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Experimental and Theoretical Optical Properties of β -Carotene in Oleic Acid Solution

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In this work we present experimental and theoretical modeling of absorbance and photoluminescence for beta-carotene in oleic acid solution. The results show that it is possible to identify the signature of β -carotene in oleic acid liquid for small concentrations. However, for high concentrations the prominent characteristics of β -carotene band presents a deformation due the molecule–molecule interaction. The photoluminescence of oleic acid, centered at 540 nm, presents a red shifted when increases the β -carotene concentration. The experimental results were very well described by sequential Monte Carlo/quantum mechanics methodology.

Keywords: Beta-Carotene, Molecular Dynamics, Oleic Acid.

1. INTRODUCTION

The oleic acid (OA) is one of the most important fatty acid because it is one of the major components present in any vegetable oil.¹ The large interest in the properties of the oleic acid molecule is in part due to the need of understanding the applications of this class of material in industries such as cosmetic, foods, pharmaceutical, etc.² The understanding of the process of how an absorbed photon can be converted to chemical energy requires that the nature of the isomerization can be described in molecular details.³

The oleic acid is also important, because it is present in all animal specimens being its principal source of energy. The β -carotene (BC) is a substance presented in several fruits and greens and it is a natural antioxidant capable of producing good influence over human health.⁴ There are many scientific works about OA and BC system.⁵

In Figure 1 we show the structures of oleic acid on its *trans* and *cis* conformations and the β -carotene molecules. We have previously investigated similar chemical structures of other group of carotenoids derivatives. In the present work we present an experimental and theoretical investigation of these molecules.

We analyze how the solvation affects the transition energy of BC + OA and compute the experimental and

theoretical absorption and emission spectra of these derivatives. In the next section the adopted methodology will be discussed.

2. METHODOLOGY

2.1. Sample Preparation

We have prepared a standard solution diluting 10.000 IU of β -carotene from Merck in 50 mL of oleic acid from Sigma-Aldrich both with 99.9 percent of purity, at room temperature. A set of samples with various β -carotene concentration was prepared by dilution of the standard solution.

2.2. Absorbance and Luminescence

The absorbance spectra were obtained by the experimental setup shown in the Figure 1(a) constituted by a monochromator model 308i manufactured by ACTON Inc., controlled by a microcomputer through a NCL interface. We use also a silicon photodetector and a 75 W Xenon light according to the schema in Figure 2(a). For the emission spectra we illuminate the sample with an ultraviolet light at 350 nm filtered from the Xenon light as showed in Figure 2(b). For both cases (absorbance and luminescence) we have used a silicon photodetector to collect the light and to generate a signal.

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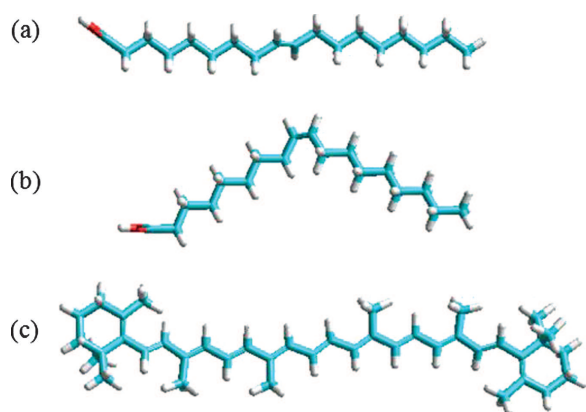


Fig. 1. (a) The structures of trans oleic acid, (b) cis oleic acid and (c) all-trans- β -carotene.

3. THEORETICAL MODELING

3.1. Liquid Simulations

In this work, to build the liquid structure simulations were executed on beta-carotene structure surrounded by 200 oleic acid molecules. This procedure was performed

at NVT ensemble (298.15 K and normal pressure conditions). The cited monte carlo (MC) treatments were administrated by DICE⁶ program for liquid simulation. The cubic box size ($L = 25 \text{ \AA}$) was regulated by the experimental water density 0.9966 g/cm^3 . The Restricted Hartree-Fock (RHF) procedure and the Pople complete basis set with one polarization function were applied to obtain the molecular geometries of minimal energies used in our simulations.⁶ As a real liquid structure is composed by a huge quantity of molecules, periodic boundary conditions implemented by the image methods were used to build the aqueous environment. Under these conditions, if one particle escapes of the box side its image enters by the other extremity, then the quantity of molecules is kept constant and the computational expense is reduced. The molecular interactions were described by Lennard-Jones plus Coulomb potential. To water molecules these parameters were obtained by single point charge (SPC) potential developed by Gunsteren and co-workers.⁷ To beta-carotene molecule we describe de intermolecular interaction by OPLS developed by Jorgensen et al.⁸ In respect to beta-carotene charges were adjusted from RHF using the well known CHelpG methodology.⁹

To perform DFT calculations was used the hybrid functional B3LYP.¹⁰ The molecular interactions were truncated to a specific cutoff radius $r_c = 12.50 \text{ \AA}$ and defined as half box size. For regions beyond this point was used the long range correction of potential energy. For the Coulomb potential, this correction was evaluated using the reaction field methodology considering dipole interactions (dielectric constant of water $\epsilon = 78.5$) and to the Lennard-Jones potential we use the pair radial distribution function.

In this work, the MC simulations can be summarized in two different thermalization and average stages. On thermalization, first a randomly MC configuration is generated.⁶ Then MC steps were performed to obtain only structures that decrease the energy of the system to finish the thermalization stage, it is initiated an average stage where several equilibrium configurations are generated. In MC simulations, new molecular positions are modified translating the molecule by $\delta \mathbf{r}$ and rotating in $\delta \theta = 15^\circ$ a chosen axis randomly [6, 11, 12 and references therein].

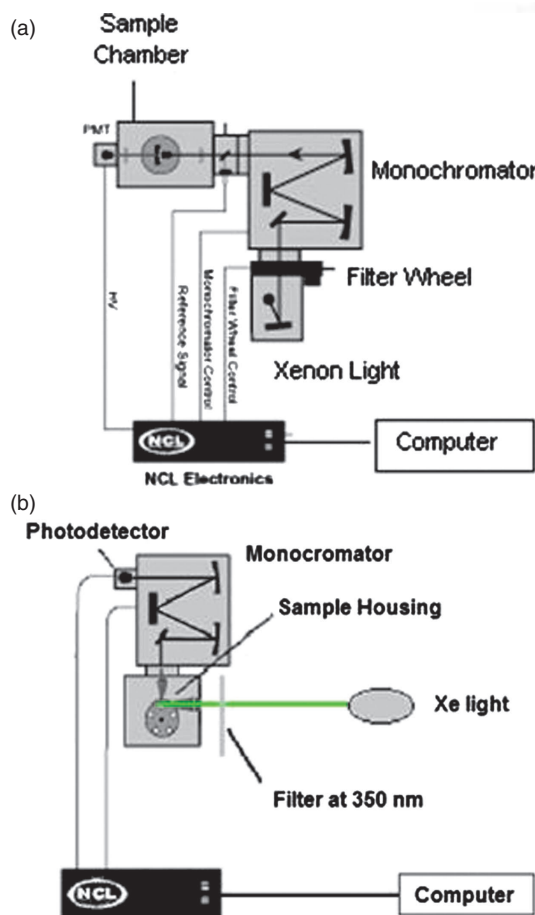


Fig. 2. (a) Absorbance spectra experimental setup and (b) emission spectra arrangement for all investigated solutions.

3.2. Quantum Mechanics Calculations

Proceeding the liquid structure simulations we would like to obtain the electronic properties, as the absorption spectra. This in way was applied on MC configurations the well known INDO/CIS-S (Intermediate Neglect of Differential Orbital/Configuration Interaction Spectroscopic - Single excitations) procedure performed by the ZINDO¹³ program. The ZINDO methodology was especially formulated to treat electronic transitions reasonable for to computational effort.

Considering that MC configurations produce different eigenvalues, the physical properties of the system must be

measure by statistical procedures. This way, the quantum observables were obtained although an average, in another way, the Metropolis sampling technique includes the Boltzmann distribution, implying that all structures were generated with appropriate Boltzmann factor.

4. RESULTS AND DISCUSSION

Figure 3 shows the absorbance visible spectra for several concentration of β -carotene (BC) diluted in oleic acid. The spectra characteristic appears as high as the concentration of β -carotene function, so we can guarantee the incorporation in the solution of OA + BC. The curve A is absorbance to the pure OA, i.e. without β -carotene showing that the OA is a practically transparency medium to 1 cm thick sample. In the B, C, D, E and F curve are, respectively, the absorbance for 9.35, 18.75, 37.5, 75.0 and 150 $\mu\text{g}/\text{cm}^3$ of β -carotene in OA. It is interesting to observe that for concentration represented by E and F curves, begins appear deformations in the characteristic beta-carotene band reflecting probably the interaction amongst β -carotene molecules. In the curves B, C and D the deformation in the band none appear because of the distance between each two β -carotene molecules is large enough due to low concentration.

Theoretically the average $\pi \rightarrow \pi^*$ transition energies of the BC in OA were computed using only 70 configurations. It is important to mention that these configurations were properly selected by means of the autocorrelation function of the energy and due to this fact they are considered nearly uncorrelated. The quantum mechanical technique used in these 70 statistically relevant configurations

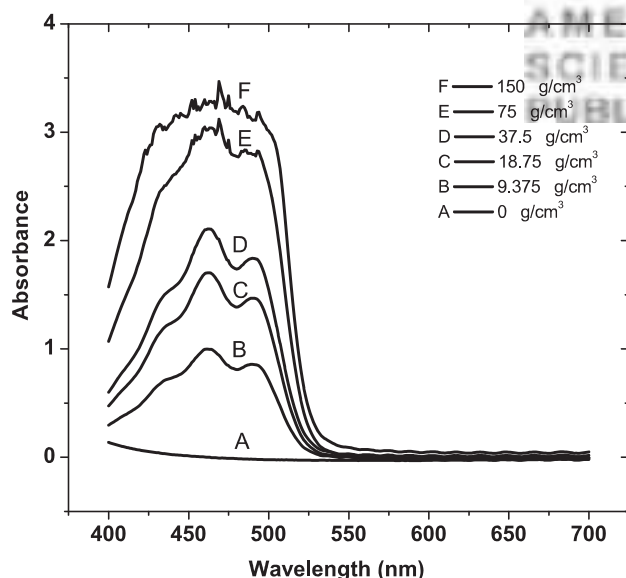


Fig. 3. Experimental absorbance spectra obtained for several concentrations of beta-carotene in oleic acid. (A) pure oleic acid, (B) 9.35 $\mu\text{g}/\text{cm}^3$, (C) 18.75 $\mu\text{g}/\text{cm}^3$, (D) 37.5 $\mu\text{g}/\text{cm}^3$, (E) 75.0 $\mu\text{g}/\text{cm}^3$ and (F) 150 $\mu\text{g}/\text{cm}^3$.

was the well known Intermediate Neglect of Differential Overlap/Spectroscopy-Configuration Interaction technique.

To compute the average values of the $\pi \rightarrow \pi^*$ transition energies of BC in OA it is necessary to obtain the liquid structure of OA around the BC. This is indeed obtained by means of the radial distribution function between the center of mass of the solute and solvent molecules under investigation. We took into account only the first solvation shell structure.

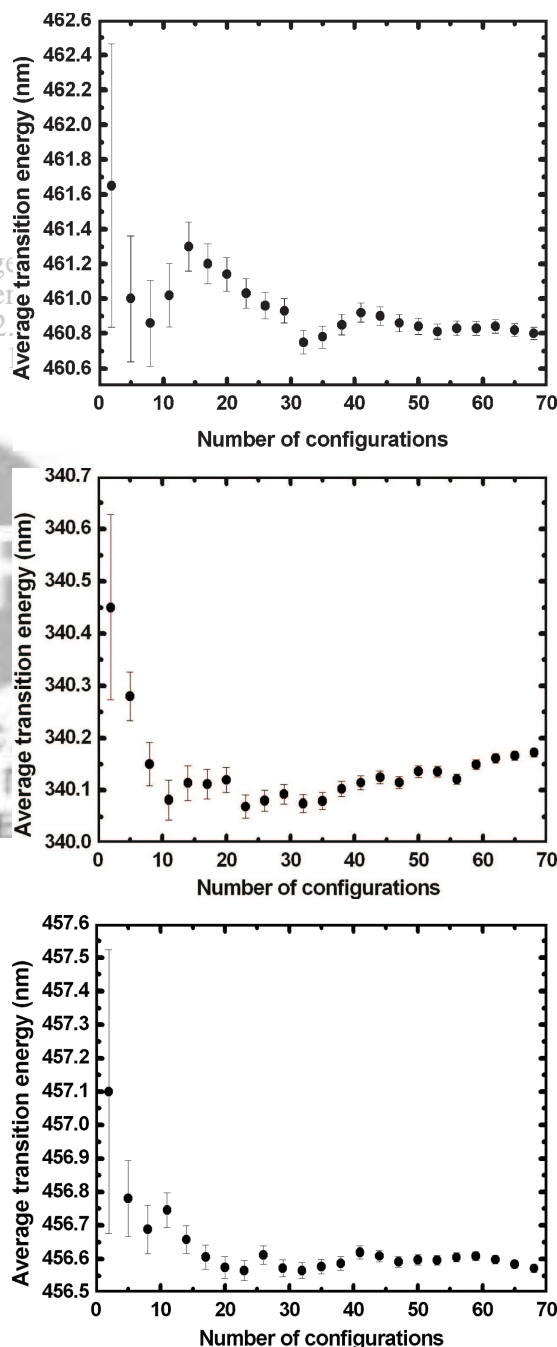


Fig. 4. Convergence of calculated absorption for the $\pi \rightarrow \pi^*$ transition energies of the BC in oleic acid.

Therefore, the first solvation shell initiates at 12.2 Å and finishes at 13.6 Å. A coordination number of one OA molecule is computed by the spherical integration in the previously mentioned interval. As discussed before, 70 statistically relevant configurations were sampled and each computed value for the $\pi \rightarrow \pi^*$ transition energy was averaged out.

Thus, using the liquid structure of the first solvation shell we computed three average values of the $\pi \rightarrow \pi^*$ transition energies. For the first band of the electronic absorption spectrum of the BC in OA an average value of 460.82 nm was computed. For the second and third bands, average values of 340.17 and 456.64 were obtained respectively. These average values computed for the first up to the third bands of the BC in OA match very well with the experimental results of 463, 350 and 500 nm, respectively (Fig. 4).

Figure 5 shows how the 490 nm band increases as β -carotene concentration function. The results presented show that the dependence on BC concentration increases with respect to the absorption of respective band. Also it was not observed shifts in this band with β -carotene concentration. We also observed how luminescent band, centered at 430 nm, in pure oleic acid is affected when β -carotene is gradually placed in the solution. The luminescent band is red shifted with β -carotene inclusion.

The Figure 6 show luminescence curves for several concentration of β -carotene in OA. By the Gaussian fit in each curve of the Figure 6 we can monitor the intensity and position of the absorption band. These results allow us to affirm that the pure oleic acid shows a photoluminescence spectra, centered in at 540 nm (green color), which is displaced to the region of the red in electromagnetic spectrum when we increase the concentration of BC in the solution. This luminescence takes place after the absorption and the non-radioactive internal conversion. Another effect caused for the presence of the BC in the solution is the reduction of intensity of the photoluminescence spectra effect.

In Figure 7 we establish a relation between the respective wavelength of each peak of luminescence in function of the concentrations OA + BC. With these results we find

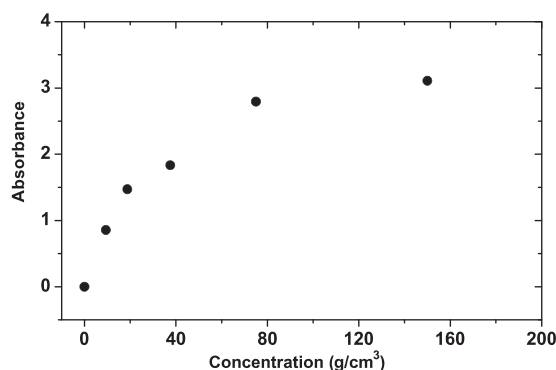


Fig. 5. Absorption concentration intensity of beta-carotene at 490 nm.

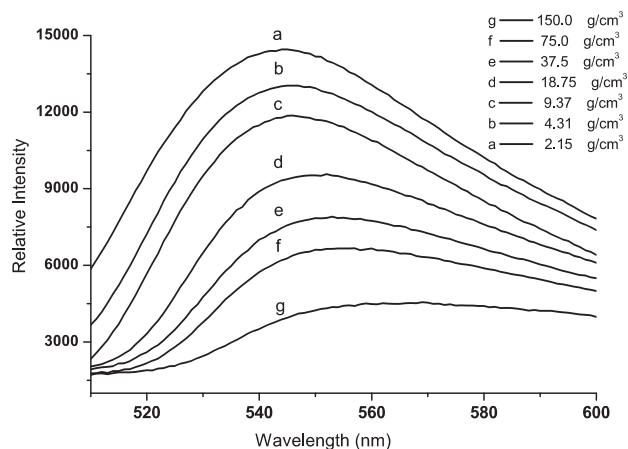


Fig. 6. Set of emission spectra for different concentrations of the β -carotene solution diluted in oleic acid.

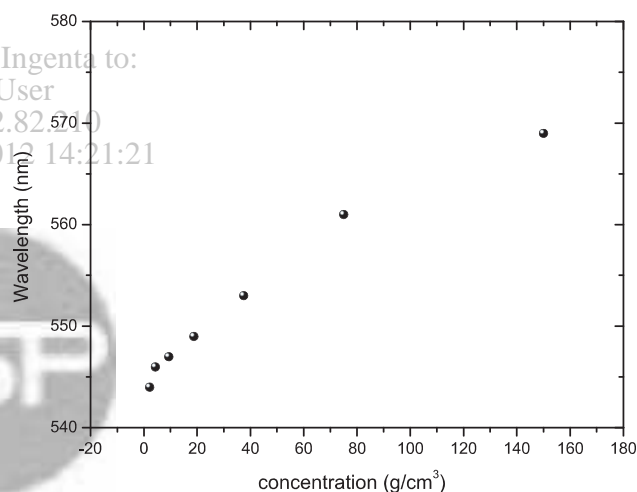


Fig. 7. Wavelength of the peak of the luminescence band in function of the concentration OA + BC.

to be possible, to identify the concentration of one determinate sample, knowing the respective wavelength of the most intense peak, for data spectra of luminescence of the solution.

Also, for high concentration deformation of the band appears because the BC are close each other provoking distortion in the electronic levels. Also, the background between the UV bands and the usual bands of BC suffers an increase of absorbance. This process is reversible by increasing the quantity of OA into the all system.

5. CONCLUSIONS

Design of vegetable oils is important to understand their physical and electronic properties and the oleic acid and β -carotene molecules belong to this category. In this paper we have investigated how the absorbance and luminescence properties change as the concentration function does and utilizing a sequential Monte Carlo/quantum mechanics

methodology to simulate the interaction of BC and OA. The molecules studied gives us some insight about the behavior of the solute-solvent interaction in biological molecules and help us to understand the influence of the beta-carotene over the optical properties of OA. The results presented show us the possibility of improving the optical properties of chemical modifications that combine: (a) increasing in the insaturation and (b) modifications of the acceptor/donor properties of the substituents.

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