Solvent Effects on The Nonlinear Refractive Index of Bromocresol Purple at Three Excitation Wavelengths

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Abstract. In this study, the linear properties and the nonlinear refraction of Bromocresol purple (BCP) dye are studied in water and ethanol at three different wavelengths (405, 473 and 532 nm). The study is to assess the effect of the solvent properties on the dye optical characteristics at different wavelengths. Beside the differences in the linear response, the nonlinear refractive index $n_2$ of the dye changes by changing the solvent. The type of the solvent-induced change in $n_2$ depends on the excitation wavelength. In addition, the value of $n_2$ in the same solvent depends on the wavelength of light. The changes in $n_2$ in the two solvents are not likely to be due to the differences in the linear absorption or the thermal effects. The polarity and the hydrogen bonding ability of the solvent can be the main reason of the solvent effects on the nonlinearity of the dye. The effect of wavelength on the nonlinearity of the dye can be due to the change in the physical mechanisms that originate the nonlinear refraction or the change in their individual contributions to the overall nonlinear refraction of the dye.

1. Introduction

Directly after the generation of laser light in 1960, the field of nonlinear optics (NLO) started attaining great interest. Although, nonlinearities have limiting effects in laser active media and optics, nonlinear phenomena have been employed in a great number of applications in various fields [1]. Among the large number of nonlinear materials, organic molecules, especially organic dyes, have special importance in the field of NLO due to their outstanding optical characteristics. In addition to their photo-thermal stability, dissolvability, and easy preparation, they possess large nonlinearity and rapid response [2]. These properties have nominated organic materials to be essential components in various applications [3-8].

The nonlinear properties of material have been extensively investigated over the past decades. There have been different techniques to characterize the nonlinear parameters of materials [9-13]. In comparison with the z-scan technique, these techniques have complex experimental setups and/or required detailed analysis and measurements [14]. However, z-scan measurement [15, 16] is a proficient technique for characterizing the nonlinearity of material. The type and the magnitude of the nonlinear refractive index $n_2$ and the nonlinear absorption coefficient $\beta$ can be concluded from this technique by using a simple and sensitive apparatus.

The nonlinear refractive index of material is an essential parameter in photonics and other optical applications of NLO. It can be caused by different physical effects [17]. In different liquids $n_2$ can be a result of anisotropic molecules arrangement, isotropic molecular redistribution, electronic clouds distortion, resonance effects, and thermal effects [18]. In addition, the value of the nonlinear refractive index of the same material depends on the properties of the surrounding molecules. For instant, in liquids the solvent can significantly alter the nonlinear properties of the solute molecules via different
mechanisms. In general, the solvent-solute interactions which can affect the nonlinearity of the solute molecules can be either specific or non-specific interactions [19]. In addition, there are many processes that can contribute to the determination of the nonlinear properties of the solute. For example, the parameters that can modify the nonlinearity of solute are the thermal capacity and heat distribution of the solvent, different energy transfer mechanisms, the ability of aggregation and dimers formation, collisions between solution molecules, and other parameters [21].

The ability of tailoring the nonlinear properties of materials can be considered as an important advantage in the field of material science. The nonlinear response of organic molecules can be modified either by performing molecular structure changes to the molecules or via the interactions of the solute with the surrounding solvent molecules [20]. Extensive theoretical and experimental works have studied the effects of the environment on the nonlinearity of materials, e.g. [18-23]. In these studies the effects of the environment on the nonlinear refractive index and the nonlinear absorption processes have been investigated for different materials. The outcome of these studies indicated that the effects of the same solvent can be different on different solute molecules and for different light intensities.

In this work the effects of the solvent on the nonlinear refractive index of Bromocresol purple (BCP) dye at three different excitation wavelengths have been investigated. The nonlinearity of the samples has been characterized by using z-scan technique. The value of the nonlinear refractive index of the dye is found in water and ethanol at three different wavelengths (405, 473, and 532 nm). The light sources used are CW diode lasers.

2. Experimental setup

2.1. Z-scan method

Figure (1) depicts a simple scheme of the used z-scan setup [15, 16]. The laser beam is focused by a converging lens and the transmitted power through a small circular aperture located at the far field is measured by a digital power meter as a function of the sample position.

\[
T(z) = \frac{\int_0^L |E(0,r,z)|^2 r dr}{\int_0^L |E(0,r,z)|^2 r dr}
\]

with

\[
S = 1 - \exp\left(-2r^2/w_a^2\right)
\]

\[
\Delta \Phi_0 = kn_2I_0L_{\text{eff}}
\]

\[
L_{\text{eff}} = \frac{1-e^{-at}}{a}
\]
where \( r_a \) is the aperture radius, \( E \) is the electric field component of the light, \( r \) is the spatial coordinate, \( w_a \) is the beam radius at the aperture, \( k \) is the wavenumber, \( I_o \) is the peak intensity, \( \alpha \) is the linear absorption coefficient.

For \(|\Delta \Phi_o| < \pi\), the difference between the maximum of the aperture transmittance curve and its minimum \((\Delta T_{p-v})\) is a linear function of \( \Delta \Phi_o \), and the relation between them can be given by [16]

\[
\Delta T_{p-v} \approx 0.406(1 - S)^{0.25}|\Delta \Phi_o| \tag{5}
\]

As the quantity \( \Delta T_{p-v} \) can be easily obtained from the transmittance curve, \( n_2 \) of the sample can be easily concluded from equations (3) and (5).

### 2.2. Material and instruments

The Bromocresol purple dye is obtained from CDH and used without further purification. The solvents used in this work are of spectroscopic purity. The physical properties and the polarity parameters of water and ethanol are listed in [19]. The samples of the dye are prepared by dissolving a calculated weight of the dye in water and ethanol. The dye is prepared with different concentrations.

The lasers used in this work are diode lasers having Gaussian beams profile. The wavelengths of the used lasers are 405, 473 and 532 nm. The absorption spectra of the BCP dye is measured by using a UV-visible spectrometer, model CECIL CE 7200 (ENGLAND). A 1 mm thick quartz cell is used to contain the samples of the dye in the z-scan setup.

The z-scan curves of the BCP dye in the two solvents are obtained by translating the sample cell across the focal plane of the laser and recording the transmitted power through the aperture as a function of the sample position. The transmittance curve is normalized to the value of the linear transmittance.

### 3. Results and discussion

The linear absorption spectra of the BCP dye dissolved in water and ethanol are shown in figure (2). The absorbance of BCP in ethanol has a slightly higher value and its peak happens in a wavelength 11 nm shorter than that of the dye dissolved in water. Furthermore, the curve of the dye solution in water is slightly wider than that in ethanol.

The differences in the linear absorption in the two solvent can be caused by the difference in the polarity of the solvents. The effect of solvent on the linear properties of the dye can be due to different solvent-solute interactions. These interactions are mainly influenced by the Kamlet-Aboud-Taft (KAT) parameters of the solvent [24]. These parameters are the hydrogen bond donating and accepting abilities and the dipolarity [25]. KAT parameters of the solvent affect the spectroscopic behavior of the solute with different contributions of each parameter [24].

The transmittance curves of the close aperture z-scan for the BCP dye of concentration of 0.1 mM are shown in figure (3 a-c). The appearance of the maximum of the curve before the minimum indicates that BCP has a negative nonlinear refractive index (self-defocusing) in both solvents and at all the studied wavelengths. The total refractive index of the dye in the presence of the third order nonlinearity can be given by:

\[
n = n_o + n_2 I_o \tag{6}
\]

where, \( n_o \) is the linear index of refraction.

In order to obtain the pure effect of the nonlinear index of refraction, the close aperture curve should be divided by the corresponding open aperture curve for the same sample. The curves in figure (3) of the dye in ethanol show that the nonlinear absorption process modifies the shape of the curves. The calculated values of the nonlinear refractive index of the dye in water and ethanol at the three used excitation wavelengths are listed in table (1). The behaviour of the dye in the two solvents and at the three wavelengths is confirmed by the results of the study at different concentrations.

In ethanol, the absolute value of the nonlinear refractive index at the excitation wavelength 405 nm is about 5.85 times larger than its values at the excitation wavelengths 473 nm and 532 nm. In water, the absolute value of the nonlinear refractive index at the excitation wavelength 405 nm is also much higher than its absolute values at 473 nm and 532 nm in the same solvent. The differences in the values...
of the linear absorption at different wavelengths can cause a variation in the nonlinearity of the sample. The differences in the linear absorption at the mentioned excitation wavelengths suggest an increment of 7.2% in the nonlinear index of refraction at 473 nm and 13.69% at 532 nm relative to its value at 405 nm. However, the experimental results show that the change in the nonlinear refractive index is not in this scale and the change is opposite to the suggestion of the linear absorption variations. This indicates that the differences in the nonlinear refractive indices at different excitation wavelengths are not due to the differences in the linear absorbance. The change of the excitation wavelength may induce a change, enhancement or weaken, in the mechanisms that are the origin of the self-defocusing effect in material. In addition, at different wavelengths the nonlinear diffraction can be caused by different physical mechanisms or the contribution of each mechanism to the nonlinearity of the material can change with the change in the excitation wavelength.

The value of the nonlinear refractive index of the BCP dye is also changing by changing the solvent. At excitation wavelengths 405 nm and 473 nm, dissolving the dye in water leads to enhance the nonlinearity of the dye, as can be seen from table (1). However, at wavelength of 532 nm, the value of the refractive index of the dye in ethanol is more than double its value in water. These changes are also not likely to be due to the differences in the linear absorption because they are not in the scale or the direction of the linear absorption-induced changes.

The absorption of the excitation light in the focus of the beam can result in a local temperature increase in the medium. This change in the temperature can have spatial distribution around the focus of the light. The localized heat distribution can act as a lens that significantly modifies the phase of the light beam. This phenomenon has been employed in many studies including charactering the third order nonlinearity of material [26]. In dyes solutions, the value of the thermal-induced nonlinear index of refraction of the dye is mainly affected by the thermal characteristics of the solvent [18]. The thermal conductivity and the specific heat of water are much higher than those of ethanol. This indicates that the effect of thermal lensing of the dye dissolved in water should be much lower than that in ethanol. In other words, the thermal-induced nonlinearity of the dye in water is smaller than its value in ethanol. However, the results shown in table (1) do not agree with the indications of the heat-induced lensing, except at the excitation wavelength 532 nm. This means that the nonlinear refraction of BCP at the wavelengths 405 nm and 473 nm is not due to the thermal effects or, at least, the thermal lensing has minimal contribution to the nonlinearity of the dye at these wavelengths.

The other parameters that can influence the nonlinearity of the solute are the polarity parameters of the solvent. These parameters can cause several solvent-solute interactions. These interactions can cause modifications in the geometrical properties of the organic molecules, hence, influencing the nonlinearity of the molecules [20]. Therefore, the specific and the non-specific interactions of the
solvent can be the main reason for affecting the nonlinearity of the BCP dye. In this case, the effect of the solvent can be studied by investigating the effect of the KAT parameters. Water has dielectric constant, dipolarity/polarizability ability, and hydrogen bond donating ability higher than ethanol [19]. The increase of these parameters leads to change the interactions type of solvent molecules with the dye molecules which can affect the nonlinearity of the dye. In addition, the increase in these

Figure 3. The close aperture curves of the BCP dye at excitation wavelength (a) 405 nm, (b) 473 nm, and (c) 532 nm.
parameters can change the contribution of each one to the overall influence of the solvent on the dye nonlinearity. Furthermore, from the results of the present study, it is obvious that the effects of the solvent parameters are not the same at all wavelengths. Water properties induce an increase in the nonlinearity of the dye at wavelengths within the resonance band of the dye. However, at wavelength located slightly outside the resonance band of the dye, the characteristics of water lead to weaken the nonlinearity of the dye. Therefore, in order to employ the dye nonlinearity in a certain application a correlation between the environment effect and the wavelength of the excitation light should be taken into account.

Table 1. The values of the nonlinear refractive index of BCP dissolved in water and ethanol with concentration of 0.1 mM.

| Solvent | $n_2 \times 10^{-12}$ (m$^2$/W) at 405 nm | $n_2 \times 10^{-12}$ (m$^2$/W) at 473 nm | $n_2 \times 10^{-12}$ (m$^2$/W) at 532 nm |
|---------|---------------------------------|---------------------------------|---------------------------------|
| Ethanol | -8.89                           | -1.52                           | -1.51                           |
| Water   | -11.8                           | -2.62                           | -0.647                          |

4. Conclusion

The linear properties and third order nonlinear refraction of Bromocresol purple (BCP) dye are studied in water and ethanol at three different excitation wavelengths. The study was undertaken to investigate the effect of solvent on the properties of the dye at different wavelengths. This is to specify the optimum conditions of the dye for using in different applications.

The position, the value and the width of absorption spectra of the dye have some differences in the two solvents. In addition, the results of the study show that the highest nonlinearity of the BCP dye is obtained at wavelengths of 405 nm in water and ethanol, relative to that at the other used wavelengths. This can be due to that at different wavelengths the physical origin of the nonlinear refraction changes. Also, it can be due to wavelength-induced changes in the individual contributions of the mechanisms to the overall nonlinear refraction.

The properties of water lead to enhance the nonlinearity of the dye at excitation wavelengths 405 nm and 473 nm. However, at 532 nm, the nonlinear refractive index in ethanol is more than double its value in water. These changes are not likely to be due to the differences in the linear absorption of the dye. Furthermore, at wavelengths 405 and 473 nm the thermal effects cannot be the reason for the nonlinearity changes. The higher polarity of water and the better ability of donating a hydrogen bond can be the main cause of the changes in the dye optical properties. In addition, the influence of the solvent on the nonlinearity of the dye changes by changing the excitation wavelength.

References

[1] Christodoulides, D. N., Khoo, I. C., Salamo, G. J., Stegeman, G. I. and Van Stryland, E. W. 2010 Nonlinear refraction and absorption: mechanisms and magnitudes Adv. Opt. Photonics 2.1 60-200.
[2] Ali, Q. M. and Palanisamy, P. K. 2006 Z-scan determination of the third-order optical nonlinearity of organic dye nile blue chloride Mod Phys Lett B 20.11 623-32.
[3] Bellier, Q., Makarov, N. S., Bouit, P. A., Rigaut, S., Kamada, K., Feneyrou, P and Andraud, C. 2012 Excited state absorption: a key phenomenon for the improvement of biphotonic based optical limiting at telecommunication wavelengths Phys. Chem. Chem. Phys. 14.44 15299-307.
[4] Sreenath, M. C., Joe, I. H. and Rastogi, V. K. 2018 Third-order optical nonlinearities of 1, 5-Diaminoanthraquinone for optical limiting application Opt Laser Technol 108 218-34.
[5] Geethakrishnan, T. and Palanisamy, P. K. 2006 Optical phase conjugation and double-exposure phase-conjugate interferometry in dye-doped thin film using He–Ne laser Appl. Phys. B 82.2 169-72.

[6] Jeyaram, S., Hemalatha, S. and Geethakrishnan, T. 2020 Nonlinear refraction, absorption and optical limiting properties of disperse blue 14 dye Chem. Phys. Lett. 739 137037.

[7] Hernandez, F. E., Alvarado, Y., Biondi, A. and Maillotte, H. 1998 Measurement of nonlinear refraction index and two-photon absorption in a novel organometallic compound Opt. Commun. 152.1-3 77-82.

[8] He, G. S., Zhao, C. F., Bhawalkar, J. D. and Prasad, P. N. 1995 Two-photon pumped cavity lasing in novel dye doped bulk matrix rod Appl. Phys. Lett. 67.25 3703-05.

[9] Williams, W. E., Soileau, M. J. and Van Stryland, E. W. 1984 Optical switching and n2 measurements in CS: Opt. Commun. 50.4 256-60.

[10] Weber, M. J., Milam, D. and Smith, W. L. 1978 Nonlinear refractive index of glasses and crystals Opt. Eng. 17.5 175463.

[11] Adair, R., Chase, L. L. and Payne, S. A. 1987 Nonlinear refractive-index measurements of glasses using three-wave frequency mixing JOSA B 4.6 875-81.

[12] Friberg, S. T. E. P. H. E. N. R. and Smith, P. E. T. E. R. W. 1987 Nonlinear optical glasses for ultrafast optical switches IEEE J. Quantum Electron. 23.12 2089-94.

[13] Owyoung, A. 1973 Ellipse rotation studies in laser host materials IEEE J. Quantum Electron. 9.11 1064-69.

[14] Geethakrishnan, T. and Palanisamy, P. K. 2007 Z-scan determination of the third-order optical nonlinearity of a triphenylmethane dye using 633 nm He–Ne laser Opt. Commun. 270.2 424-28.

[15] Sheik-Bahae, M., Said, A. A., Wei, T. H., Hagan, D. J. and Van Stryland, E. W. 1990 Sensitive measurement of optical nonlinearities using a single beam IEEE J. Quantum Electron. 26.4 760-69.

[16] Sheik-Bahae, M., Said, A. A. and Van Stryland, E. W. 1989 High-sensitivity, single-beam n2 measurement Opt. Lett. 14.17 955-57.

[17] Shen, Y. R. 1984 The Principles of Nonlinear Optics Wiley, New York.

[18] Sinha, S., Ray, A. and Dasgupta, K. 2000 Solvent dependent nonlinear refraction in organic dye solution J. Appl. Phys. 87.7 3222-26.

[19] Sadigh, M. K., Zakerhamidi, M. S., Rezaei, B. and Milanchian, K. 2017 Environment effects on the nonlinear absorption properties of Methylene blue under different power of excitation beam J. Mol. Liq. 229 548-54.

[20] Jeyaram, S. and Geethakrishnan, T. 2020 Solvent dependent linear and nonlinear optical characteristics of acid blue 3 dye J. Fluoresc. 30.5 1161-69.

[21] Thankappan, A., Thomas, S. and Nampoori, V. P. N. 2013 Solvent effect on the third order optical nonlinearity and optical limiting ability of betanin natural dye extracted from red beet root Opt. Mater. 35.12 2332-37.

[22] Manzoni, V., Modesto-Costa, L., Del Nero, J., Andrade-Filho, T. and Gester, R. 2019 Strong enhancement of NLO response of methyl orange dyes through solvent effects: A sequential Monte Carlo/DTF investigation Opt. Mater 94 152-59.

[23] Yu. Balakina, M. and Nefediev, S. E. 2006 Solvent effect on geometry and nonlinear optical response of conjugated organic molecules Int. J. Quantum Chem. 106.10 2245-53.

[24] Khadem Sadigh, M. and Zakerhamidi, M. S. 2018 A comparative study of media polarity effects on the linear and third-order nonlinear optical responses of thiazine dyes Can. J. Phys. 96.3 337-42.

[25] Sherwood, J., Granelli, J., McElroy, C. R. and Clark, J. H. 2019 A Method of Calculating the Kamlet–Abboud–Taft Solvatochromic Parameters Using COSMO-RS Molecules 24.12 2209.

[26] Terazima, M. 1994 Transient lens spectroscopy in a fast time scale: Photoexcitation of rhodamine 6G and methyl red solution Chem. Phys. Lett. 230.1-2 87-92.