The Influence of pH on Nonlinear Refractive Index of Bromophenol Blue

F.Z. Henari and K.G. Culligan
Department of Basic Medical Science, Royal College of Surgeons in Ireland,
Medical University of Bahrain, Kingdom of Bahrain

Abstract: Problem statement: Bromophenol blue is a pH indicator, a kind of chemical that changes colour when pH goes up or down over a narrow linear dynamic range of 3.0-4.6 pH units. Therefore a good approach must be taken to extend the linear response of the indicator in order to have simple calibration and precise measurements of PH sensors. The purpose of this experiment is to measure the nonlinear refractive index of Bromophenol blue in a PH range of 2-9. **Approach:** Samples of Bromophenol blue solutions at an optimized final concentration of 5.25µg mL^{-1} were prepared each having one unit pH intervals from a pH of 2 using 10 mM Tris-Cl as a buffering agent. The nonlinear refractive index response of the samples were investigated at CW laser at 514 nm using z-scan technique. **Results:** The closed aperture z-scan of the samples displayed a prefocal peak followed by a postfocal valley (self defocusing). A variation of the nonlinear refractive index within a pH range over 2-9 is observed. This reflects the interaction of the Bromophenol molecules with the environment. The nonlinear refractive values measured range was from 1.0×10^{-12}-5.5×10^{-12} m^2/w for pH varying from 2-9 pH units. The correlation between the peak of the absorption and measured nonlinear refractive index is reported. **Conclusion/Recommendations:** The z-scan showed that Bromophenol blue exhibits a nonlinear effect of thermal origin. The experiment illustrated that the nonlinear refractive index measurements can be considered as a good indicator of pH values.

Key words: Nonlinear optics, nonlinear refractive index, z-scan, Bromophenol, pH indicator

INTRODUCTION

Bromophenol blue is a halochromic chemical that indicates, through characteristic colour changes, the degree of acidity or basicity of solutions. Acid-base indicators are commonly employed to measure the existing pH of a solution. Most halochromic indicators change gradually from one colour to another over a range called visual transition interval (Bishop, 1972). These changes for Bromophenol blue occur in a very narrow interval of 3-4.6 pH units from yellow at pH 3.0 to purple at pH 4.6. Beyond a pH of 4.6 it is impossible to determine the pH of the solution visually. Optical sensors (optodes) technique is widely used for determination of pH. This technique is restricted to narrow pH ranges (Wolfbeis, 2002; Ferreira and Girotto, 2009). It is important to have a linear response because is leads to more precise pH measurements over the entire linear range. Therefore techniques such as absorption measurements, colorimetric pH sensors and fluorescent measurements are necessary in order to monitor the extent response range of Bromophenol blue as a pH indicator. Recently the third order optical nonlinearities have been exploited in different ways to characterize organic materials (Passad and Williams, 1991; Shen, 2003), amino acid solutions (Rodrigues *et al*., 2003) and measurement of blood glucose levels (Dhinna *et al*., 2008). Among the various techniques used to measure the nonlinear response of materials, the z-scan technique (Sheik-Bahae *et al*., 1990) proved to be an effective tool. This method can measure both nonlinear refractive index and nonlinear absorption in solid and liquid samples.

In this article we report the nonlinear refractive index measurements of Bromophenol blue solutions at different pH intervals, ranging from 2.0-9.0 with 514 nm cw laser using z-scan technique. By using nonlinear refractive index measurement, the linear response of bromophenol blue pH indicator could be extended from pH 3.0-4.6-3.0-7.5. The correlation between the measured nonlinear refractive indices and absorption peaks are also reported.

Corresponding Author: F.Z. Henari, Department of Basic Medical Science, Royal College of Surgeons in Ireland,
Medical University of Bahrain, Kingdom of Bahrain

MATERIALS AND METHODS

Solutions of Bromophenol blue at an optimized final concentration of 5.25 µg mL^{-1} were prepared each having one unit pH intervals from a pH of 2 using 10 mM Tris-Cl as a buffering agent. A physiological pH (pH 7.4) was also included. Figure 1b shows the plot of the absorption peak intensity at 591 nm as a function of pH for the Bromophenol blue solution.

The z-scan technique was used to measure the nonlinear refractive index. The experiment was performed with an air-cooled Ar ion laser beam operating at 514 nm with an average power of 40 mW. The beam was focused to a beam waist of 20 µm with a lens of 5 cm focal length, giving a typical power density of 6.3×10^7 W/m^2. The sample was placed in a 1mm path length quartz cuvette. The transmission from the sample was measured through an aperture (closed-aperture case) in the far-field of the lens, as the sample moved through the focal point.

The difference between normalized peak-valley transmittance ΔT_{p-v} is given by:

$$\Delta T_{p-v} = 0.406(1-S)^{0.25} |\Delta\phi| \qquad (1)$$

Where:

$|\Delta\phi|$ = The on axis nonlinear phase shift at focus
S = The linear transmittance of the aperture and is given by:

$$S = 1 - \exp(-2r_a^2 / w_a^2) \qquad (2)$$

Where:

r_a = The radius of the aperture
w_a = The radius of the laser at the entrance of the aperture

The nonlinear phase shift is given by:

$$\Delta|\phi| = \frac{2PL_{eff}}{\lambda w_o^2} n_2 \qquad (3)$$

Where:

n_2 = The nonlinear refractive index
P = The laser power
λ = The laser wavelength
L_{eff} = (1-exp(-αL))/α with α is linear absorption coefficient at 514 nm
L = The sample thickness
L_{eff} = The effective thickness of the sample

RESULTS

The absorption spectra of Bromophenol blue measured at different pH values ranging from 2-9

are shown in Fig. 1a. From the absorption spectrum for pH 2 it can be clearly seen that the spectrum is characterized by one absorption band in the region of 453 nm. As the value of pH of solution increases a new band in the region 591 nm appears in the spectrum. These absorption bands correspond to the colour changes of the Bromophenol blue from yellow to purple in pH ranges 3-4.6. An increase in pH, results in decrease in peak intensity at 453 nm and an increase in the peak intensity around 591 nm. At higher pH values the absorption spectrum shows only one band at 591 nm with a small shift to lower wavelengths at higher pH, which may be due to the existence of more Bromophenol blue species. The isosbestic point, at 490 nm present in the absorption spectra confirms the existence of an equilibrium between acid and basic forms in the Bromophenol blue samples (Sedjil *et al.*, 1998).

As shown in Fig. 1b, the useful linear range of this solution is limited to a range pH 3-4.6 and with a maximum absorption about pH 7.5. This pH range value is in agreement with the working pH range reported in (Ferreira and Girotto, 2009; Taib *et al.*, 1996).
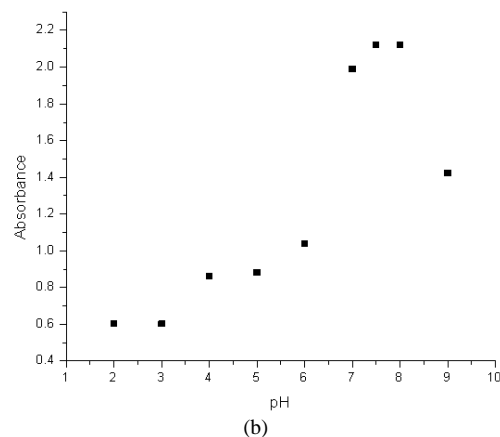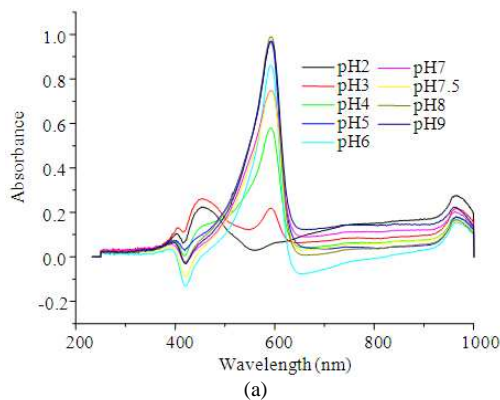

(a)

(b)

Fig. 1: (a): Absorption spectra of Bromophenol solutions at various pH values. (b): Peak of absorption spectra with variation pH values

The absorption is higher in the range of 591 nm than the absorption at 453 nm. Therefore the nonlinear experiment performed at a wavelength close to absorption peak at 591 nm i.e., at the nearly resonance condition.

This technique relies on the fact that the intensity varies along the axis of the convex lens and is maximum at the focus. Hence, by shifting the sample through the focus, the nonlinear refraction can be measured by observing the spot size variation at the plane of finite aperture/detector combination.

The normalized transmittance through closed aperture for Bromophenol blue at different pH values are shown in Fig. 2. This normalized transmission curve is characterized by a prefocal peak followed by a postfocal valley. This peak valley configuration implies that the nonlinear refractive index of solution is negative ($n_2 < 0$). The changes of linear and nonlinear absorption properties are related to the protonation or deprotonation of the Bromophenol blue molecule, Thus, the variation of the z-scan transmission with pH can be explained as follows: The localized absorption of the focused Gaussian beam by the sample produces a spatial distribution of the temperature in the sample solution which results in spatial variation of refractive index (Gomeze *et al.*, 1999 Henari and Al-Saie, 2006). This light induced change of refractive index can have considerable effect on the laser propagation in the nonlinear medium, which leads to the well known self action effect phenomena such as self defocusing, self focusing and self-phase modulation. Therefore the observed nonlinear effect can be attributed to the thermal nonlinearity resulting from 514 nm absorption by the sample.
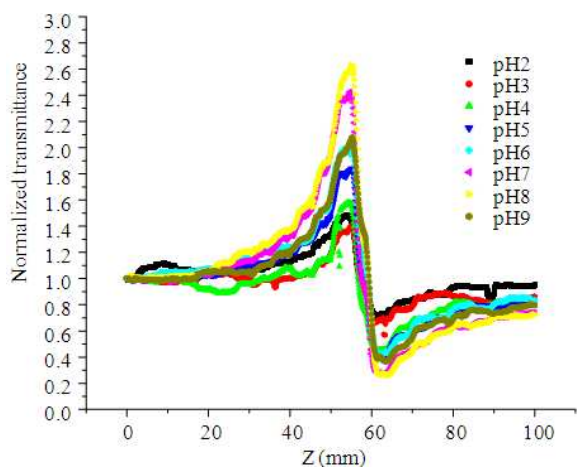
DISCUSSION

Figure 2 shows the results of z-scan measurement for Bromophenol blue pH indicator at different pH's ranging from pH 1-9. As can be seen as the pH value increases, the peak-valley intensity varies. The nonlinear refractive index (n_2) is calculated from the normalized transmittance value of ΔT_{p-v} using equations 1-3 for different values of pH's.

Figure 3 shows the calculated values of nonlinear refractive index n_2 variation for different pH values of the solution. As can be seen, the n_2 values are vary linearly with pH up to the pH value 7.5, while the absorption spectra of Bromophenol blue show a useful linear range up to pH 4.6 (Fig. 4).
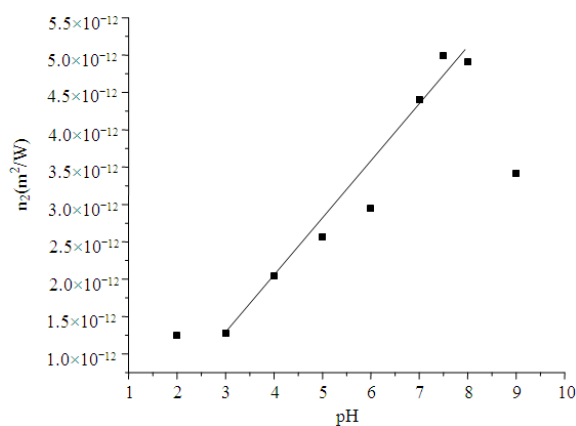

Fig. 3: Variation of the nonlinear refractive index for Bromophenol solutions at various pH values. The drawing line is for the guide
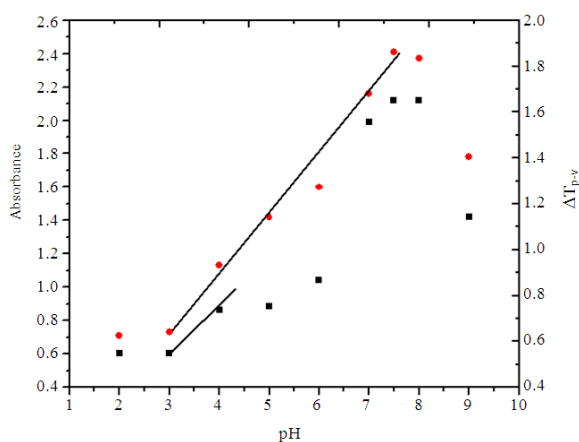

Fig. 2: z-scan results for various pH values of the bromophenol blue

Fig. 4: Variation of peak absorption value for various pH values (squares) and changes ΔT_{p-v} for various pH values (circles). The drawing line is for the guide

This extended linear range observed by z-scan measurements can be considered as an advantage over the traditional absorption spectra. The above results demonstrate an important practical achievement since the z-scan measurements may be used to determine the pH of solutions.

An important point to be considered is that the calculation of n_2 is not needed since the transmission change ΔT_{p-v} is proportional to n_2. Figure 4 shows the plot of the of ΔT_{p-v} variation for Bromophenol blue solution as a function of pH values. Also plotted in Fig. 4 are the peak values of absorption spectra at 591 nm for comparison.

CONCLUSION

We have measured the nonlinear refractive index for Bromophenol blue indicator at different pH values using the z-scan technique with 514 nm cw Argon laser. The z-scan shows that Bromophenol blue exhibits a nonlinear effect of thermal origin. The extended linear range of Bromophenol blue was observed. The experiment illustrated that the nonlinear refractive index measurements can be considered as a good indicator of pH values. Technically the z-scan has an advantage over conventional spectrometric method because it is easy to be employed and less expensive.

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