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Nonlinear properties of Acid Blue 29 Dye in CTAB/1-butanol/water microemulsion

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The nonlinear optical properties of Acid Blue 29 dyes inside of microemulsion have been studied using Z-scan technique. Experiments are performed using a CW Diode laser at 532nm wavelength and 80mW power. The nonlinear refractive index (n_2), nonlinear absorption coefficient,(ß) hyperpolarizabilities(γ_R), nonlinear susceptibility(χ_R) and are measured at three concentrations in microemulsion. The droplets were produced by mixture of water, cetyltrimethylammonium bromide (CTAB) and 1-butanol. The results show that there is an increasing trend in the value of the NLO as the concentration increases. The dynamic light scattering and SAXS experiments are used to understanding the effect of dye in dynamic and structure of droplets. Oil dispersions of water droplets are shown the collective diffusion coefficients reduce linearly with the increase of volume fraction and the increase with the increase of Acid Blue 29 (AB29) concentration. A theoretical model based on mixtures of hard spheres droplets, is applied to X-Ray Scattering data. The result shows, the size of droplets is constant with change of droplet concentration, but it varies from 9.5 to 7.6nm with the increase of Acid Blue 29 amount from 1.0 to 2.3mM and the size polydispersity is constant for all samples.

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Keywords: Acid Blue, CTAB, Nonlinear Optics, SAXS

1. Introduction

The use of the first lasers in 1960 made possible the creation of the field of nonlinear optics (NLO) which at present plays a major role in the development of laser techniques and opens up many prospects in the study of mechanisms based on light-matter interaction [1-3]. The study of nonlinear effects, which is interesting for its applicative potential, allows a thorough characterization of new materials with strong NLO properties [4,5]. As a matter of fact, the knowledge of such phenomena produced in excited media by laser light is a key element in enhancing the performances of optoelectronic compounds. The content of this work corresponds to this research topic and aims at studying the NLO properties and structure, organic dye mixed by microemulsion(MC). The NLO properties of mixtures of dye with MC are new interesting topic. The first work was done before on nonlinear optic of mixture of Fluorescein sodium salt (FSS) with, Bis(2-ethylhexyl) sulfosuccinate sodium salt (AOT) microemulsion [6]. In that work, the concentration of droplets can affect the NLO properties of FSS.

Nonlinear optical properties of organic dye molecules such as a large nonlinearity, broadband spectral response and fast response time are important for realizing the potential for using organic dyes and their applications in optical limiting and processing fields [7].

Following our recent investigations on optical limiting behavior of acid blue 29, this paper reports the use of Z-scan technique to measure the nonlinear optical properties of acid blue 29 dye. Acid Blue 29 molecule is an acid dye that is water-soluble and anionic [8]. The structure of Acid Blue 29 is presented in Fig. 1.

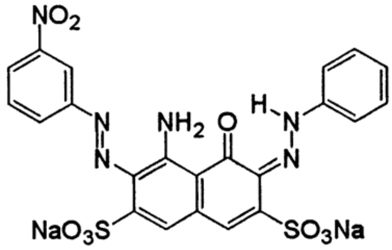

Fig. 1. The chemical structure of Acid Blue 29

Acid Blue 29 has an interesting potential for application in electronics and in photonics. The molecules have good second-order nonlinear optical (NLO) response because of noncentro-symmetric structure. They have p electron conjugation in the electronic structure that it is interesting for getting enhanced third-order NLO properties.

A cationic surfactant cetyl trimethylammonium bromide (CTAB) was used for the preparation of microemulsions. It is one of the components of the topical antiseptic cetrimide. The CTAB cation is an effective antiseptic agent against bacteria and fungi [9,10]. It is also one of the main components of the buffer for the extraction of DNA [11]. The closely related compounds CTAB are also used as topical antiseptics and may be found in many household products such as shampoos and cosmetics. CTAB, due to its relatively high cost, is typically only used in select cosmetics. In this work, the water to oil phase microemulsion is prepared by mixing of CTAB with 1-butanol in aqueous solution of dye. In this work, the interaction of Acid Blue 29 on structure and dynamic of droplets in microemulsion was studied by using dynamic light scattering (DLS) and small angle

X-ray scattering (SAXS). The Acid Blue 29 can easily solve inside of water droplets and the ion of Acid Blue 29 can interact with the ion of CTAB. This type of interaction can affect the size and the interaction of droplets.

The several researches were demonstrated that the increases the ground state dipole moment resulting the substantial increase of NLO coefficient in this system [12]. As we know that the dipole moment of dye depends on the polarity of the medium and electrostatic interaction of medium with dye. The dynamic light scattering and SAXS are techniques to understand interaction of droplets and the structure. The Acid Blue 29 in water has a negative charge, but CTAB ion has a positive charge. So, the attractive interaction between dye and surfactants can change the dipole moment and it can affect the NLO properties of the samples.

2. Experimental

Microemulsions were formulated by mixing CTAB with water and 1-butanol at fixed CTAB to water molar ratio (W=8) different concentration of Acid Blue 29. The droplet volume fraction (Φ) is the volume of droplets to total volume. The microemulsions were prepared at molar ratio (W=8) and the different volume fraction of droplets, which varies by the respective volume of 1-butanol. We observed that all samples were transparent at 20°C. The mixing of Acid Blue 29 with microemulsions is described by molar of Acid Blue 29 in microemulsion. The dynamic of the CTAB/1-butanol /water droplets are founded by dynamic light scattering. The Malvern dynamic light scattering instrument at the Medical University of Mashhad was used in this experiment. The light source is a He-Ne laser, operating at a wavelength of 632.8 nm, with vertically polarized light. Small-angle X-ray scattering (SAXS) measurements were performed using the pinhole SAXS instrument.

The Z-Scan was executed with a continuous wave (CW) laser at a 532nm wavelength with a power of 80mW as the excitation source. Solutions of three dye concentrations (1, 1.8 and 2.3mM) placed in 1 mm glass cuvette. The beam waist ωo of the Gaussian beam at the focal point is measured to be 0.5 mm. For this technique a sample thickness of 2 mm was used. The sample is moved in the direction of negative -Z to positive +Z axis (laser beam direction). The intensity of transmission was monitored by the change in the transmitted intensity through a small aperture with respect to the sample position.

3. Results and discussion

The nonlinear absorption coefficient (ß), of Acid Blue 29/CTAB/water/1-butanol was evaluated with open and closed aperture Z-scan measurements. Figure 2 displays, the open aperture Z-scan data of Acid Blue 29/CTAB/water/1-butanol at a constant molar ratio (W=8) and constant droplet volume fraction (0.04) and different dye/water concentration (Y=0.04, 0.07, 1.0mM) and Figure 3 displays, the close aperture Z-scan data of the same samples. The open aperture data are expected to be symmetric with respect to focus and there is a minimum transmittance in focus. The non-linear refractive index (NLR) is obtained from the close aperture, the peak-valley transmittance change, and using equation 1, [5,13]

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

Where s and L_{eff} are the linear transmission of the aperture and the effective length of sample and ΔT_{P-V} is peak-to-valley height of close aperture transmitted intensity and I_0 is the intensity of light. In order to calculate the NLA coefficient from the experimental observations, we have done the curve fitting (Fig.2) by numerically calculating the normalized transmittance using Equation 2, [5,13]

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

Where $q0=(ßI_0L_{eff})/(1+(z/z_0)2)$ and z_0 is the Rayleigh length [5,13]. The Z_0 is founded from $Z_0=\pi w_0^2/\lambda$. Where λ=532nm and w_0=20µM and α_0=0.2.

The results of NLR and NLA as a function of Z are presented in the Table1.

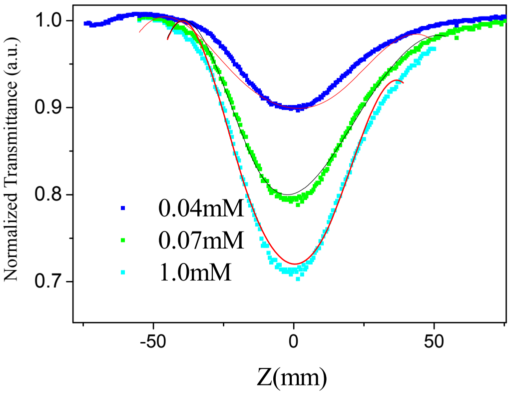

Fig. 2. Z-scan curves of Acid Blue 29 /CTAB/1-butanol/water microemulsion at W=8 for a constant droplet volume fraction (0.04) different concentration of Acid Blue 29 (0.04, 0.07, 1.0mM) for open aperture

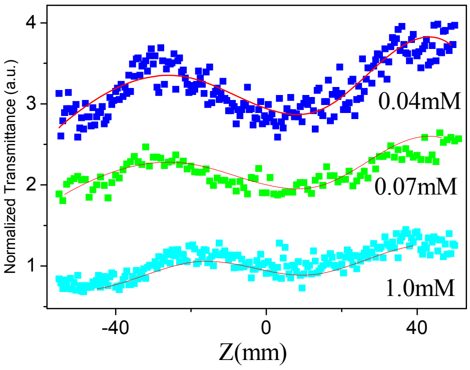

Fig. 3. Z-scan curves of Acid Blue 29 /CTAB/1-butanol/water microemulsion at W=8 for constant droplet mass fraction (0.04) different concentration of Acid Blue 29 (0.04, 0.07, 1.0mM) for open aperture

The third order nonlinear susceptibility (χR) are given (in SI units) in terms of the nonlinear refractive index, n2,

$$\chi_R^{(3)} = 2n_2 n_0^2 \varepsilon_0^2 c \tag{3}$$

where n_0 is the ordinary refractive index that it was considered the refractive index of 1-butanol, c the velocity of light. To compare one molecular species to another, it is convenient to define molecular nonlinear properties, termed molecular hyperpolarizabilities γ. The real part γ_R is given by

$$\gamma_R = \frac{\chi_R^{(3)}}{L^4 N} \tag{4}$$

where L is the Lorenz correction factor, [14]. The results of the second-order hyperpolarizabilities (γ_R) and the real susceptibilities (χ_R) are presented in table 1. The results shows, the real susceptibilities (χ_R) depend on the concentration of dye in microemulsion.

The previous studied showed that the relation between Second-Order Hyperpolarizabilities directly depend on the difference between the dipole moment of ground to excited state [15].

So, the dipole moment of dye change by increase of dye concentration in the droplet.

Table 1. The nonlinear refractive index (n_2) and nonlinear absorption coefficient (ß). The second-order hyperpolarizabilities(γ_R) and the real third order susceptibilities (χ_R) of samples

Concentration (mM)	ß (cm/W)	$n_2(10^{-7}cm^2/W)$	$\gamma_R(10^{-21}m^5V^{-2})$	$\chi_R^{(3)}(m^2V^{-2})$
0.04	0.00339	1.512	2.40248	7.10229
0.07	0.00674	6.145	9.76407	28.8648
1.0	0.00941	8.306	13.1978	39.01563

The nonlinear absorption in the dyes is due to reverse saturable absorption or two-photon absorption. For organic sample two photon absorption or reverse saturable absorption is the dominant mechanism leading to increase in absorption with intensity. The previous studied showed that the nonlinear behavior of the measured output power as a function of the input power is related to the nonlinear absorption, which is in turn originated from the RSA mechanism in the acid blue 29 [16].

In general, a four energy-level model was used for described the nonlinear absorption processes of organic dye [17], whereas the change of the nonlinear refractive index of the sample at high powers (80 mW) can induce self-diffraction pattern [18].

A studied show that higher concentration of Acid blue 29 at ethanol have better nonlinear optical properties. Also, it was found that the nonlinear parameters increase linearity with increase of dye concentration [19].

In DLS experiments, the normalized field correlation function $g^{(1)}(q,t)$ is obtained by measures the intensity correlation function from. The modulus of the wavevector $q=4\pi(n/\lambda_0)\sin(\theta/2)$, where the, θ is the angle of detection, n is the refractive index of the solvent and λ_0 is the laser wavelength. From the effective structure factor, we can find the normalized field correlation, eq.5, [9,10].

$$g^{(1)}(q,t) = \frac{S_M(q,t)}{S_M(q)} \tag{5}$$

Where $S_M(q)=S_M(q,t)$ is the measured static structure factor. Rather, the intensity scattered at a certain time and angle from colloidal particles is [16,17],

$$I(q,t) = n\overline{f}^2(q)\, S_M(q,t) \tag{6}$$

Where n is the total number density of particles and The $f_2(q)$ is form factor of the system is obtained from a static scattering measurement at high dilution where $SM(q)\approx 1$.

$$\overline{f}^2(q) = \sum_{\alpha=1}^{m} x_\alpha f_\alpha^2(q) \tag{7}$$

For monodisperse systems, the short-time diffusion coefficient define as

$$D_M(\mathrm{q}) = \frac{-1}{q^2}\lim_{t\to 0}\frac{\partial}{\partial t}\ln S_M(\mathrm{q},\mathrm{t}) \tag{8}$$

And so, we can write

$$D_M(\mathrm{q}) = \frac{1}{S_M(\mathrm{q})\,\bar{\mathrm{f}}^2(\mathrm{q})}\sum x_a\,\mathrm{f}_a^{\,2}(\mathrm{q})\,\mathrm{D}_\alpha^0 \tag{9}$$

Where $D_{R0} = k_BT/6\pi\mu_R$ is the Stokes-Einstein diffusion coefficient of a sphere with a radius of R with a viscosity of μ. In the dilute limit, diffusion coefficient is

$$D_M(\mathrm{q}) \approx k_BT/6\pi\mu a_H \tag{10}$$

Where a_H is the hydrodynamic or z-average radius, [20,21]. The dynamic behavior of the CTAB/1-butanol/water ME was probed with photon correlation spectroscopy. A single stretch exponential decay was observed in the correlation function for all samples, Fig.4. In the figure 4, the collective diffusion coefficient as the function of the droplet volume fraction is presented form mixture of CTAB/1-butanol/water MC with 1mM (square points) and 1.8mM (down triangle) of dye. The collective diffusion coefficient as function of droplets volume fraction has a negative slope. In addition, the D_c of microemulsion/dye samples with higher of dye concentrations have considerably bigger value. In general, D_c depends on the shape and interactions of droplets. Several authors indicate that the negative slope of D_c as function of volume fraction is due to the attractive interaction of droplets [22,23]. In the Fig. 5, the collective diffusion coefficient as function of molar of Acid Blue 29 at CTAB/1-butanol/water MC with W=8 with 1mM with two droplet volume fractions, 0.01 (up triangles) and 0.04(cubic points) at 293 K.

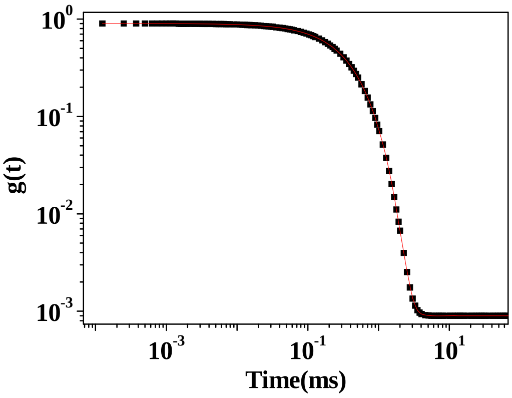

Fig. 4. The correlation function of CTAB/1-butanol/water ME with W=8 and volume fraction 0.05 and 1mM of Acid Blue 29 at 293 K

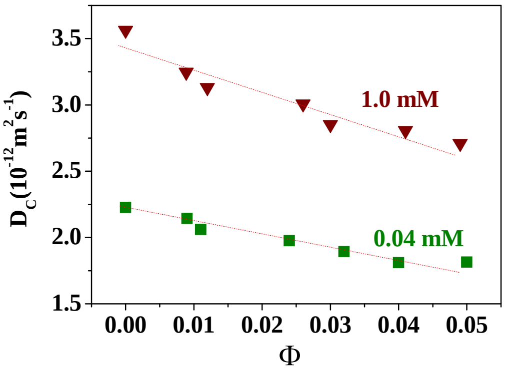

Fig. 5. The collective diffusion coefficient as function of droplet volume fraction of CTAB/1-butanol/water microemulsion with W=8 with 0.04mM (square points) and 1.0 mM (down triangle) of Acid Blue 29 at 293 K

In this work, the shape of droplets is spherical in all concentrations of droplets. So, the morphology of droplets cannot change the interaction of them.The SAXS experiment is used for understanding of the interaction of dye by structure of droplets. In the figure 6, the SAXS experiment of CTAB/1-butanol/water MC at W=8 with different concentration of Acid Blue 29 (0.01, 0.05, 0.1, 0.5 and 1.0mM), fig.6(a), and different droplet volume fraction (0.01, 0.05, 0.09), fig.6(b), at constant Acid Blue 29 concentrations (1mM).

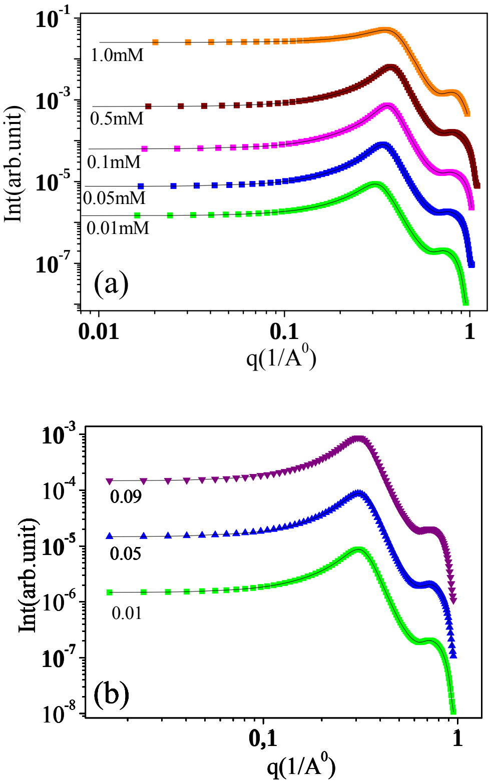

Fig. 6. The SAXS experiment of CTAB/1-butanol/water microemulsion with W=8 at 293 K with (a) different concentration of MC, (b) three droplet volume fraction (0.01, 0.05, 0.09) at constant Acid Blue 29 concentration (1mM)

The SAXS experiments are fitted with spherical model, that it can describe with a form factor P(q), and a structure factor S(q), [23]:

$$I(q) = cP(q)S(q) \tag{11}$$

c, is the number density of scattering particles.

$$P(q) = \frac{1}{V}\{\iiint dV\rho(r)e^{-iq.r}\}\{\iiint dV\rho(r)e^{-iq.r}\}^{*} \tag{12}$$

ρ(r) is the scattering length density and the integration is done over the volume V of the scattered. The structure factor, S(q), is the Fourier transform of the pair correlation function g(r), [26].

$$S(q) = 1 + 4\pi n\int_{0}^{\infty}(g(r)-1).r^{2}\frac{\sin(qr)}{qr}dr$$

$$S(q) = 1 + 4\pi n\int_{0}^{\infty}(g(r)-1).r^{2}\frac{\sin(qr)}{qr}dr \tag{13}$$

It is closely related to the total correlation function h(r)=g(r)−1 and it can by means of the Ornstein–Zernike equation. In the figure 7, the lines are fitted data's with sphere model and the results of analyzing of SAXS data's of CTAB/1-butanol/water microemulsion with W=8 and different dye concentrations (0.01, 0.05, 0.1, 0.5 and 1.0mM) are presented in the Table 2. The results of analysis of SAXS experiments at CTAB/1-butanol/water at W=8 with constant dye concentration (1mM) and different droplet concentration (0.01, 0.05, 0.09) with hard sphere model are presented in the Table 3.

Table 2. Parameters used in the hard sphere core shell model of CTAB/1-butanol/water microemulsion at W=8, the PDI is polydispersity.

Dye concentration (mM)	mean core+shell radius (nm)	mean core radius(nm)	PDI
0.01	9.5	8.0	0.2
0.05	9.1	7.5	0.2
0.1	8.7	7.2	0.2
0.5	8.3	7.0	0.2
1.0	7.6	7.1	0.2

Table 3. The results of analyzing SAXS data's of CTAB/1-butanol/water at W=8 with constant dye concentration (1mM) and different droplet concentration (0.01, 0.05, 0.09) with hard sphere model.

ϕ	mean core+shell radius (nm)	mean core radius (nm)	PDI
0.01	9.5	8.0	0.2
0.05	9.5	8.0	0.2
0.09	9.5	8.0	0.2

The results show that the core radius is changing from 9.5Å to 7.6Å and polydispersity is constant (0.2) with increase of dye concentrations from 0.01 to 1.0mM. The reducing of size can describe increase of the collective diffusion by the increase of dye concentration. The interaction of dye by surfactant increase by decrease of size and increase of dye concentration. Also, the size of droplets is constant at constant dye concentration (1mM) and different droplet concentration (0.01, 0.05 and 0.09). To understand the interaction between droplets, the Generalized Indirect Fourier Transformation (GIFT) software is used to determine the structure factor of the SAXS and the results are presented in the Fig. 7. The structure factor has a broad peak at q=0.4(1/Å) for the microemulsion that the peak slightly moved to lower value with the increase of concentration of Acid Blue 29. Moreover, the structure factor at low q increases with amount of Acid Blue 29. Increase of structure factor at low q, the attractive interaction increase by increase of dye concentration.

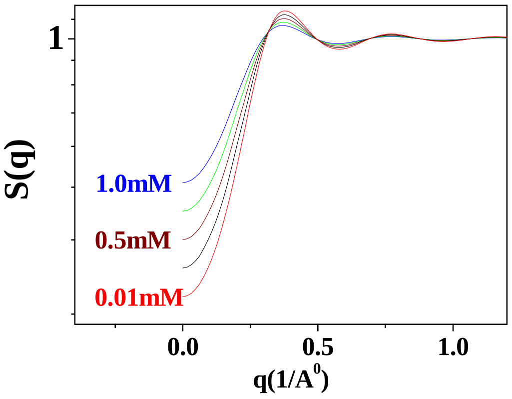

Fig. 7. The structure factor of CTAB/1-butanol/water microemulsion with W=8 with (a) different concentrations of Acid Blue 29 (0.01, 0.5, 1.0mM)

4. Conclusion

The two photon absorption, nonlinear refractive index, second-order hyperpolarizabilities and the real third order susceptibilities, were calculated from theory. The results show, the third order susceptibilities increase by dye concentration and it can increase NLO properties of the medium. The NLA study shows that the dipole moment of the ground state of the dye has been changed by dye concentration. Dilute dispersions of CTAB/1-butanol/water nano-droplets have been investigated by dynamic light scattering. Collective diffusion coefficients as functions of nano-droplets concentrations exhibit a linear and negative concentration dependence. X-ray scattering measurements conducted at small angles, explains why the collective diffusion coefficient has a negative slope in the dilute limit. Decreasing the size of droplets can influence Dc of droplets at CTAB/1-butanol/water. Moreover, the concentrations of droplets cannot affect the size of droplets. So, the negative slope of diffusion of droplets can show interaction between droplets. This type of interaction can affect the dipole moment of dye in solution and for this reason the NLO properties are changing.

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