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Study the Absorption and Fluorescence Spectra of Some Organic Dyes

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Abstract: In this study, the absorption and fluorescence spectra of (Azure-A and B) dyes dissolved in ethanol and different concentrations were studied. The optical properties (absorbance, transmittance, linear absorption and linear reflective index) were calculated as well as the calculation the lifetime and quantum efficiency of fluorescence. The results shows the increasing of absorption values and decreasing of transmittance values when the concentration increase, this is accordance with Lambert's law. Also, the results shows increasing the values of the lifetime of fluorescence and decreasing the quantum efficiency.

Key words: Azure-A dye, Azure-B dye, absorption, fluorescence, laser dyes, reflective index

INTRODUCTION

The organic dyes are an unsaturated hydrocarbon compound with a rather complex structure because it contains a series of carbon atoms that are bonded to a single and double bond, called the chromophore system (Demtroder, 1981; Lumb, 1978). The chromophore is differentiated by absorption ($S_0 \rightarrow S_1$) occurs in the visible region (Sahar and Treves, 1977). Chromophores are the group that is responsible for giving the particle a chromatic character, so that, the dye molecule pigments that absorb wavelength (400-700 nm) (visible light) in a certain color.

Each organic dyes has a special absorbance and fluorescence spectra which is triggered by the use of flashlights or by using a solid state laser such as a double-frequency sapphire laser or a gas laser such as an argon ion laser or a nitrogen laser (Lumb, 1978).

The theoretical part

Linear optical properties: The interaction between the nature and distribution of charges within the material (electronic, molecular, ionic) and electromagnetic radiation falling on the material results in the appearance of the optical properties of the material (Klinowski, 2005). A number of processes can occur when an electromagnetic beam falls on the material and their interaction together as part of the light radiation turns to heat by absorbing it by the material. The other part is called the transmitted radiation as the input passes through the material without losing energy. While the remaining portion of the light radiation is reflected from the surface of the material (reflected) (Al-Sherbini *et al.*, 1982). For information about the internal structure of the material and the nature of its bonds, the permeability, absorbance and reflectivity of the electromagnetic radiation falling on the material should be known. For example, energy beams and the quality of transitions within the material are recognized by ultraviolet spectroscopy. For the field of practical applications in which materials are used, visible should be studied (Klinowski, 2005; Fowles, 1975).

Absorbance (A): The amount of sports that binds the density of the particles (concentration) in the sample and the thickness of the sample (optical path length) is the Absorbance (A) or the optical density:

$$A = \log\left(I_0/I\right) \tag{1}$$

Where:

I = The Intensity of light at the wavelength of λ that passes through the sample (the intensity of light is in force)
I_0 = The Intensity of light before entering the sample or the intensity of the light falling

The absorption of the material in the falling rays causes an electron activity that may lead to the disintegration of its molecules, if the absorbed energy value is greater than the value of the dissociation of a bond or its transition to a higher energy level. The absorption potential increases by increasing the concentration of matter at the low energy level and increasing the number of fallen photons. The probability

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Corresponding Author: Afrah M. AL-Hussainey, Department of Physics, College of Science, University of Babylon, Babylon, Iraq, afrahalsherefy@yahoo.com of photon absorption is directly proportional to the concentration of the absorbed molecules in the sample and the thickness of the model (the length of the optical path), according to the law of Per-Lambert which is an experimental relationship that binds the absorption of light to the properties of the material through which the light passes. The law states that the number of absorbent particles in the material is directly proportional to the absorbed radiation fraction passing through. If the radiation passes through a solution, the amount of absorbed or activated light is an exponential function of the solute concentration. As in Eq. 2 (Fowles, 1975):

$$I = I_0 e^{-\alpha_{op} C_m L} \tag{2}$$

α_{op} = The optical absorption coefficient
L = Optical path Length
C_m = Molars Concentration

Equation 3 can be written as follows:

$$\ln I_0/I = \alpha_{op} C_m L = A \tag{3}$$

The Lambert-Beer Law can be applied in different spectral areas such as UV rays, visible radiation, etc., provided that the radiation used is monochromatic light (Li *et al*., 2008).

Transmittance (T): Transmittance is defined as "the percentage of light Intensity (I) to the intensity of the falling light (I_0)" or the energy of the radiation from the medium to the energy of the radiation falling on it" (Parikh, 1974; Demtroder, 2010):

$$T = (I/I_0) \tag{4}$$

According to the Per-Lambert, van transmittance decreases as the molar concentration increases and the length of the optical path L passes through the light (Straughan and Walker, 1976). The permeability of the medium is related to the absorbance of the solution with the following relationship:

$$A = -\log(1/T) = -\log(I/I_0) = \log(I_0/I) \tag{5}$$

From this relationship, we observe that the permeability increases as the absorption of the medium decreases.

Florescence and quantum efficiency: It is a radiative process resulting from the transition of molecules between two electronic states having the same multiplicity with short lifetime are typically (8-10 sec) which a spin-allowed process. The fluorescence transition is occurring from first excited singlet state to the ground state $S_1 \rightarrow S_0$ is the inverse of the $S_0 \rightarrow S_1$ absorption transition.

The lifetime of the excited electronic singlet State S_1 is sufficiently long for the excited molecules to attain thermal equilibrium, the fluorescence emission occurs primarily from the zero-point vibrational level of S_1. This condition is generally, valid if the molecules are in a condensed medium, e.g., in solution but it may not be true in rarefied vapour in which the molecules cannot lose their excess vibrational energy in collision (Lakowicz and Balter, 1982).

The molecular fluorescence quantum efficiency (q_{fm}) is defined as the ratio of the number of fluorescence photons emitted by a system of molecules in dilute solution to the number of molecules excited into S_1(the number of absorbed photons). The molecular fluorescence spectrum $f(\bar{\upsilon})$ is then defined as the relative fluorescence quantum intensity of frequency $(\bar{\upsilon})$, normalized by relation:

$$q_{fm} = \frac{\text{Number of photon emitted}}{\text{Number of photon absorbed}} \tag{6}$$

$$q_{fm} = \frac{K_{fm}\left[M^*\right]}{I_a} \tag{7}$$

Where:
K_{fm} = The rate of fluorescence emission
M^* = The Molar concentration of excited molecules
I_a = The Intensity of light absorbed

Can be calculation the quantum efficiency from total area under the fluorescence curve by used the relation:

$$q_{fm} = \int_0^\infty f(\bar{\upsilon})\,d\bar{\upsilon} \tag{8}$$

$f(\bar{\upsilon})$ the intensity of fluorescence spectrum. Quantum efficiency of most important parameter of dye molecular and its values between (0-1) dependence on nature, concentration, viscosity, temperature and natural of molecular structure of solvent (Birks, 1970; Singh *et al*., 2003). Quantum efficiency in higher concentration for solvent is called (Quantum yield) Φ_{fm} (Parikh, 1974; Demtroder, 2010). We can calculate quantum efficiency by used the relation (Hana, 2010):

$$q_{fm} = \frac{\tau_f}{\tau_{fm}} \tag{9}$$

Where:
τ_{fm} = The radiative life time
τ_f = The fluorescence life time

MATERIALS AND METHODS

Practical part

Devices used: The absorption was recorded using a two-band spectrometer (UV-Visible-spectrophotometer), this spectrometer covers a wide area of the electromagnetic spectrum from the ultraviolet to the nearby infrared region. The device contains two sources of irritation: the deuterium lamp covers the area within the wavelengths 360-190 nm and the tungsten lamp and covers spectral distribution within the wavelength zone 360-1100 nm. The F96PRO fluorescent spectrometer was also, used to measure fluorine spectra for fluorine dye solution. It consists of a 150 W xenon arc lamp, an emission and irritability spectrum 200-700 nm, a scanning ratio (200, 400, 600 nm/min) and a high sensitivity-Photomultiplier Tube (PMT) detector.

Materials used

Azure A: Organic dye Azure A is a class of thiazine compounds and a container of nitrogen and sulfur atoms within the middle ring. Its structural formula ($C_{14}H_{14}N_3SCl$), its molecular weight (291.8 g/moL). Dissolve in water and low in ethyl alcohol, it has a peak absorption at a range of wavelengths (620-634 nm), so, its color is blue. The molecular structure of Azure-A dye is shown in Fig. 1.

Azure B: Azure B is also a class of thiazine and a container of nitrogen and sulfur atoms within the middle ring. Its structural formula ($C_{15}H_{16}N_3SCl$), its molecular weight (305.8 g/moL) dissolves in water and is low in ethyl alcohol. Its peak absorption lies at a range of wavelengths (648-655 nm) for this to be a blue color. The molecular structure of Azure-B dye is shown in Fig. 2.

Ethanol: Ethanol is an organic chemical solvent and its partial formula (C_2H_5OH). It is a polar compound that has the properties of hydrogen bonding between its molecules as it contains the hydroxyl group which increases bonding. Volatile colorless liquid and its molecular weight (46.07 g/mol) and density (0.789 g/cm^3).

Preparation of solutions: To prepare a dye solution (Azure-A) at a concentration of (1×10^{-3} mL), dissolve (0.0029 g) of the dye powder in the size of (10 cm^3) of the ethanol solvent used in the research, according to the relationship:

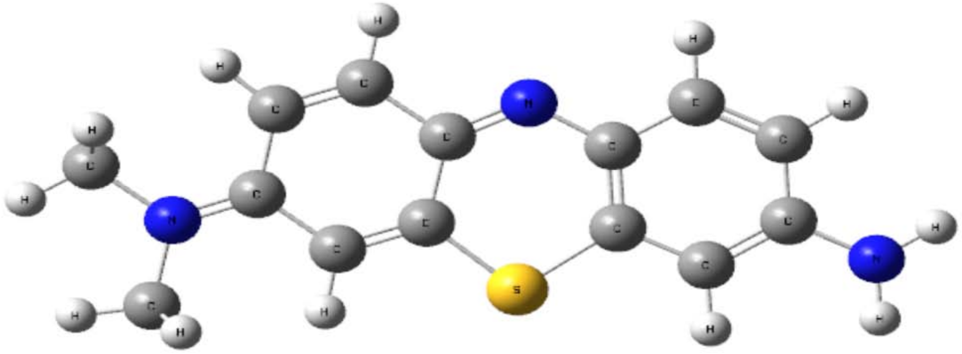

Fig. 1: Molecular structure of (Azure-A) dye

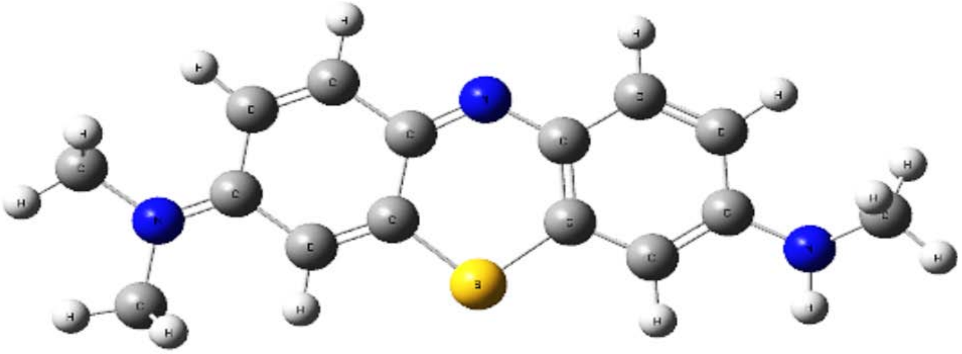

Fig. 2: Molecular structure of (Azure-B) dye

$$W_m = \frac{C \times V \times M.W}{1000} \quad (10)$$

Where:

W_m = The Weight of the dye needed to get the desired concentration (g)
C = Concentration to be prepared (mL)
V = The size of the solvent cm^3 to be added to the material
M.W = Molecular Weight of dye used (g/mol)

To prepare a dye solution (Azure-B) at a concentration of (1×10^{-3} mL), melt (0.0030 g) of the dye powder in the size of (10 cm^3) of ethanol solvent using Eq. 11.

To prepare lighter concentrations (1×10^{-4} mL) (1×10^{-5} mL) from the concentration prepared, the following relationship called the dilution relationship is used:

$$C_1V_1 = C_2V_2 \quad (11)$$

Where:

C_1 = First Concentration (higher)
C_2 = The second focus (lightest)
V_1 = The required Volume of the first concentration
V_2 = The size needed to be added to the first concentration for the second concentration

RESULTS AND DISCUSSION

The absorption spectra of the (Azure-A) solution dissolved in an ethanol solvent with different concentrations of (1×10^{-3}, 1×10^{-4} and 1×10^{-5} mL) were studied using UV-Visible spectrophotometer shown in Fig. 3 and Table 1.

Fluorescence spectra were measured for the samples prepared for the Azure-A solution dissolved in ethanol with different concentrations using fluorescence spectrophotometer. The results of the measurements were as shown in Fig. 4 and Table 2.

The calculations show that the absorption peak does not match with the top of the fluorescence, meaning that the fluorescence energy is less than the absorption capacity because of the non-radiation processes, since, the excited particles lose part of their energy in heat, so, the energy of the photon emitted is less than the absorbed photon energy. For the absorption of the adsorption indicates that the Stokes shift and is shown in Fig. 5 and Table 3. Fluorescence lifetimes (τ_f) and Quantum yield fluorescence (Q_f) were calculated using the results of fluorescence spectra and the results were

Table 1: Absorption at the maximum wavelengths of dye (Azure-A) dissolved in ethanol with different concentrations

Intensity	λ_{max} (nm)	C (m)
0.136	612	3×10^{-6}
0.234	611	5×10^{-6}
0.296	611	7×10^{-6}

Table 2: Values of the fluorescence intensity at the maximum wavelengths of the dissolved dye (Azure-A) dissolved in ethanol with different concentrations

Relative intensity	λ_{max} (nm)	C (m)
0.13585	644	3×10^{-6}
0.17884	646	5×10^{-6}
0.19581	648	7×10^{-6}

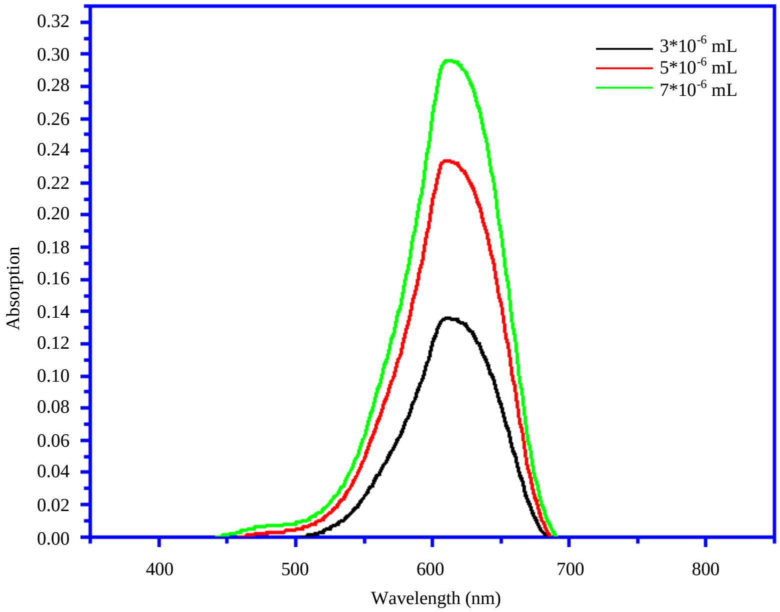

Fig. 3: Absorption spectrum curves for a dye solution (Azure-A) dissolved in ethanol with different concentrations

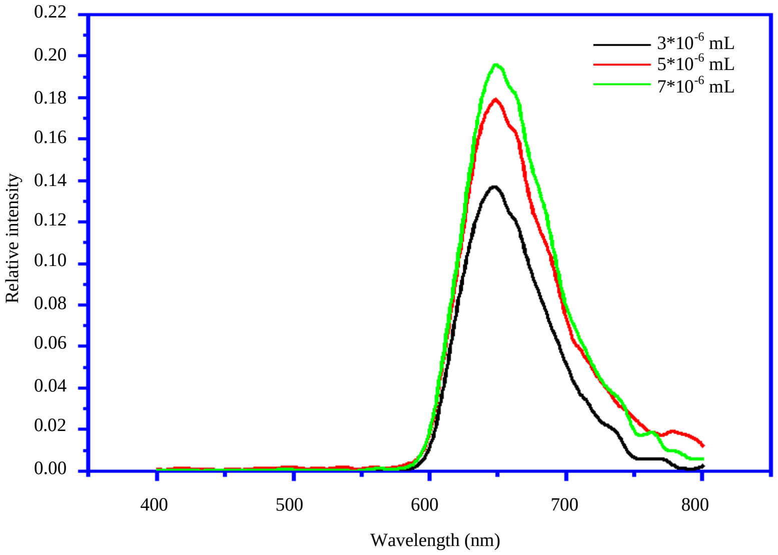

Fig. 4: Fluorescence spectrum curves for dye solution (Azure-A) dissolved in ethanol with different concentrations

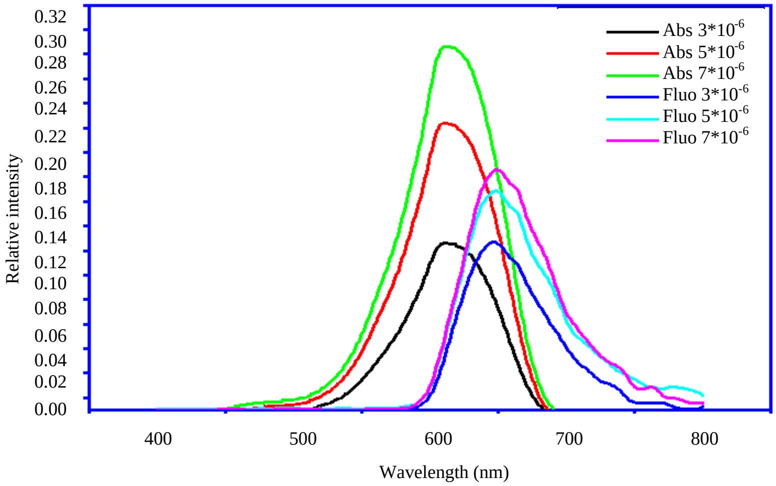

Fig. 5: Absorption and fluorescence spectra of the Azure-A solution dissolved in ethanol with different concentrations

Table 3: The values of the maximum wavelengths of a dye solution (Azure-A) dissolved in ethanol with different concentrations

Stokes shift	λ_{abs} (nm)	λ_{fluo} (nm)	C (m)
32	612	644	3×10^{-6}
35	611	646	5×10^{-6}
37	611	648	7×10^{-6}

Table 4: The lifetimes and quantum yield fluorescence for a dye solution (Azure-A) dissolved in ethanol with different concentrations

Q_f	τ_f (nsec)	C (mL)
0.95	0.1523	3×10^{-6}
0.76	0.2114	5×10^{-6}
0.61	0.2178	7×10^{-6}

Table 5: Absorption at the great wavelengths of pigment (Azure-B) dissolved in ethanol with different concentrations

Intensity	λ_{max} (nm)	C (m)
0.098	603	3×10^{-6}
0.135	602	5×10^{-6}
0.216	602	7×10^{-6}

shown in Table 4. The absorption spectra of the dissolved (Azure-B) solution in an ethanol solvent with different concentrations of (1×10^{-3}, 1×10^{-4} and 1×10^{-5} mL) were also, studied using UV-Visible spectrophotometer as shown in Fig. 6 and Table 5. Fluorescence spectra were measured for the samples prepared for the Azure-B solution dissolved in ethanol with different concentrations using fluorescence spectrometer. The results of the measurements were shown in Fig. 7 and Table 6.

The calculations show that the absorption peak does not match with the top of the fluorine, meaning that the

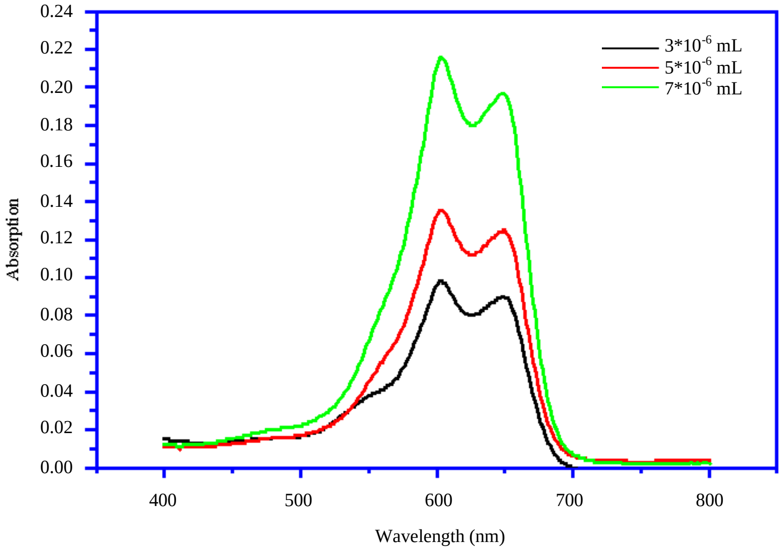

Fig. 6: Absorption spectral curves of the Azure-B solution dissolved in ethanol with different concentrations

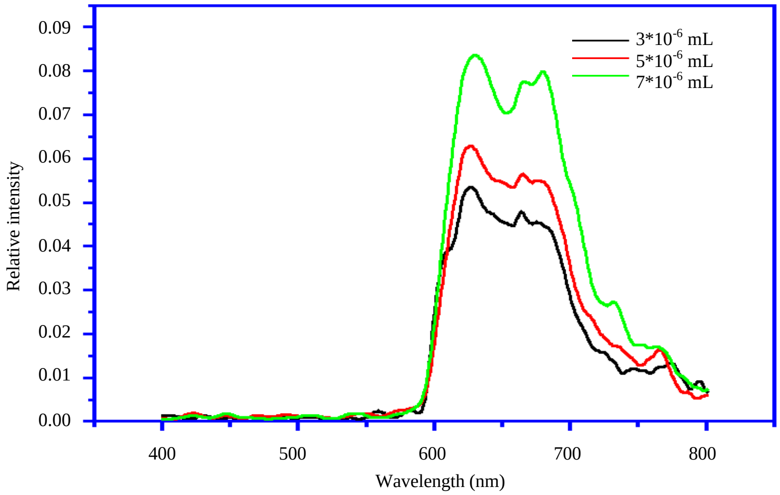

Fig. 7: Fluorescence spectrum curves for dye solution (Azure-B) dissolved in ethanol with different concentrations

Table 6: Values of the fluorescence intensity at the maximum wavelengths of the Azure-B solution dissolved in ethanol with different concentrations

Relative intensity	λ_{max} (nm)	C (m)
0.0533	626	3×10^{-6}
0.0628	626	5×10^{-6}
0.0835	629	7×10^{-6}

Table 7: Values of the maximum wavelengths of a solution of dye (Azure-B) dissolved in ethanol with different concentrations

Stokes shift	λ_{abs} (nm)	λ_{fluo} (nm)	C (m)
23	603	626	3×10^{-6}
24	602	626	5×10^{-6}
27	602	629	7×10^{-6}

Table 8: The lifetimes and Quantum yield fluorescence for a dye solution (Azure-B) dissolved in ethanol with different concentrations

Q_f	τ_f (nsec)	C (mL)
0.59	0.1109	3×10^{-6}
0.49	0.1355	5×10^{-6}
0.46	0.1993	7×10^{-6}

fluorescence energy is less than the absorption capacity because of the non-radiation processes, since, the excited particles lose part of their energy in heat, so, the energy of the photon emitted is less than the absorbed photon energy and is shown in Fig. 8 and Table 7. Fluorescence lifetimes (τ_f) and Quantum yield fluorescence (Q_f) were calculated using the results of fluorescence spectra and the results were shown in Table 8.

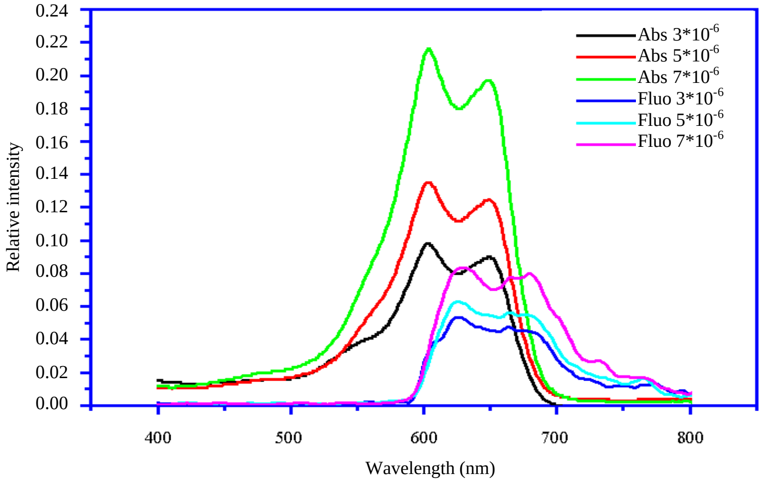

Fig. 8: Absorption and fluorescence spectrum curves for a solution of Azure-B dissolved in ethanol with different concentrations

CONCLUSION

In the study of the spectral properties of Azure-A and B, dissolved in ethanol with different concentrations, the decrease in concentration leads to the appearance of spectra with peaks of less intensity and moving towards the longer wavelengths (red shift). The highest relative intensity at the top of the absorption spectra of the dye (Azure-A) at (612 nm) at (7×10^{-6} mL). This is due to the increase in the number of molecules which increases the probability of absorption. This confirms the true absorption of pigments and is in line with the law of Per-Lambert. Concentration leads to a decrease in the intensity of the fluorine spectra and its direction towards the short wavelengths (blue shift) A decrease in concentration leads to a reduction in the lifetime of the fluorine. This results in an increase in the quantitative product of fluorine where we observed the highest quantitative efficiency recorded for the dye (Azure-A) where (95%) at concentration (3×10^{-6} mL), therefore, this dye can be used as an effective medium in dye lasers.

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