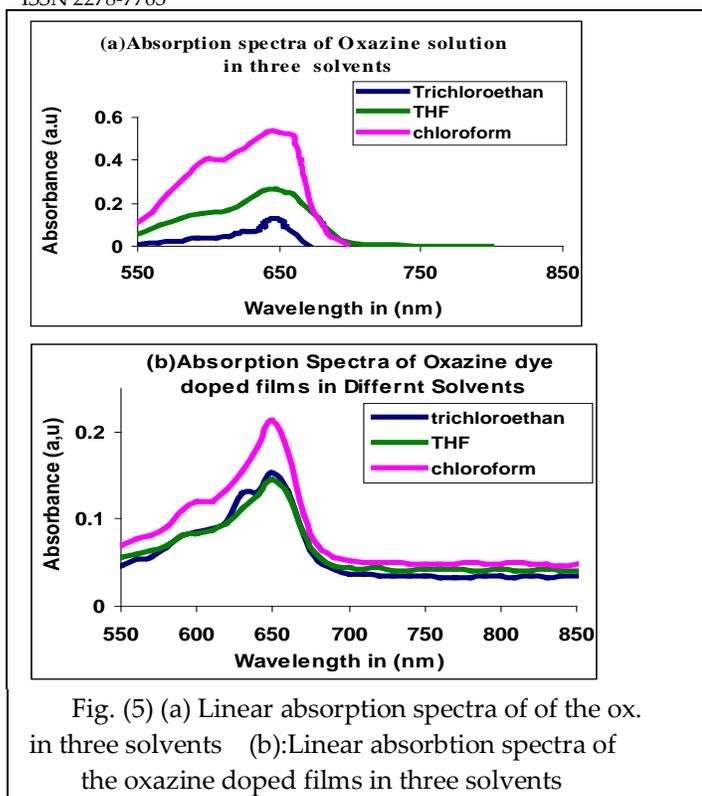


The thickness of the films produced by this method is dependent on concentration and the volume of the liquid in the dish. The liquid volume was (10) ml, yielding film of different thickness.

The thickness of the films was measured with an electrical device (Mini-test 3000 microprocessor coating thickness) from electro, phyisk, Germany (ERICHSEN). The doping ratio was 1:2 dye to the polymer.

4 Results and Discussion:

Fig. (5a), shows the absorption spectra of the dye of concentration 10⁻⁵ M in different solvents, Fig. (5 b) shows the absorption spectra of the dye of concentration 10⁻⁵ M doped polymer films in three solvents. The spectra were carried out by using (UV/Vis SP – 3000, plus, 2003) Spectrophotometer Optima / Japan, which operates in wavelength range of 190-1100 nm. The light source is Tungsten- Halogen and D₂ lamp. Its monochromator is modified (turner type with 1200 lines /mm holographic grating. Its detector is Silicon photodiode with automatically rotating Position cell holder [19].



solvent	Oxazine solution of 10 ⁻⁵ M		Oxazine doped polymer films of 10 ⁻⁵ M	
	λ abs.	Abs. at λ max.	λ abs.	Abs. at λ max.
Trichloroethan	640	0.1125	650	0.154
THF	647.5	0.263	650	0.146
Chloroform	649.5	0.528	650	0.214

The absorption spectra of the doped films shows no change in $\lambda_{abs,max.}$, with the change of solvents or concentration and this is due to (i) a lack of translational freedom for the dye; intermolecular collisions deactivation is thus avoided. Each molecule is trapped in its own cage (ii) This implies that no exciplex is formed between the dopant. [20].

Experiment was performed for different solvents. Figure 6 shows the typical OA Z-scan profiles of the dye doped films in the three different solvents.

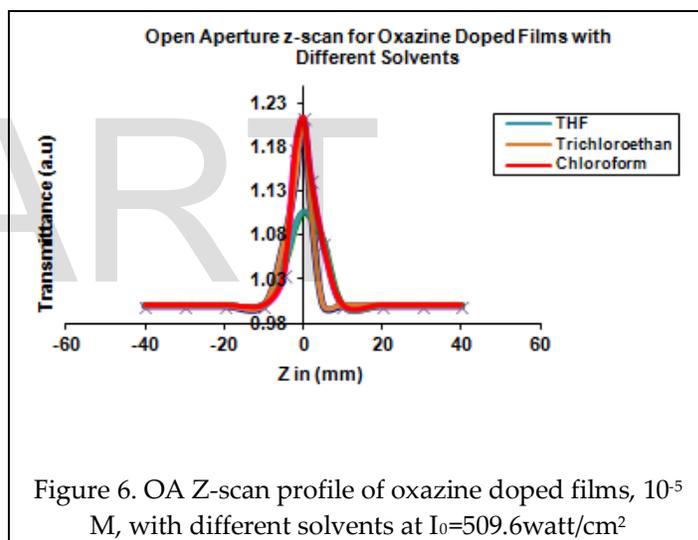


Figure 6. OA Z-scan profile of oxazine doped films, 10⁻⁵ M, with different solvents at $I_0=509.6\text{watt/cm}^2$

From Fig.5(a) we can see that the absorption spectra of Oxazine dye solutions in all the three species of solvent have a broad absorption band of (550 -700) nm. Also the UV-VIS spectra show that the absorption peaks of the dye solution shift towards the longer wavelength region proportional to the polarity of the solvents (Bathochromic shift). This can be attributed to solute – solvent interaction where the absorption spectra of many organic dyes in liquid solutions depend on the local electric fields generated by the surrounding polar solvent molecules. It is found that the polar solvent strongly influences the more polar state of the molecule. Since molecular electronic transitions lead to redistribution of charge, the dipole moment of the ground state and an excited state of a molecule will, in general, be different. If the excited state of the molecule has a larger dipole moment than the ground state, an increase in solvent polarity will more strongly stabilize the excited state lowering its energy, and red shifting $\lambda_{max.}$ [20,21].

Table 2: The spectral parameters of oxazine doped films in different solvents at 10⁻⁵ M concentration

(Fig.6) shown that the nonlinear absorption can be attributed to a saturation absorption process, The linear transmittance is normalized to unity. Measurements of β_2 are performed using the following equation [14]:

In case of saturation type of nonlinear absorption we can estimate the value of $\text{Im}[\chi^{(3)}]$ from the nonlinear absorption coefficient β (cm/W) using the relation :

$$\beta = \sigma_0 / I_s \dots\dots\dots(8)$$

where σ_0 is the ground state absorption coefficient in cm^{-1} provided the value of I_s (Saturation Intensity) is $> I_0$ (Peak Intensity).

For nonlinear refraction we can estimate the value of $R[\chi^{(3)}]$ from the nonlinear refractive index n_2 (cm^2/W) using the relations :

L_{eff} : - the effective length of the sample, can be determined from the following formula: [4]

$$L_{\text{eff}} = [1 - \exp(-\alpha_0 L)] / \alpha_0 \dots\dots\dots (9)$$

Where, L is the sample length, α_0 is the linear absorption coefficient,

$$\alpha_0 = \frac{1}{L \ln\left(\frac{1}{T}\right)} \dots\dots\dots (10)$$

Where T: linear transmittance

$$I_0 = 2P_{\text{peak}} / \pi\omega_0^2, \dots\dots\dots (11)$$

where, ω_0 : - the beam radius at the focal point, P_{peak} : - the peak power,

$$Z_0 = k\omega_0^2 / 2 \dots\dots\dots (12)$$

Z_0 is the diffraction length of the beam, $k=2\pi/\lambda$, the wave number, and λ , the wavelength of the laser light [14].

For closed aperture z- scan we define the change in transmittance between the peak and valley in a Z-scan as:

$$\Delta T_{\text{pv}} = T_p - T_v \dots\dots\dots (13)$$

Where T_p and T_v are the normalized peak and valley transmittances as seen in figure (3). The empirically determined relation between the induced on axis phase shift, $\Delta\Phi_0$, and ΔT_{pv} for a third-order nonlinear refractive process in the absence of nonlinear absorption (NLA) is, [12]

$$\Delta T_{\text{pv}} \cong 0.406(1-s)^{0.27} \left| \Delta\phi_0 \right| \dots (14)$$

S: the size of the aperture.

The size of the aperture is signified by its transmittance. In most reported experiments, $0.1 < S < 0.5$ has been used for determining nonlinear refraction. S the aperture linear transmittance is given by[13]:

$$S = 1 - \exp(-2r_a^2/\omega_a^2) \dots (15)$$

with r_a denoting the aperture radius(it is 0.5 mm),and, ω_a denoting the radius of the laser spot before the

aperture (it is 0.015 mm). In our experiment $S = 1.12 \times 10^{-4}$ then $(1 - 1.12 \times 10^{-4})^{0.27} \approx 0.999999999 \approx 1$ so:

$$\Delta T_{\text{pv}} \cong 0.406 \left| \Delta\phi_0 \right| \dots\dots\dots (16) \quad [14]$$

The nonlinear refractive index is calculated from the valley to peak difference of the normalized transmittance by the following formula: - [12 and 14]

$$n_2 = \Delta\phi_0 / I_0 L_{\text{eff}} k \dots (17)$$

Linear refractive index n_0 was calculated from equation:

$$n_0 = 1/T + [(1/T^2) - 1]^{0.5} \dots\dots\dots (18)$$

Where T is the linear transmittance of the films.

A typical closed aperture Z-scan curve of the dye doped films (at 10^{-5} M concentration) exhibiting the normalized transmittance is shown in the Fig.7 at incident intensity $I_0 = 509.6 \text{ W/cm}^2$. The curve is characterized by a pre-focal vally followed by a post-focal peak, which implies that the nonlinear refractive index is positive ($n_2 > 0$). We have, while the nonlinear refraction leading to focusing in this dye may be due to thermal lensing.

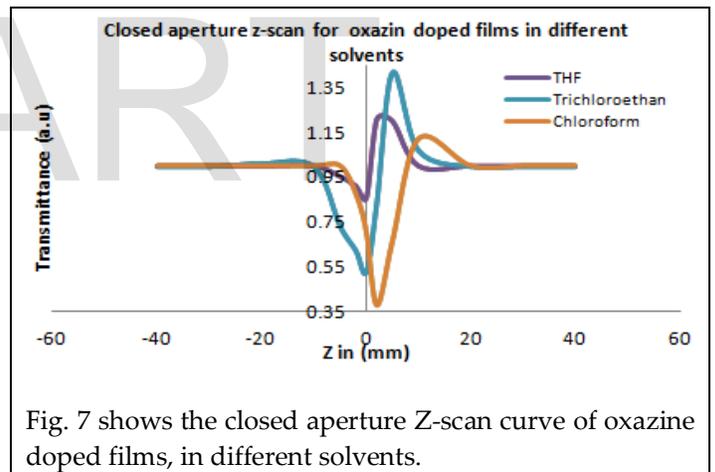


Fig. 7 shows the closed aperture Z-scan curve of oxazine doped films, in different solvents.

The experimentally determined values of T_{p-v} , n_0 , n_2 , $\Delta\phi_0$ and $R\chi^3$ are given in Table 3. The experimentally determined values of β , $\text{Im}\chi^3$, χ^3 are given in Table 4.

Table (3) show nonlinear refractive index parameters for dye doped polymer Films.

Table (3): Nonlinear refractive index parameters for PMMA Films Doped with Ox. for different solvents by using CW diode laser at 650 nm for closed aperture.

solvent	Tmax.	Tmin.	ΔT	Δφo	n ₂ cm ² /watt	no	RX ³ (esu)
THF	1.21	0.86	0.35	0.85	2.84E-06	2.38	1.16E-5
Trichloroethan	1.42	0.53	0.89	2.19	6.19E-06	2.44	5.78E-5
chloroform	1.12	0.38	0.74	1.82	5.62E-06	2.93	6.88E-5

Table (4): Nonlinear absorption parameters for oxazine doped films in three different solvents with Concentrations of 10⁻⁵ M by using CW diode laser at 650 nm for open aperture.

Solvents	T(z)	β (cm/watt)	Im χ ³ (cm/watt)	χ ³ cm/watt
THF	1.091	1.959E-16	7.51	1.16E-5
Trichloroethan	1.214	1.782E-16	7.43	5.78E-5
Chloroform	1.214	2.54E-16	11.5	6.88E-5

With cw pumping we expect major contribution to the observed third-order nonlinearities to be thermal in nature. The energy from the focused laser beam is transferred to sample through linear absorption and is manifested in terms of heating the medium leading to a temperature gradient and there by the refractive index change across the sample which then acts as a lens. The phase of the propagating beam will be distorted due to the presence of this thermal lens. It can be seen that for a third -order nonlinearity the following relation holds:

$$\Delta Z = Z_{\min} - Z_{\max} \approx 1.7 Z_R, \dots\dots(19)$$

where Z_{min} and Z_{max} represent the positions of the minimum and maximum transmittance, respectively. The peak-valley separation of more than 1.7 times the Rayleigh range of ~ 4.754 mm also suggests the presence of thermal component. It is well established that a separation of ~ 1.7z₀ indicates Kerr-type of nonlinearity [22 and 23].

Table (5): shows that the solvent chloroform is the best solvent for which the relation (19) is hold, which confirms the presence of the third order optical nonlinearity for this the solvent chloroform has the highest third order susceptibility, and this agree with [25], where third order susceptibility increased with decrease of solvent dielectric constant and dipole moment (see table 1).

Table (5): shows the corresponding between solvents ΔZ and 1.7 Z_R

solvents	1.7 Z _{Rmm}	ΔZ = Z _{min} - Z _{max}
trichloroethan	8.075	5-0=5 < 8.075
THF		2-0 =2 < 8.075
Chloroform		10-2= -8≈ 8.075

It is worth noting that the value of χ³ for the dye studied is larger than those of some representative third-order nonlinear optical materials such as safranin O [22] dye and its derivatives and organic dyes like Mercurochrome [15].

The NLO efficiency at the specific wavelength is of primary importance for accessing the suitability of a material for all-optical integrated devices.

Measurements were performed on the pure solvents taken in the quartz cell under the same measuring conditions. The experimental results show that pure solvents do not exhibit any nonlinearity contribution. This verifies that the valley and peak in the Z-scan curves originate from the dye molecules and not from the solvent or the quartz cell. All the experiments were done at room temperature.

According to the results obtained from the Z-scan experiment of the dye Oxazine doped films in three species of solvent, we found that n₂, β and χ³ of the dye doped films are dependent on the surrounding medium parameter, especially on solvent dielectric constant, dipole moment and polarity (the kind of solvent: polar or not polar), and this has a good agreement with [24].

The physical and chemical properties of organic molecules utilized in different scientific and technological applications can strongly depend on the properties of surrounding media. For liquid solutions, the solvent plays a fundamental role in photo physical processes, leading to the modification of the ground and excited-state energies of the molecules. The interaction of solute with surrounding solvent leads to solvation effect, which refers to the reorientation of the solvent molecules around a solute molecule. The result of interaction of solute with solvent molecules depends on the nature of arising forces (specific, such as hydrogen bonding, and/or nonspecific, universal interactions), which are determined by charge distribution and polarizability of the solvent and solute molecules. Considerable changes in the energy of solvated solute molecules may occur with changes in the solvent, especially in polar media [24].

Typically one of the two phenomena may cause the direct rotation of solvent molecules in a solution: 1) interaction of molecules with a strong optical field leading to the optical Kerr effect and: 2) interaction of polar solvent molecules with the electric field of the dye molecules, which possess the permanent dipole moment. The first mechanism is the major one responsible for self focusing of picoseconds pulses in liquids while the other one plays an important role in the processes of formation of the solvent shell, surrounding the dye molecule [25].

5. Conclusions

Z-scan has been carried out on Oxazine dye doped films in three species of solvent that are different in their polar properties using CW diode laser at 650 nm. The nonlinear optical properties and nonlinear absorption spectra were influenced by solvent polarity. The observed nonlinearities were large and positive in nature. The experimental results show that χ^3 of Oxazine dye doped films are strongly dependent on the polarity of the solvent and film of Oxazine dissolved in chloroform has the largest third order susceptibility χ^3 . The latter property provides the possibility of adjusting the optical windows by changing the solvents, which may offer the potential of tuning an optical limiter to a desired spectral range.

The reported nonlinearities are primarily thermal in nature owing to the CW excitation based on nonlinear refraction.

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