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Low Optical Limiting and Nonlinear Optical Properties of Vanadyl Phthalocyanine using a CW Laser

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Abstract
Vanadyl phthalocyanine complex has been prepared and characterized by FT- IR, Differential Scanning Calorimetry (DSC) and elemental analysis. The third-order nonlinear optical and optical limiting properties for solution of vanadyl phthalocyanine have been investigated using a continuous wave laser at 635 nm. We have employed the Z-scan technique to evaluate the sign and magnitude of nonlinear refractive index and nonlinear absorption coefficient. The concentration dependent nonlinear refractive index was observed in this medium. We have observed low power optical limiting action, with low limiting thresholds, based on nonlinear refraction in the medium. It indicates that the vanadyl phthalocyanines could be promising candidates for optical limiting materials.
Keywords: Z-scan, Optical material, Optical limiting

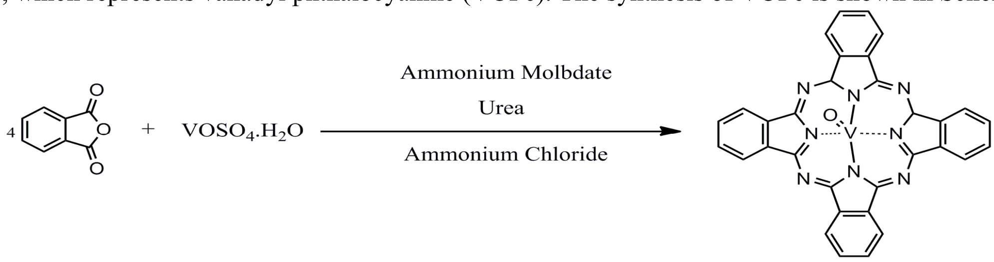
1. Introduction
Nonlinear optical materials continue attracting attentions because of their potential application in optical communications, optical storage, optical computing, harmonic generation, optical switching, optical limiting, etc. [J.V. Moloney, 1998].Among all the nonlinear optical applications, optical limiting is one of the most promising in practice, such as the protection of human eyes and optical sensors [M. Hanack, 2002]. Several mechanisms could lead to optical limiting behaviour, such as reverse saturable absorption, two photons absorption [G.S. He, 1995], nonlinear refraction [B. L. Justus, 1993] and optically induced scattering [K. M. Nashold 1995, K. Mansour,1992].
Phthalocyanine is known to exhibit large optical nonlinearity and photostability than many of the organic dyes [D.R. Coulter,1989, K. Sathiyamoorthy,2008, S.J. Mathews 2007] arising from certain characteristic features of charge distribution. But most of the available literature are concerned with nonlinear response to laser excitation at high laser intensities [J.W. Perry, 1996, Tai-Huei, 1998, G. de la Torre,1998]. Interestingly, only few reports are available on low power nonlinearity in metal substituted phthalocyanine compounds and its application in optical limiting. However, these compounds show interesting features arising from thermal variation of the refractive index at relatively low laser powers [Liang Song, 2006, A. Shevchenko, 2004, S. Brugioni, 2002, K. Sendhil, 2006], which can be described by an intensity dependent term in the refractive index. Due to changes in their refractive index, these compounds are able to show both self-focusing and self-defocusing effects, leading to the reduction of their transmittance at far field (due to distortion of spatial profile of Gaussian beam).
Reduced transmittance in the far field gives better optical limiting performance. Z-scan is a standard technique for measuring the sign of nonlinearity and change in magnitude of refractive index within the material [M. Sheik-Bahae, 1989, M. Sheik-Bahae, 1990].
In this paper, we chose a solution of vanadyl phthalocyanine (VOPc) in the solvent nitrobenzene as sample, and investigated experimentally the nonlinear optical properties of this sample under cw laser illumination using Z-scan technique. The optical limiting behavior of the sample has been studied too.

2.Experimental
2.1 Materials
Vanadyl sulfate monohydrate was obtained from Fluka, ammonium chloride, ammonium molybdate, nitrobenzene, phthalic anhydride and urea were obtained from Merck .Solvents were used after being purified according to the standard method.
2.2 Instruments
IR spectra was recorded on FT-IR (type Shimadzu model 4800S) as KBr disk in wave-number region 4000-400 cm^{-1}. The elemental analysis was performed on Euro Vectro EA 3000A. Differential Scanning Calorimetric (DSC) was performed using a Shimadzu apparatus DSC-60 model, (Japan). The sample was placed in open

aluminum pans under nitrogen atmosphere, with heating range (35-270) C^o and heating speed 10°C/min. The UV-vis absorption spectra of VOPc in nitrobenzene was recorded using Cecil Reflected-Scan CE 3055 reflectance spectrometer.

2.3 Preparation Method

The synthesis of vanadyl phthalocyanine is as stated in reference [B. N. Achar, 1987]. In three neck round bottom flask with condenser, 11.848 g (80 mmol) of phthalic anhydride was mixed in 25ml nitrobenzene and 3.62 g (20 mmol) vanadyl sulfate monohydrate, then excess urea 25 g (416 mmol) , 0.1 g ammonium chloride and 0.1 g ammonium molybdate were added with stirring under reflux for 3 hours, the color changed to dark blue . The hot mixture was filtered and washed twice with ethanol, the product was dried and added to 250 ml of 1N HCl, then refluxed for 2 hours, cooled to room temperature , filtered, then treated with 250 ml 1N NaOH ,filtered and washed with distilled water. Finally a dark blue to purple fine powder was obtained, yield with 68% , which represents vanadyl phthalocyanine (VOPc). The synthesis of VOPc is shown in Scheme (1)



Scheme (1) Synthesis of VOPc.

2.4 Z-scan technique

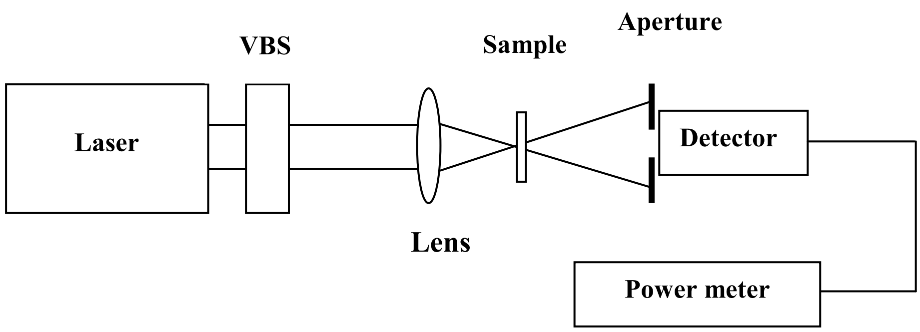
The Z-scan technique [M. Sheik-Bahae, 1990] was used to determine the nonlinear optical properties of the investigated sample. This technique is a simple and sensitive method for measurement of nonlinear refractive indices and nonlinear absorption of nonlinear optical materials.

A beam from continuous SDL laser operating at 635 nm and power of 40 mW is used to perform the measurement. The beam was focused on the sample using 5 cm focal length lens. The beam waist at the focal point was estimated to be 19.36 µm and the corresponding Rayleigh range was Z_R= 1.85 mm. The sample was moved along the z-axis using a translation stage. An aperture of 5 mm diameter was mounted in front of the photo detector placed about 10 cm away from the beam focus. The intensity transmitted by the sample was measured as a function of the sample position along the z-axis, there by obtained the closed aperture data. The measurements were repeated after removing the aperture in order to obtain the open aperture data.

2.5 Optical limiting

Optical limiters are devices, that strongly attenuate optical beams at high incident intensities while exhibiting high transmittance at low intensities. An ideal optical limiter is perfectly transparent at low intensities up to a predetermined intensity level, above which the transmitted intensity clamped at a constant value. These materials have important applications for the protection of the human eye and optical sensors from intense irradiation fields [M. Hanack, 2001].

The limiting effect for solution of VOPc in the solvent nitrobenzene was studied by using the 40 mW SDL cw laser at 635 nm. The experimental setup for the demonstration of optical limiting is shown in Fig. 5. A 1mm quartz cuvette containing VOPc solution is kept at position where the transmitted intensity shows a valley in closed aperture Z-scan curve. A Variable Beam Splitter (VBS) was used to vary the input power. This beam is then made to fall on the photo detector. The input laser intensity was varied systematically and the corresponding output intensity values were measured by the photo detector(Scheme 2).



Scheme (2) Experimental set-up for measuring limiting effect.

3. Results and discussion

3.1 Structure characterization and thermal property of VOPc

The vanadyl phthalocyanine complex was established from its FT-IR, elemental analysis and DSC, and are given in Table 1. The IRs spectrum (Fig. 1) exhibited, C-H stretching of aromatic rings at 3040w cm^{-1}. The weak band at 1652 cm^{-1} was due to the stretching vibration of C=N, in addition the spectrum show bard resulting from the OH stretching band at 3443 cm^{-1} that refered to the moisture with complex, the stretching of vanadyl group V=O stretching was at 900-1090 cm^{-1}.

Table 1. FT-IR absorption bands (cm^{-1}) of vandyl phthalocyanine.

VOPc	Assignment
3443w	OH (moisture)
3040w	υ(C–H Ar) symmetric stretching
1652w	υ(C=N) stretching
1603w	υ(C=C) stretching
1288m	υ(C–N) in isoindole
1164m	υ(C–N) in plane
900m-1090s	υ(V=O) stretching
1059w	υ(C–N) stretching

Ar: Aromatic, m: Medium, s: Strong ,w: Weak, υ : Vibration frequency.

The results of the characterization by elemental analysis agreed with those possessed by $C_{32}H_{18}N_8OV$, i.e. C, 66.10 %; H, 3 .12% and N, 19.27%. The following percentages error in element for, C,H,N , respectively , 0.012 % , 0.112 % , 0.0125 % are calculated.

The DSC tests were performed using a Shimadzu apparatus DSC-60 model, made in Japan. The samples (10 mg) were sealed in aluminum pans under nitrogen atmosphere in a temperature range 27-356 °C at a heating rate of 10°C/min which proved that the complex is thermally very stable, and the melting point occurs in 174.76 °C (Fig. 2).

3.2 UV–Visible spectroscopic studies

The optical absorption of the VOPc in the solvent nitrobenzene with four concentrations of 0.05, 0.06, 0.07 and 0.08 mM showed an absorption peak at 680 nm as shown in Fig.3. The value of absorbance increases with increasing concentration. The code of VOPc with 0.05, 0.06, 0.07 and 0.08 mM concentrations are S1,S2,S3 and S4, respectively.

3.3 Absorption coefficient (α)

The spectrum of the optical absorption was computed from the absorbance data. The absorption coefficient (α) has been obtained directly from the absorbance against wavelength curves using the relation [F. Yakuphanoglu, 2007]

$$\alpha = 2.303A/d$$

where A and d are the sample absorbance and thickness, respectively.

Fig. 4 shows the variation of the absorption coefficient (α) at the wavelength 635 nm with respect to concentration of the solution of VOPc. The absorption coefficient (α) is found to be linearly dependent on the concentration.

3.4 Nonlinear optical properties

The third-order nonlinear refraction index n_2 and the nonlinear absorption coefficient β of VOPc were evaluated by the measurements of Z-scan technique. Fig. 5 shows the closed aperture Z-scan data for 0.05 , 0.06 , 0.07 and 0.08 mM solution of VOPc in the solvent nitrobenzene at incident intensity I_o= 6.79 kW/cm^2. The peak followed by a valley-normalized transmittance obtained from the closed aperture Z-scan data, indicates that the sign of the refraction nonlinearity is negative, i.e. self-defocusing. Self-defocusing effect is due to local variation of refractive index with temperature. Moreover, the peak valley separation in all samples is found to be approximately $\Delta Z_{pv} \approx 5.4 Z_R$ which agrees well with literature on thermally induced nonlinearities [J.-G. Tian, 1993], in contrast to $|\Delta Z_{pv}| \approx 1.71\ Z_R$ that is observed for Kerr nonlinearity.

Fig.6 shows the normalized transmittance without an aperture (open aperture) for different concentrations of VOPc in the solvent nitrobenzene. Here, the sample showed a minimum transmittance at z = 0, which indicated the presence of nonlinear absorption in the sample. Since the observed absorption is due to resonant excitation, the decrease in the normalized transmittance is due to reverse saturation absorption process.

Generally, the measurements of the normalized transmittance, allow determination of the nonlinear refractive index n_2 and the nonlinear absorption coefficient β. Here, since the closed aperture transmittance is affected by the nonlinear refraction and absorption, the determination of n_2 is less straight forward from the closed aperture scans. It is necessary to separate the effect of nonlinear refraction from that of the nonlinear absorption. A

method to obtain purely effective n_2 is to divide the closed aperture transmittance by the corresponding open aperture scans [M. Sheik-Bahae, 1990]. The ratio of Figs. 5 and 6 scans is shown in Fig. 7. The data obtained in this way reflects purely the effects of nonlinear refraction.
The nonlinear absorption coefficient β (cm/W) can be calculated using the equation [G. Vinitha, 2008].

$$\Delta T = \frac{\beta I_o L}{2\sqrt{2}} \tag{1}$$

where ΔT is the normalized transmittance for the open aperture, L is the thickness of the sample and I_o is the intensity of the laser beam at focus. The nonlinear refractive index n_2 is estimated by the following equation [M. Sheik-Bahae, 1990]

$$n_2 = \frac{\lambda \Delta T_{p-v}}{0.812\pi(1-S)^{0.25} L_{eff} I_O} \tag{2}$$

where L_{eff} = [1-exp(-αL)]/α is the effective thickness of the sample, λ is the laser wavelength, S is the aperture linear transmittance and ΔT_{p-v} is the difference between the normalized peak and valley transmittances for the closed aperture. The nonlinear absorption coefficient β and nonlinear refractive index n_2 are calculated from the open and closed aperture normalized transmittance in Figs. 6 and 7 respectively and they are given in Table 2.

Table 2: Nonlinear optical parameters for VOPc in the solvent nitrobenzene.

Concentration mM	n_2 x 10^{-8} cm^2/W	β x 10^{-3} cm/W
0.05	1.08	0.95
0.06	4.30	1.32
0.07	6.76	1.84
0.08	8.52	2.11

It is worth noting that our values of n_2 and β are difference than that obtained for other phthalocyanine with different central metal such as CIAI-phthalocyanine [K. Sathiyamoorthy,2008] and octakis-(heptyloxy)-phthalocyanine [S.J.Mathews,2007]. We think the difference in the values of n_2 and β coming from the central metal and solvent used because the axially substituted halogen atom which connect to the central metal could greatly influence the solubility and nonlinear optical properties behaviors of the phthalocyanine.

3.5 Optical limiting

Figs. 8 and 9 show the optical limiting experimental results, namely, transmitted output power curves and normalized transmission curves as a function of incident input power for 0.05, 0.06, 0.07 and 0.08 mM concentrations of VOPc in the solvent nitrobenzene. The transmitted output power is found to vary linearly with the incident input power at low power for all the samples, but starts to deviate at high incident power. With further increase of the input power, the transmitted power reaches a plateau and is saturated at a point defined as the limiting amplitude. i.e., the maximum output intensity, showing obvious limiting property. However, their optical limiting abilities are quantitatively different. As shown by points A,B,C and D in Fig. 9, the optical limiting thresholds (defined as the incident input power where the transmission reduces by 50%) are approximately 12,10.4,8.8 and 6.2 mW for 0.05, 0.06, 0.07 and 0.08 mM concentration of VOPc solution, respectively. The optical limiting responses of the low concentration solutions are generally much weaker than those of high concentrated solutions, while high concentrated solutions exhibits strong optical limiting. This indicates that the number density of dye molecules in the laser beam is the main factor affecting the clamped level. From the threshold intensity for optical limiting for each sample, it can be seen that the optical power limiting threshold is inversely proportional to the concentration. The limiting behaviour observed in all the samples is attributed mainly to nonlinear refraction. Since the samples were pumped with cw laser beam, the arising nonlinearities are predominantly thermal in nature. The experiment was repeated for the pure solvent (nitrobenzene) to account for its contribution, but no limiting was observed. The results were comparable to some of the reports of low power optical limiting materials, such as copper phthalocyanines solution and poly chloro copper phthalocyanines solution [F. Li, 2008]. So the sample possesses limiting effect for the light of 635 nm.

4. Conclusion

In summary, we have measured the nonlinear refraction index n_2 and nonlinear absorption coefficient β. for solution of VOPc in the solvent nitrobenzene for various concentrations using the Z-scan technique with the 635 nm of SLD laser. The Z-scan measurements indicated that the VOPc exhibited large nonlinear optical properties. Also we have shown that the nonlinear refraction leads to self-defocusing at 635 nm. The origin of optical nonlinearity observed in the cw regime is attributed to the thermal variation of refractive index in the medium. Based on nonlinear refraction the sample behaved as good optical limiter even at low power with threshold of 6 mW. Furthermore, vanadyl phthalocyanines are very economical, if they are made into thin films or doped in polymeric matrix, they can be widely used in devices.

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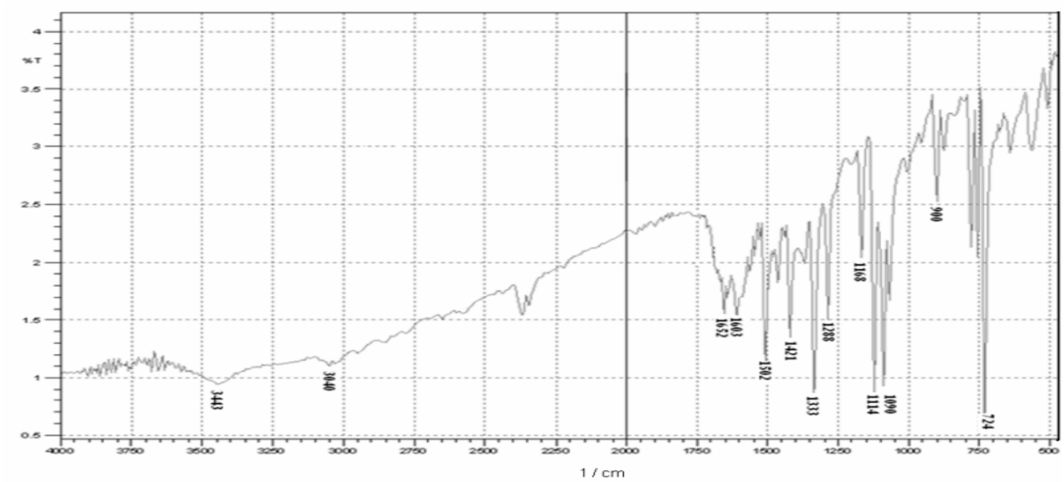

Fig. 1. FT-IR spectrum of VOPc.

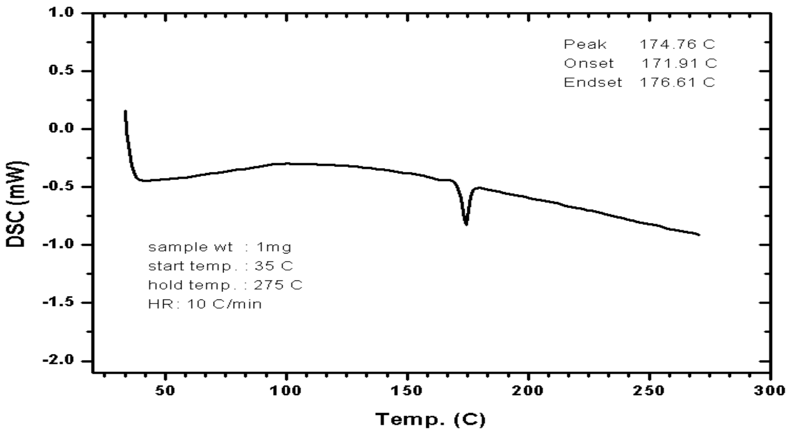

Fig. 2. DSC curve of VOPc.

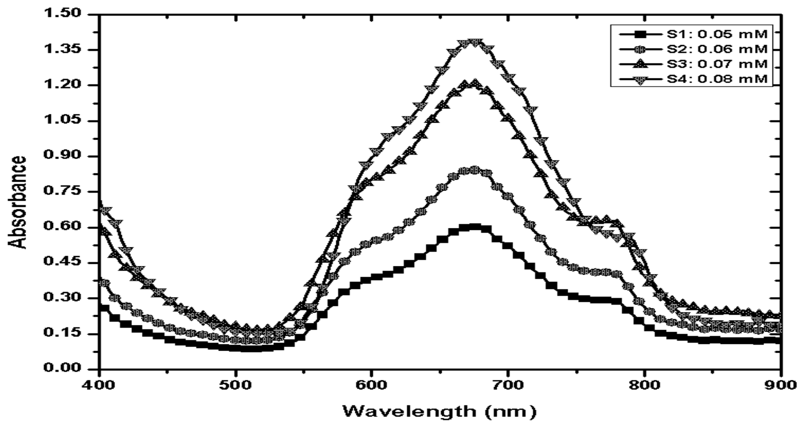

Fig. 3. UV-VIS absorption spectrum of VOPc at various concentrations.

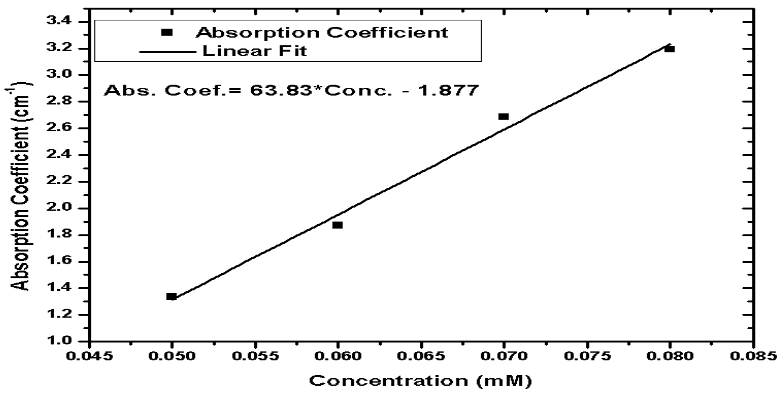

Fig. 4. Variation of absorption coefficient with concentration for VOPc.

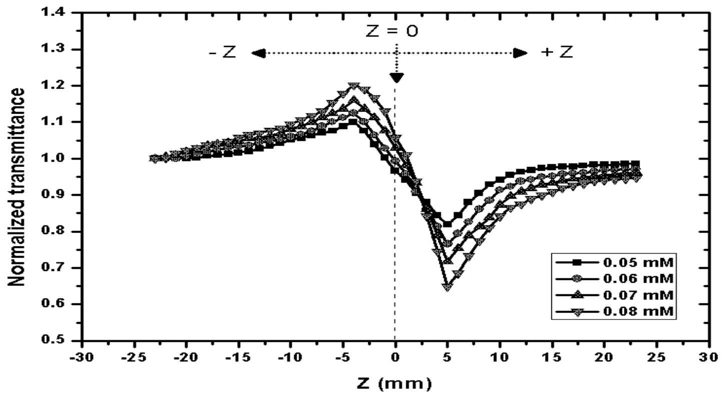

Fig.5 Closed-aperture Z-scan data for different concentrations of VOPc in the solvent nitrobenzene.

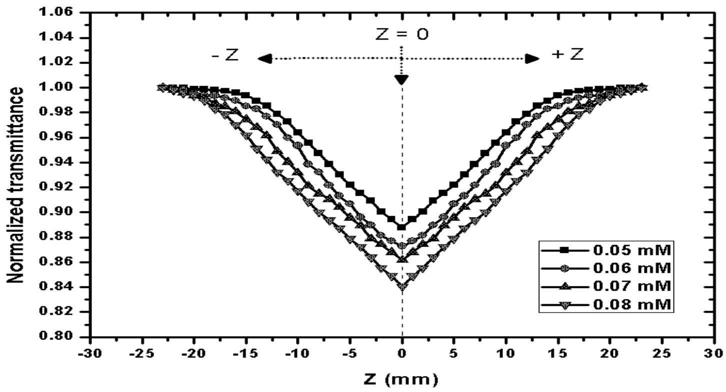

Fig. 6 Open-aperture Z-scan data for different concentrations of VOPc in the solvent nitrobenzene.

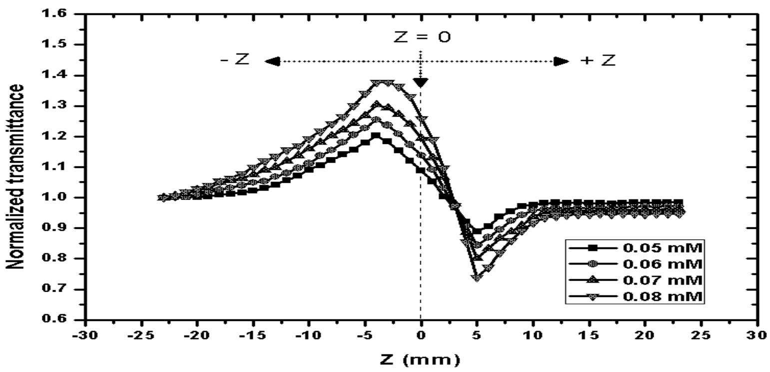

Fig. 7. Z-scan data obtained by dividing the closed aperture data by open aperture data for VOPc in the solvent nitrobenzene.

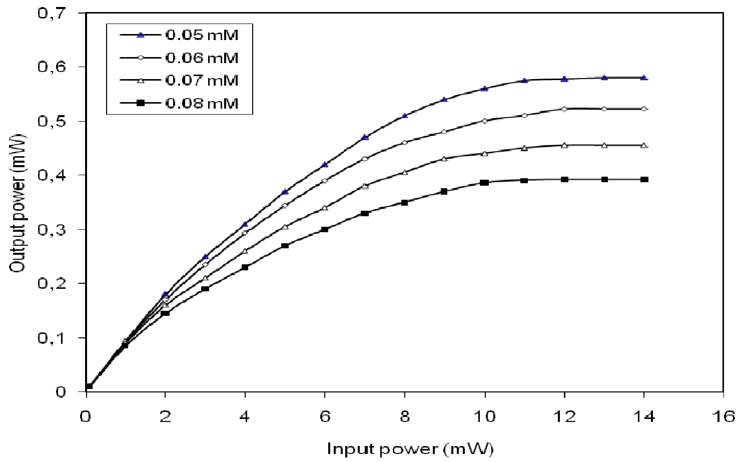

Fig. 8. Optical limiting curves for VOPc in the solvent nitrobenzene for different concentrations.

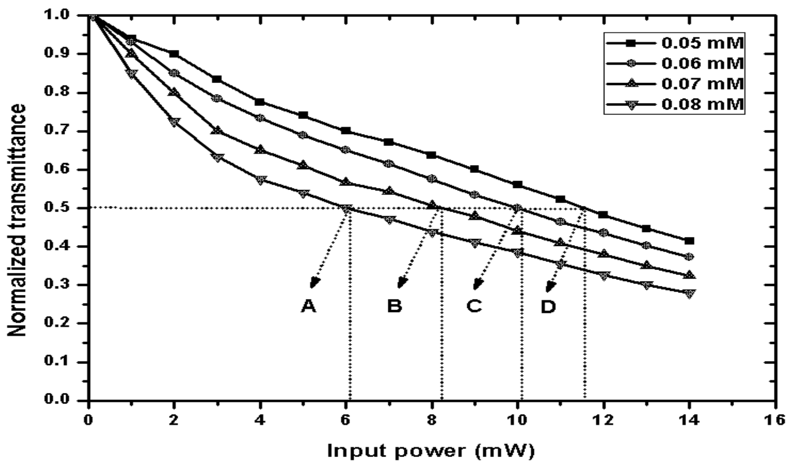

Fig.9. Normalized transmission curves of optical limiting for VOPc in the solvent nitrobenzene for different concentrations.