Effect of L-alanine concentration on linear and nonlinear optical properties of two dyes in water and nano-confined water

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The effect of L-alanine concentration with anionic Erythrosin B (EryB) and cationic Rhodamine 6G (R6G) dye in water and nano-confined water was studied by absorption, fluorescence and Z-Scan instruments. The nano-confined water was prepared with a mixture of water and n-decane and Sodium bis(2-ethylhexyl) sulfosuccinate (AOT) that the size of nano-confined water can change with molar ratio of water to AOT (X). By the change of L-alanine concentration up to 1.5M, absorption spectra do not change and the peak position of absorption spectra is constant. The fluorescence spectra of AOT/n-Decane/Water/EryB with W=40, shows a peak at 555 nm that shifts to 553 nm by increasing of L-alanine concentration. The fluorescence intensity of mixed with AOT/n-Decane/Water/EryB with W=40 quenches by increasing of L-alanine concentration that this behavior was not observed in other samples. The nonlinear absorption (β) of EryB and also R6G nano-confined water is enhanced compared to bulk water. Moreover, the slope of β as function L-alanine concentration of for both of dyes in nano-confined water is higher than that of in bulk water. Therefore, the nano-confined water and the nonlinear absorption are suitable medium and parameter to detection of the L-alanine concentration.

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1. Introduction

Non-linear optical (NLO) materials have shown to have wide applications such as, second electro optic switches, optical power limiting, optical data storage technology and optical signal processing[1–3]. The study of NLO properties of biological systems is a chalange on condensed matter physics. Most of studied base on NLO properties of acid amine in crystal structute. Different amino acids have been reported as interesting materials for NLO applications [4–6]. Due to presence of a protonated amino group and deprotonated carboxyl group they have zwitterionic structure. This groups will improve the nonlinear polarization [7]. Amongst the amino acids, L-alanine is the simplest acentric structure, ionic organic crystal with a side chain methyl group (CH_3) and displays molecular chirality features. The L-alanine is the fundamental part of more complex amino acids. The NLO values of L- alanine is improved when it combined with different organic and inorganic compound to form novel materials [6,8].

Among different experimental techniques accessible, the Z-scan method is the most advantageous and effective tool and also a highly sensitive and an exact method for determining the NLO parameters. Nonlinear absorption coefficient and non-linear refractive index can be evaluated by the Z-scan measurements [6,9–11]. K. Rajesh et al. determine the nonlinearity of the β alanine β alaninium picrate (βAβAP) single crystal using a Q-switched Nd:YAG laser of 1064 nm wavelength in Z-scan technique [6]. The non-linear optical properties in five different amino acids water solutions were reported using the Z-scan method with femto-second laser pulses [12]. The study shows, that it is not easy to find the NLO values of L-analine in solution by Z-scan with continuous laser. In order to improve the NLO properties, the L-alanine was mixed in crystal.

Regarding of the fluorescence quenching effects of dyes in the presence of amino acids is crucial for the advancement of new fluorescence-based experiments. By these considerations, in the literature the fluorescence quenching of different fluorophores by several amino acids were reported [13–16]. Among the dyes investigated, Rhodamine 6G [14], the red-absorbing oxazine derivative MR121, the dyes ATTO 655, ATTO 680 [13,16] and AuNPs–βCD–dye assembly as a fluorescent probe [15] show the most enounced quenching efficiency by tryptophan. Other aromatic and aliphatic amino acids (L-valine, L-alanine, norvaline, tyrosine, L-phenylalanine, methionine, and histidine) showed only less quenching efficiencies. Valine, alanine and norvaline have insignificant effect on the fluorescence recovery of the

dye. Owing to their smaller aliphatic side chain and their higher hydrophilicity than L-tryptophan such amino acids can not form suitable inclusion complex with β-CD [15].

Mohd. Shkir et al. investigated the nonlinear optical properties of methylene blue dye added L-alanine crystal by Z-scan technique. They showed that the third order nonlinear optical parameters of dyed L-alanine crystals are enhanced and they are better than pure crystal for optical device applications [17]. As it seems, Z-scan method can be more useful technique than the fluorescence spectroscopy due to its high sinsitivity to interaction of this amino acid with dyes. One feasible liquid medium for a dye system is a two-phase medium such as microemulsions (oil in water) and reverse microemulsions (water in oil). In a microemulsion system dye molecules can be dissolved and encapsulated in one medium while it is nearly separated from any chemical interaction with the second medium. By choosing a two-phase medium it is possible to achieve the desirable thermal and optical properties with no change in the pH and molecular structure of the host medium. Additionally, the nano-droplets in microemulsion can enhance the linear and nonlinear optical properties of dye molecules [18]. Therefore, in this work we choose an AOT microemulsion medium for dyes and investigate the effect of L-alanine amino acid on the two-photon absorption coefficient of dye solution in confined water (water nano-droplets) and compare with bulk water using the Z-scan technique.

2. Experimental

2.1. Materials

Anionic Erythrosin B dye (purity>95%), Cationic Rhodamine 6G dye (purity>95%), Sodium bis(2-ethylhexyl) sulfosuccinate AOT (purity >99%), L-alanine amino acid (99% purity) and n-decane (purity >95%) were purchased from Sigma–Aldrich and used without any further purification.

2.2 Preparation of EryB and R6G nano-droplets

The microemulsion samples comprising EryB and R6Gwere prepared by weighting, in terms of water to surfactant molar ratio of W=[H_2O]/[AOT] and also the nano-droplets mass fraction [$m_{fd}=(m_{H2O}+m_{AOT})/(m_{Total})$], which $m_{Total}=m_{H2O}+m_{AOT}+m_{Dec}$. The size of the nano-droplets can be altered through variation of water to AOT surfactant molar ratio (W=40 and 6.7). The concentration of amino acid inside the nano-droplet was determined with the mass ratio of amino acid in water ($C_{L\text{-}alanine}$) that in this work, the $C_{L\text{-}alanine}$ has three different values (0, 0.09 and 1.5 M). The concentration of dye inside of microemulsion was determined with a mass ratio of dye in microemulsion (C_{dye}).

2.3. Characterization

Absorption and Fluorescence spectra of dyes were recorded using UV-1650 PC spectrometer (Labomed) and LS-45 spectrofluorometer (PerkinElmer), respectively. The open-aperture Z-Scan of samples was recorded at laser wavelengths of 530nm. A TEM00 Gaussian beam was adjusted on the samples using an 8-cm focal length lens. The samples were put in its focal area on a place where the transmittance was minimal in the Z-Scan test. The transmittance of the extruding beam from an aperture was measured as a function of the input power.

3. Results and discussion

3.1. Absorbance spectroscopy

Figs. 1 show the optical absorbance spectra of EryB and R6G in confined water (nano-droplets) and in bulk water with different L-alanine amino acid concentrations. The absorbance peak of EryB aqueous solution is composed of an intense vibronic band at about 525 nm corresponding to the allowed origin, most likely associated with a $0 \rightarrow 1$ transition and a smaller shoulder at 492 nm corresponding to the $0 \rightarrow 2$ transition [19]. As seen from Fig. 1(a), there is an intense absorbance band around 536nm and a shoulder around 498 nm in the optical absorbance spectra of the AOT/n-Decane/Water/EryB at W=40 and $C_{dye=}$0.003mM and the position of peaks do not change with the change of L-alanine amino acid concentration up to 1.5M. Even the position of absorbance spectra is constant at EryB-water solution with increase of L-alanine concentration, Fig. 1(b). The R6G has one absorbance maximum at 533nm at nano-droplet samples that its position does not change at different L-alanine amino acid concentration, Fig. 1(c). The absorbance spectrum of R6G molecules in bulk water has a peak at wavelength of 525 nm and a vibronic shoulder at around 495nm, which originated from R6G monomers [20]. Therefore, the absorption characteristics of EryB and R6G dyes are not affected by changing the L-alanine amino acid concentration, Fig. 1(d).

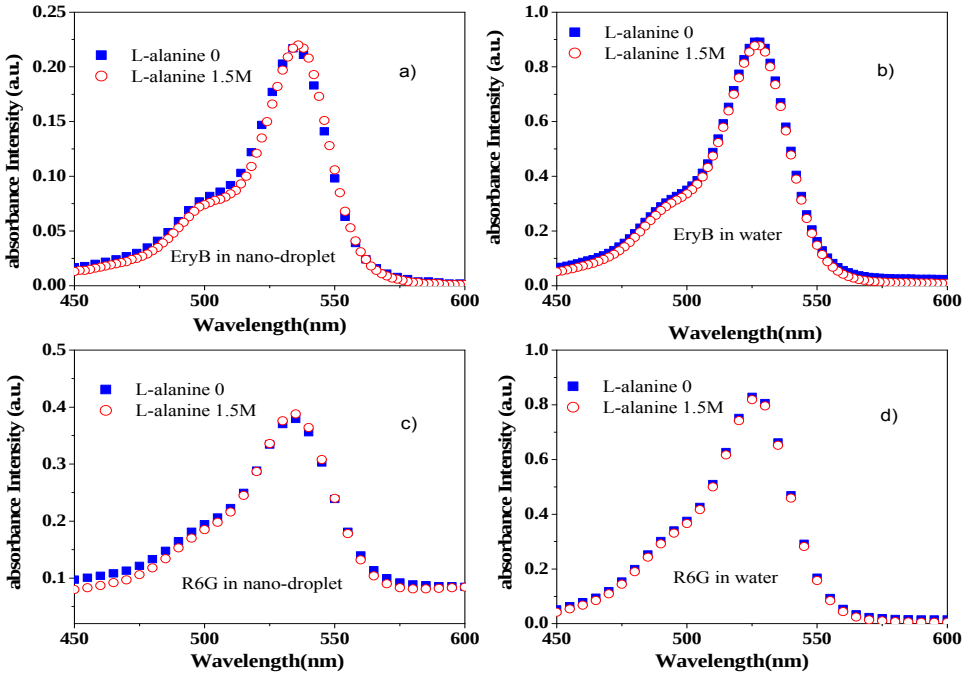

Fig. 1. The UV-vis absorbance spectra of AOT/n-Decane/Water/EryB at constant W=40 and C_{dye}=0.003mM (a), EryB in bulk water at C_{dye}=0.04mM (b) and Decane/Water/R6G at W=6.7 and C_{dye}=0.004mM (c) and R6G in water at C_{dye}=0.05mM (d) with two L-alanine amino acid concentration (0 and 1.5M), respectively

3.2. Fluorescence spectroscopy

The experimental fluorescence spectra of EryB and R6G dyes in confined water (nano-droplets) and in bulk water with different L-alanine amino acid concentration, are shown in Figs. 2(a-c). The fluorescence spectra of AOT/n-Decane/Water/EryB at constant W=40 and C_{dye}=0.003mM, shows a peak at 555 nm that shifts to 553nm by increasing of L-alanine concentration. The fluorescence intensity of AOT/n-Decane/Water/EryB Water with W=40 quenches by increasing of L-alanine concentration, Fig. 2(a). While the fluorescence intensity of Ery B in bulk water has no considerable quenching with the increase of L-alanine concentration. AOT/n-Decane/Water/R6G at W=6.7 and C_{dye}=0.004 mM and $C_{L\text{-}alanine}$=0.09M indicates fluorescence peak at 561 nm that with increase of L-alanine amino acid concentration has no remarkable enhancement, Fig. 2(b). The EryB in bulk water at C_{dye}=0.04 mM shows a peak at 555 nm that it is constant with increase of L-alanine concentration, Fig. 2(c). Therefore, we can suggest that EryB dye is more sensitive than R6G dye for detecting of L-alanine amino acid.

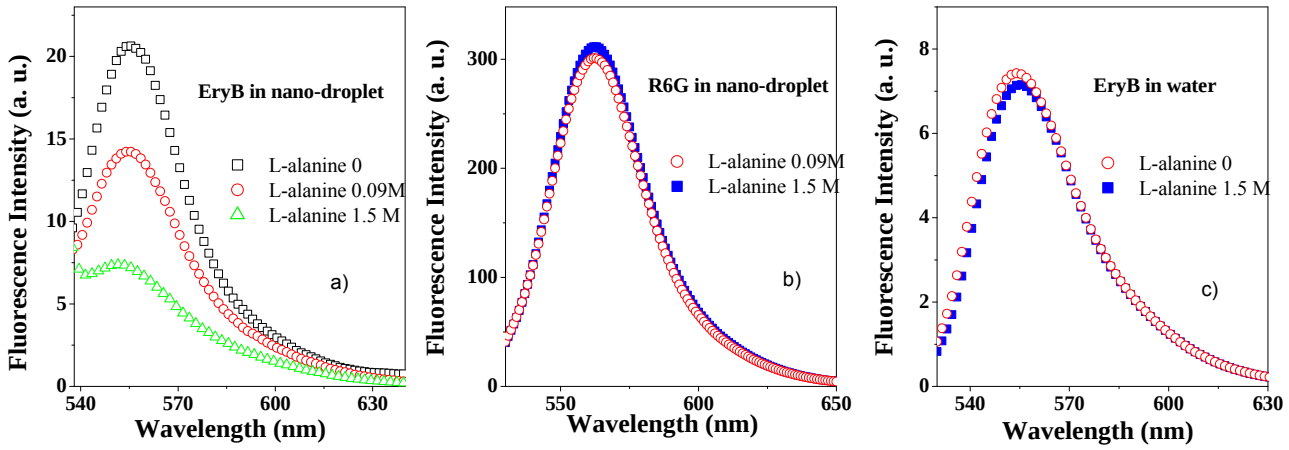

Fig. 2. The fluorescence spectra of AOT/n-Decane/Water/EryB at constant W=40 and C_{dye}=0.003mM (a), AOT/n-Decane/Water/R6G at W=6.7 and C_{dye}=0.004mM (b), respectively and EryB in bulk water at C_{dye}=0.04mM (c) with different L-alanine amino acid concentration

The maximum intensity of fluorescence as a function of L-alanine amino acid concentrations ($C_{L\text{-alanine}}$) for EryB in nano-droplet and bulk water is presented in the Fig. 3. From the Fig. 3, the fluorescence intensity is quenched by increasing of L-alanine ($C_{L\text{-alanine}}$) for both of EryB in microemulsion and water. But the variation of the EryB fluorescence intensity in nano-droplet is much more considerable than that of in bulk water. Therefore, we can suggest that the microemulsion system is more suitable than bulk water for detecting L-alanine purpose owing to its more sensitivity to the presence of L-alanine amino acid.

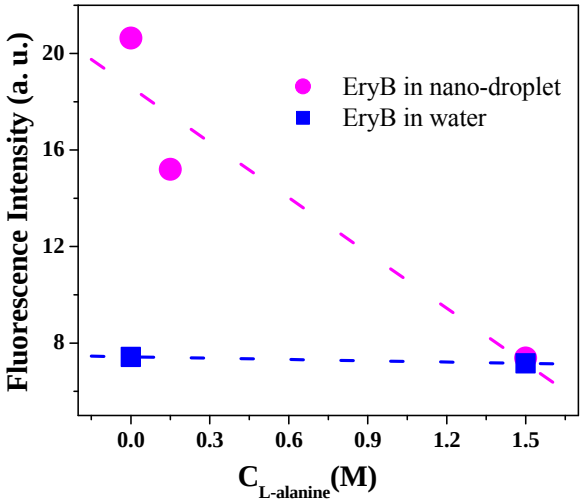

Fig. 3. The peak of fluorescence intensity of EryB dye as function of L-alanine amino acid concentration.

The hydrophobic interactions between dyes and amino acid can play an essential role in the formation of the dye/quencher nonfluorescent complex [21]. Hydrophobic amino acids such as L-alanine and phenylalanine mostly immigrate into the AOT interface layer. The SAXS studies indicate the increase of nano-droplets size and distortion of the symmetry infering a change in shape from spherical to cylindrical or ellipsoidal in the presence of hydrophobic amino acids molecules such as phenylalanine [22].

3.3. Z-Scan study

Fig. 4 present the open-aperture Z-scan data of EryB (a,b) and R6G (c,d) dyes in nano-droplets and in bulk water. The peak has been suppressed partly or completely due to the presence of the excited state absorption. The true change in the real part can be obtained by dividing the normalized closed aperture scan by the corresponding normalized open aperture scan [23]. From the valley transmittance change, we obtained two photon absorption using the following equation

$$T(z) = \sum_{m=0} [(-q_0)]^m / (m+1)^{\frac{3}{2}} \quad (1)$$

where, $q_0 = \left(\beta I_0 L_{eff}\right) \Big/ \left(1 + \left(Z/Z_0\right)^2\right)$, β is the two-photon absorption coefficient and z_0 is the Rayleigh length [24]. The open aperture data show, the valley depth (Figs. 4) of figures increase with the increase of L-alanine amino acid concentration. The non-linear refractive index has been obtained from the peak-valley transmittance change, using the following equation [9]

$$n_2 = \left(\lambda \Delta T_{P\text{-}V}\right) \Big/ \left(2\pi L_{eff} I_0 (0.406)(1-S)^{0.27}\right) \quad (2)$$

where $\Delta T_{P\text{-}V}$ is the peak-to-valley height of the closed aperture transmitted intensity, L_{eff} is the effective length of the sample, I_0 and S are and the intensity of light and the linear transmission of the aperture, respectively. Our experimental results approve the incidence of the two-photon absorption in the prepared samples owing to the entity of a valley in the open aperture data (Fig. 4).

The Z-scan Open aperture curves of AOT/n-Decane/Water/EryB at constant W=40 and C_{dye}=0.003mM are presented in Fig. 4(a). The results show by increase of L-alanine concentration the valley depth is increased. The same effect was observed in the mixture of EryB in water, Fig. 4(b). The Z-scan of Decane/Water/R6G at W=6.7 and C_{dye}=0.004mM and R6G in water at C_{dye}=0.05 mM with different L-alanine amino acid concentration was presented in Fig. 4(c and d), respectively. The nonlinear absorption (NLA) coefficients of EryB and R6G doped nano-droplet and bulk water as a function of L-alanine amino acid concentration ($C_{L\text{-alanine}}$) are presented in the Figs. 5(a,b), respectively.

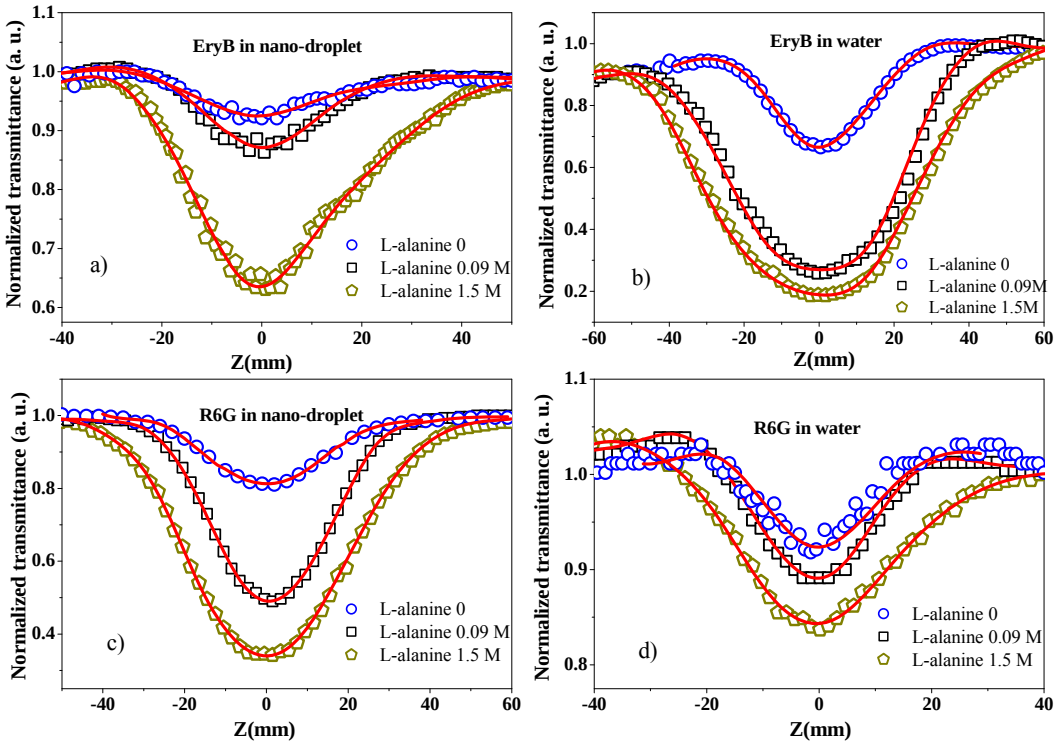

Fig. 4. The Z-scan Open aperture curves of AOT/n-Decane/Water/EryB at constant W=40 and C_{dye}=0.003mM (a), EryB in bulk water at C_{dye}=0.04mM (b) and Decane/Water/R6G at W=6.7 and C_{dye}=0.004mM (c) and R6G in water at C_{dye}=0.05mM (d) with different L-alanine amino acid concentration, respectively

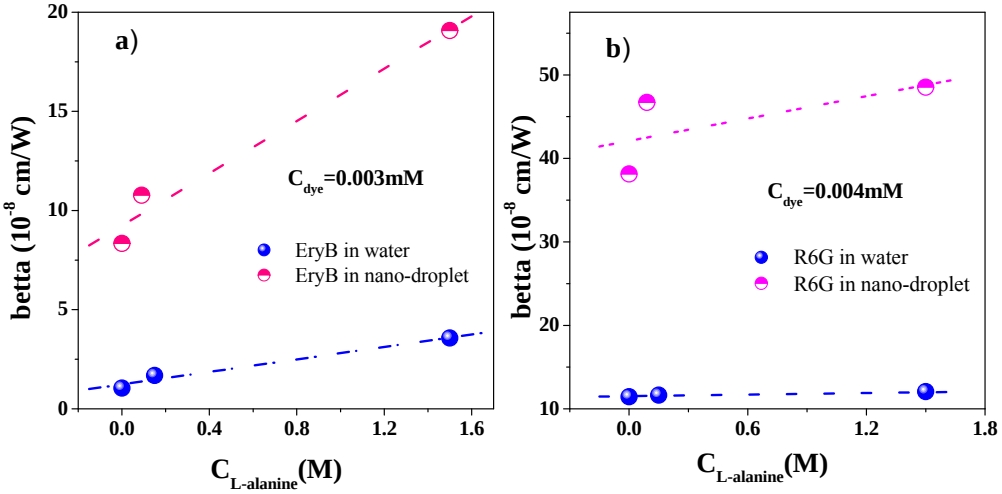

Fig. 5. Calculated values of two photon absorption coefficients as a function of L-alanine concentration ($C_{L\text{-alanine}}$) for (a) EryB and (b) R6G doped nano-droplet and in bulk water

As seen from Fig. 5(a,b), The NLA depends on L-alanine amino acid concentration ($C_{L\text{-alanine}}$) and increases by increasing of $C_{L\text{-alanine}}$. The NLA of EryB and also R6G nano-droplets are enhanced compared to bulk water. Moreover, the slope of the NLA curve for both of dyes in nano-droplet is faster than that of in bulk water. Therefore, by Z-scan technique microemulsion medium is more suitable medium for revelation of L-alanine amino acid than bulk water. In the case of R6G as a probe Z-scan method is more efficient than fluorescence spectroscopy. As seen from Fig. 2b there is no significant variation in fluorescence intensity of R6G with the increase of L-alanine concentration while the NLA of R6G shows an acceptable enhancement by increasing of L-alanine amino acid concentration.

The previous studied shows that, linear and nonlinear optical parameters of R6G dye in nano-droplet and in the bulk water have been determined, using fluorescence, UV-vis and Zscan techniques [25]. It was shown that the fluorescence intensity of R6G can be enhanced by confined water nano-droplets at higher dye to water mass ratios. Also, the Z-Scan results show, the NLO of R6G in nano-droplets are higher than that of in bulk water and increase by nano-droplet concentration [25]. Moreover,

the study on mixture of EryB in AOT microemulsion showed that the enhancement of the fluorescence intensity and two photon absorption of EryB by nano-droplets [26]. So, the materials with high fluorescence intensity and two photon absorption are suitable for detection on biological materials. For this reason, the mixture of L-alanine in different concentration was studied in this work. Our results in the present study show the effect of L-alanine concentration on the optical properties of these dyes in nano-droplet and bulk water leading to distinguish better the presence and concentration of L-alanine amino acid.

A study shows that the nonlinear optical response between an electroactive Tetrathiafulvalene based ligand and its corresponding zinc complex has been performed. The results show an enhancement of the nonlinearity upon complexation of the ligand [27,28]. It is demonstrated that the nonlinear optical properties of materials depend on the solvent polarity [29]. In general, the nonlinear optical properties can enhanced by the increase of polarity of molecule [30]. A study has shown that the nonlinear optical properties in materials depend on the absorption coefficients of the sample [31]. In our case the absorption value does not change with increase of L-alanine amino acid concentration and the change of the nonlinear optical properties can be changed with the change of the dipole moment of dye.

From Fig. 5, it is observed that the nonlinear absorption of Rhodamine 6G is higher than Erytrosin B. A study has shown that the nonlinear absorption value can be enhancement in the molecule with methyl and methoxycarbonyl end groups [32]. It is well known that Rhodamine 6G have methyl group that it can be enhance the nonlinear optical values.

4. Conclusion

A new method for determining the concentration of L-alanine in solutions is described in this work. The nonlinear absorption of AOT/n-Decane/Water/EryB and AOT/n-Decane/Water/R6G are more sensitive to change of L-alanine concentration than the water solution of the two dyes. Moreover, the NLA value, are enhanced with increase of L-alanine concentration in nano-confined water while, it is constant in the bulk solution of dyes. In the water and nano confined water, the position and shape of absorption spectra of R6G and EryB do not change with increase of L-alanine concentration.

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