Edelweiss Applied Science and Technology
ISSN: 2576-8484
Vol. 8, No. 6, 4026-4033
2024
Publisher: Learning Gate
DOI: 10.55214/25768484.v8i6.2881

Solvatochromic behavior on the absorption, transmittance and emission spectra for some organic dyes as active media

Alaa N. Hadi[1*], Talib M. Abbas[2]
[1,2]College of Education for Pure Sciences, University of Babylon; Pure243.alaa.najah@student.uobabylon.edu.iq (A.N.H.)
Pure.talib.mohsen@uobabylon.edu.iq (T.M.A.).

Abstract: This research examines the absorption and emission (fluorescence) spectra of several solutions containing mixtures of organic dyes dissolved in ethanol, analyzed at three distinct concentrations (0.1, 0.2, 0.3 mM) for each mixture. Two organic dyes were combined: (Fluorescein + Eosin), (Fluorescein + Methyl Orange), and (Malachite Green + Azure B), each with a defined weight. As the concentration of these dye mixtures decreases, so do the absorbance values and an increase in transmittance values and vice versa. This is consistent with the Beer-Lambert law, which also leads to a decrease in the values of all linear optical properties. The fluorescence spectra were obtained via a fluorescence spectrometer. The fluorescence lifespan and quantum efficiency of fluorescence were computed to derive a combination of dyes with elevated quantum efficiency suitable for use as active media in dye lasers.

Keywords: *Absorption and fluorescence, Mixtures of organic dyes, Organic dyes, Quantitative efficiency of fluorescence, Spectra.*

1. Introduction

Organic compounds have undergone extensive theoretical and experimental investigation owing to their potential applications across various life science disciplines. This study selected several organic compounds that emit in the blue-green region for analysis. These compounds' photophysical properties in various solid matrices have received attention due to their many uses in tunable a solid dye active media, energy transfer studies, medical devices, and sensing and probe instruments [1].

This text addresses the fundamental principles of electromagnetic radiation interaction with atoms and molecules of organic matter. The primary source of information regarding this interaction can be obtained through the study of the photophysical processes of these materials. In these processes, radiative and nonradiative transitions serve as the primary mechanisms for energy relaxation from an excited state of an organic molecule [2]. Fluorescent dyes, significant organic materials in this study, are organic particles characterized by perfumed ring constructions that contain delocalized π electrons, which can be readily animated by photons [3].

Fluorescent dyes also exhibit characteristic absorption and emission spectra, that are important for the design of optical setup to study these spectra [4].

The fluorescent dye molecules have the ability to dissolve in different solvents with appropriate concentrations. The absorption and emission spectra are very sensitive to the concentration and solvent used [5]. As the active medium in liquid lasers, dyes are pumped optically by other lasers or flashlamps at 10^{-2}–10^{-4} mol/l. Additionally, maximum dyes belong to one of the families of dyes such as Rhodamine or Coumarin [6,7]. The dyes emit a spectrally broad pulse, and could be tunable to cover the UV, Vis. and NIR regions of the spectrum. Most lasers dyes show strong absorption and fluorescence in the visible region [8].

* Correspondence: Pure243.alaa.najah@student.uobabylon.edu.iq

2. Theoretical Part

Laser radiation is absorbed and reflected by material surfaces. Surface heating begins with absorbed energy. Multiple parameter regimes must be explored depending on time and fluence. When a laser beam hits a substance, unbound electrons absorb its energy. Laser energy is transferred to the material via the electron subsystem carrying absorbed energy to the lattice [9].

This technique is resonant because materials absorb lasers at different wavelengths depending on their microstructure and electromagnetic characteristics [9]. The interaction of matter can be classified as linear interaction and nonlinear interaction [10]. Nonlinear optics was created when the laser emerged as a coherent light source with a in height strength. These days, it is crucial in many fields of science and technology [11].

The optical processes that are seen in solid state materials when light interacts with matter can be categorized as transmission, refraction, absorption, and reflection [12]. The transmitted, absorbed, and reflected beam intensities, represented as I_T, I_A, and I_R, must add up to the concentration I_O of the beam occurrence to the solid medium's surface, or [13,14].

$$I_o = I_T + I_A + I_R \text{.............}(1)$$

$$T + A + R = 1 \text{.............}(2)$$

The absorption coefficient (αo) and the refractive index (no) can be derived from the transmittance pattern use the following equations [14].

$$\alpha_o = \frac{1}{t}\ln\left(\frac{1}{T}\right) \text{.........}(3)$$

$$n_o = \frac{1}{T} + \left[\left(\frac{1}{T^2} - 1\right)\right]^{1/2} \text{.......}(4)$$

where t signifies the sample thickness and T indicates the transmittance The effectiveness of light absorption at a wavelength λ by an absorbing material is defined by absorbance. A or transmittance T is defined by **[15]**

$$A = \log\frac{\mathrm{I_o}}{\mathrm{I}} = -\log \mathrm{T} \text{.........}(5)$$

$$T = \frac{\mathrm{I}}{\mathrm{I_o}} \text{.........}(6)$$

Io and I represent the light intensities of the beam entering and exiting the absorbing material, respectively. The absorbance of a sample adheres to the Beer-Lambert law [15].

$$A = \log\frac{\mathrm{I_o}}{\mathrm{I}} = \varepsilon\ \mathrm{LC} \text{..........}(7)$$

Where: ε represents the molar extinction coefficient (in $l\cdot mol^{-1}\cdot cm^{-1}$), and C is the concentration (in mol/L) of the absorbing species. L represents the absorption path length, denoting the thickness of the absorbent material, measured in centimeters. The reflectivity R and the extinction coefficient K can be calculated from the following equations [15].

$$R = \left(\frac{n-1}{n+1}\right)^2 \quad (8)$$

$$K = \frac{\alpha_0 \lambda}{4\pi} \quad (9)$$

Upon excitation by photon absorption, a molecule may revert to its ground state by fluorescence emission. The absorption spectrum generally overlaps with the fluorescence spectrum, leading to the emission of light at shorter wavelengths than those absorbed. The fluorescence spectrum mirrors the absorption spectrum due to the analogous differences between the vibrational levels in the ground and

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excited states [17]. The molecular fluorescence quantum efficiency q_{fm} is the ratio of fluorescence photons emitted by molecules in dilute solution to photons absorbed: [16].

$$q_{fm} = \frac{\text{number of photon emitted}}{\text{number of photon absorbed}} \quad .... (10)$$

The quantum efficiency is a crucial property of dye molecules, with values ranging from 0 to 1, influenced by factors such as nature, concentration, viscosity, temperature, and the molecular structure of the solvent [16]. The quantum efficiency at elevated solvent concentrations is referred to as quantum yield (Φfm) [18]. Quantum efficiency can be calculated using the relation [18]:

$$q_{fm} = \frac{\tau_f}{\tau_{\text{fm}}} \quad ....(11)$$

$$\Delta\lambda = \lambda_{\text{flu.}} - \lambda_{abs} .... (12)$$

Where: τ_{fm}: The radiative lifetime. τf: The fluorescence lifetime. The Stokes shift is the difference between the peak of the absorption spectrum and the fluorescence spectrum, expressed in wavelength, as illustrated in equation [16,19].

3. Experimental Part

3.1. Material Used

Five organic dyes were used and dissolved with ethanol solvent to obtain three different dye mixtures.

Table 1.
Shows the most important characteristics of the dyes used in this study.

Dyes	Supplier company	Chemical formula	Molecular weight gm/mole	Appearance
Fluorescein	Sigma aldrich	$C_{20}H_{12}O_5$	332.311	Dark red-orange powder
Eosin yellow	Sigma aldrich	$C_{20}H_6Br_4Na_2O_5$	991.9	Yellow powder
Malachite Green	Sigma aldrich	$C_{23}H_{25}ClN_2$	364.9	Dark green powder
Methyl orange	Sigma aldrich	$C_{14}H_{14}N_3NaO_3S$	327.33	Orange-yellow powder
Azure B	Sigma aldrich	$C_{15}H_{16}ClN_3S$	305.8	Dark blue powder

3.2. Preparation of Dyes Mixtures Solutions

Three solutions of organic dyes mixtures were prepared in present study are (Fluorescein + eosin), (Fluorescein + Methyl orange) and (Malachite green + Azure B) at a concentration of 10^{-3} M, with a specific weight for each dye and dissolving them. With one solvent, which is ethanol, and according to the weight equation:

$$M = (C \times V \times M_w)/1000 \quad ....(10)$$

M: The mass of the dye required to achieve the target content in grammes. C: content to be formulated in mol/L. The volume of solvent required to be applied to the material in cubic centimeters. Mw: Molecular weight of the dye employed, g/mol. To generate diluted concentrations of 0.1, 0.2, and 0.3 mM, a certain volume of solvent is added in accordance with the following dilution equation:

$$C_1 \times V_1 = C_2 \times \mathrm{V}_2 \quad ....(11)$$

C1: initial (high) content, C2: subsequent (lightest) content, V1: the requisite volume of the initial content; V2: the volume required to be additional to the initial content to achieve the second content.

4. Results and Discussion

Absorbance values were calculated using an ultraviolet-visible spectrometer and emission intensity (fluorescence) values were calculated using a fluorescence spectrometer. Figures (1), (2) and (3) shows, respectively, the absorbance and fluorescence spectra of solutions of dye mixtures (Fluorescein + Methyl Orange). (Fluorescein + Eosin) and (Malachite Green + Azure B) at different concentrations (0.1, 0.2, 0.3) mM. It is noted from these figures that absorbance values vary from one mixture to another and occur at different wavelengths, and that a decrease in concentration leads to a decrease in absorbance values, and this is consistent with the Beer-Lambert law of absorbance. As for the fluorescence curve, a decrease in concentration leads to an increase in fluorescence values, and this is due to This is due to the decrease in the concentrations of dimers inside the dyes dissolved in the polar solvent, which often works to suppress the fluorescence and thus obtain a broad fluorescence spectrum.
The optical properties were determined by calculating the linear absorption coefficient (n) and refractive index, as well as the fluorescence lifetime time (τ_{fm}) and the quantum efficiency of fluorescence (q_{fm}) based on the curves of the absorbance and fluorescence spectra. It has been observed that when the concentration is decreased, there is a corresponding increase in the quantum yield of fluorescence (Φ_{fm}), which results in a high quantum efficiency attainment.

A reduction in dye concentration diminishes the formation of dimer aggregates, resulting in absorption cross-sections that are independent of concentration, thereby adhering to the Beer-Lambert law. This phenomenon enhances beam exposure in the low-frequency region, subsequently decreasing fluorescence lifetime and increasing quantum efficiency values, as illustrated in Table 1.

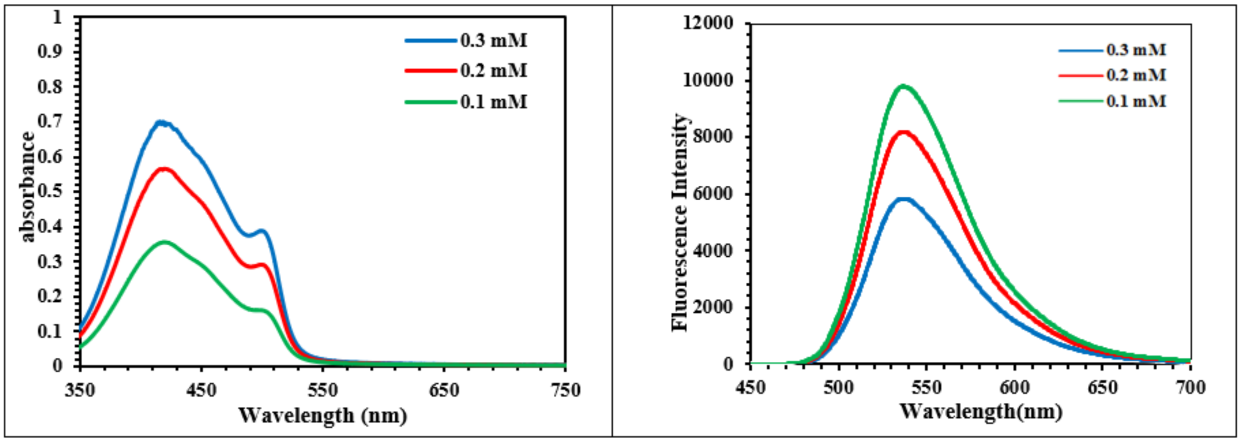

Figure 1.
Absorbance and fluorescence spectra curves of mixture solutions of dyes (Fluorescein + Methyl Orange) at different concentrations.

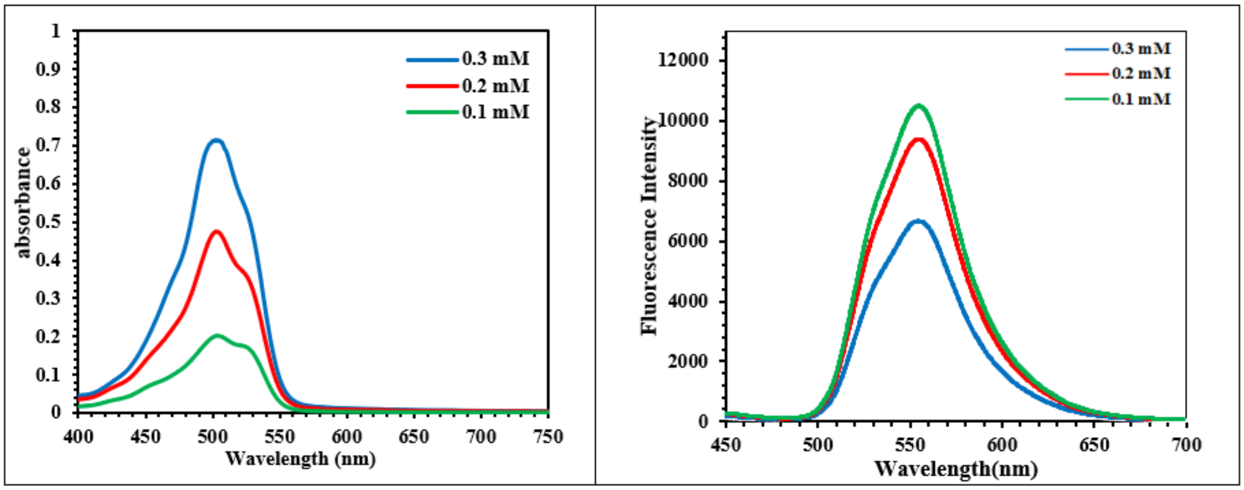

Figure 2.
Absorbance and fluorescence spectra curves for solutions of dye mixtures (Fluorescein + Eosin) at different concentrations.

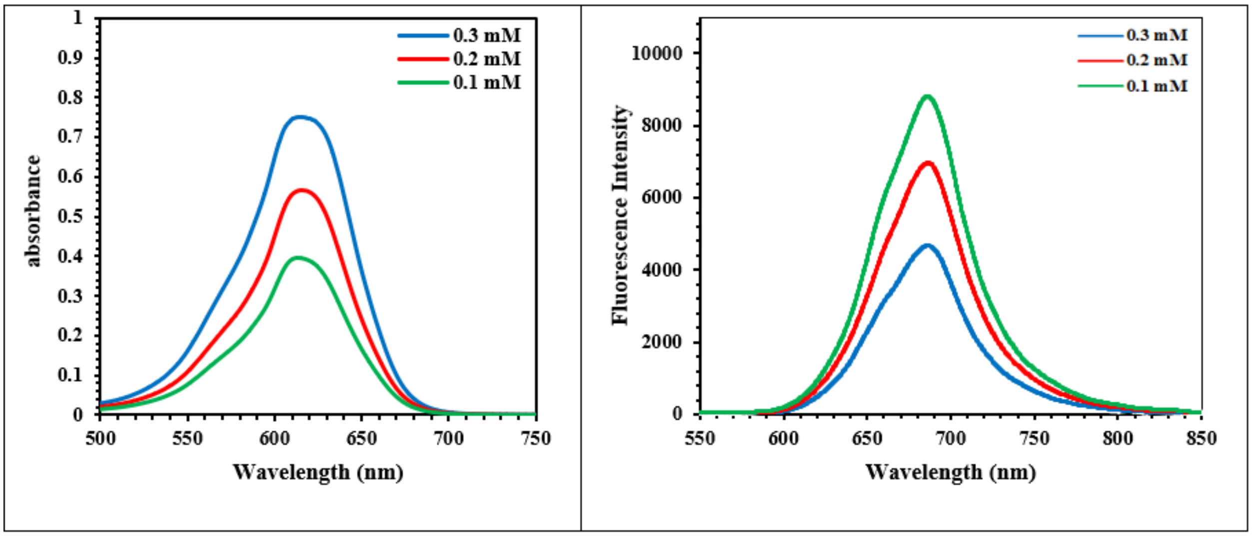

Figure 3.
Absorbance and fluorescence spectra curves of dye mixture solutions (Malachite Green + Azure B) at different concentrations.

Table 1.
The optical properties of the solutions of organic dye mixtures.

DYE mixture	**Consternations (m M)**	**A**	**λ_{ab} (nm)**	**λ_{flu} (nm)**	**λ_{flu}-λ_{ab} Stokes shift (nm)**	**α**	**n**	**τ_{fm} (nsec)**	**Φ_{fm}**	**Φ_{fm} %**
Fluorescein + Methyl orange	0.3	0.70	419	535	116	1.6	2.15	6.33	0.34	34%
	0.2	0.57	419	535	116	1.3	1.85	4.12	0.69	69%
	0.1	0.36	419	535	116	0.8	1.48	2.15	0.82	82%
Fluorescein + Eosin Y	0.3	0.71	504	558	54	1.64	2.05	6.11	0.39	39%
	0.2	0.48	504	558	54	1.09	1.90	3.87	0.76	76%
	0.1	0.20	504	558	54	0.47	1.43	1.98	0.89	89%
Malachite green + Azure B	0.3	0.75	614	690	76	1.73	2.14	7.84	0.26	26%
	0.2	0.59	614	690	76	1.29	1.85	5.73	0.65	65%
	0.1	0.39	614	690	76	0.91	1.32	2.69	0.78	78%

The transmittance values were determined using UV-visible spectroscopy. Figures (4) depict the transmittance spectra of dye mixture solutions (Fluorescein + Methyl Orange), (Fluorescein + Eosin), and (Malachite Green + Azure B) at varying doses (0.1, 0.2, 0.3 mM). These figures show that transmittance varies amongst mixtures and at different wavelengths, and that a drop in concentration leads to an rise in transmittance standards, which is compatible with the Beer-Lambert law. The transmittance spectra curves were used to determine linear optical coefficients (linear absorption coefficient, refractive index, extinction coefficient, and real and imaginary dielectric constants). It should be noted that a drop in concentration causes a decrease in all standards of optical belongings, as indicated in Table (2), which is attributable to a fall in transmittance values, and vice versa.

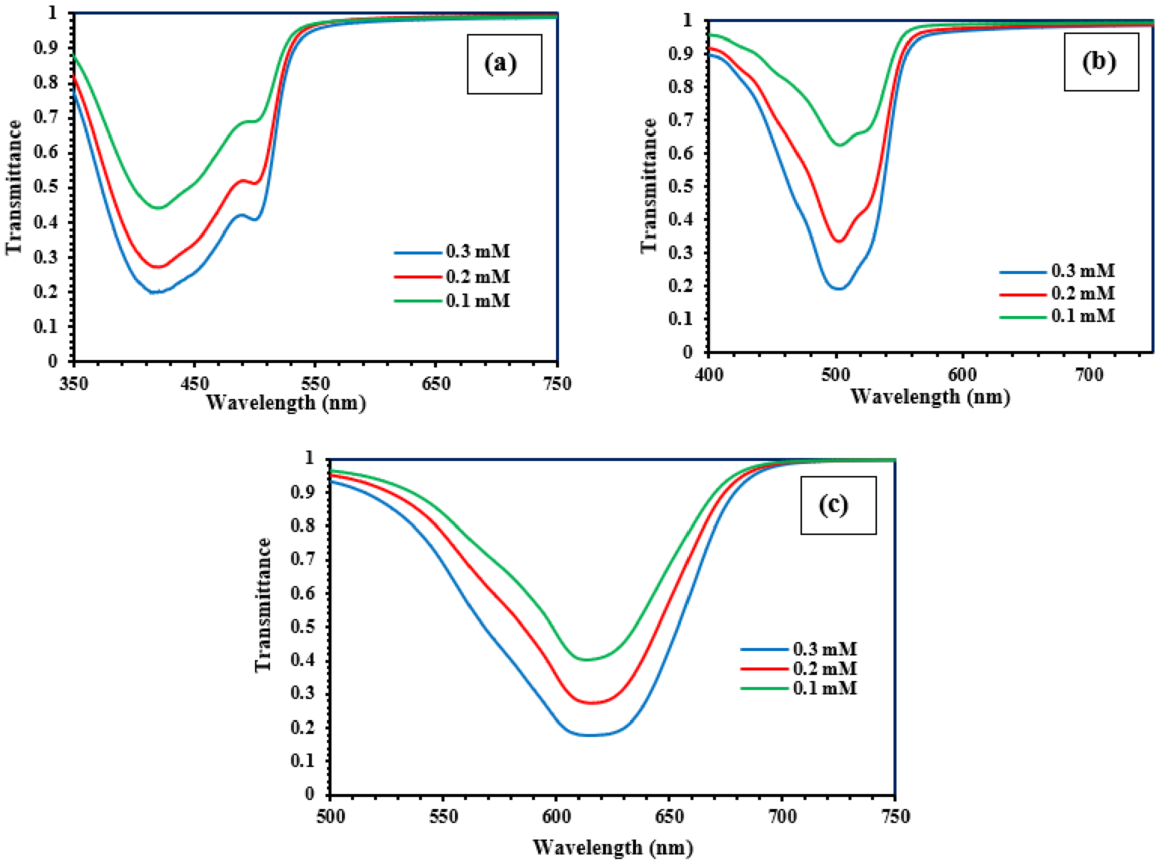

Figure 4.
The transmittance spectra curves for solutions of a mixture of dyes a: (Malachite Green + Azure B), (b): (Fluorescein + Methyl Orange) and c: (Fluorescein + Eosin) dissolved in ethanol solvent at different concentrations.

Table 2.
The most important linear optical properties of the solutions of organic dye mixtures.

DYE mixture	Consternations (m M)	$(\lambda_{ab})_{max}$ (nm)	A	T	α	n	k	ε_1	ε_2
Fluorescein + Methyl orange	0.3	419	0.70	0.2	1.6	2.15	5.4	4.6	1.62
	0.2	419	0.57	0.27	1.3	1.85	4.4	3.4	1.60
	0.1	419	0.36	0.44	0.8	1.48	2.7	2.2	1.58
Fluorescein + Eosin	0.3	504	0.71	0.19	1.64	2.05	6.6	4.2	1.88
	0.2	504	0.48	0.33	1.09	1.90	4.3	3.6	1.79
	0.1	504	0.20	0.62	0.47	1.43	1.9	2.05	1.64
Malachite green + Azure B	0.3	614	0.75	0.18	1.73	2.14	8.46	4.59	2.35
	0.2	614	0.59	0.28	1.29	1.85	6.35	3.44	2.22
	0.1	614	0.39	0.40	0.91	1.32	4.45	1.73	1.91

5. Conclusion

In this work, new mixtures of organic dyes in an ethanol solvent are prepared, exhibiting optical properties that differ from those of the individual dyes. As the concentration of these dye mixtures decreases, so do the absorbance values and an rise in transmittance standards and vice versa. This is dependable with the Beer-Lambert law, which also leads to a decrease in the values of all linear optical properties. Lowering the concentration in the dye mixture solutions in this study leads to shorter fluorescence lifetimes, thereby enhancing the quantum efficiency of fluorescence. This proceed enables the creation of organic dye mixtures suitable for use as active media in dye lasers.

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