Study the effect of thickness change on optical properties of Rhodamine B

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Abstract:
The optical properties of an organic laser dye, Rhodamine B in water is an important for modern applications, the linear optical properties of the absorption and fluorescence spectrum of the liquid dye were discussed, and the highest value of quantum yield was reached at 96% at a concentration of \(10^{-7}\) Ml a high quantum yield allow numerous applications of used doped host in optoelectronics applications and after knowing the most appropriate concentrations, a thin film of polyvinyl alcohol was dye, Study of the effect of film thickness on optical properties, the film has optical properties, reflexivity, refractive index, extinction coefficient, real and imaginary isolation constant, and the best thickness was at (4) µm. The energy gap was calculated and was inversely proportional to the thickness.

Key word: Rhodamine B, PVA, Quantum yield, Optical properties.

1. Introduction
One of a family of related chemical compounds fluorone dyes is Rhodamine B, with the chemical formula \(C_{28}H_{31}ClN_2O_3\) and Fig. (1) shows its chemical structure [1]. The molar mass of the dye is \((479.02)\) g·mol\(^{-1}\). With its spectral luminescence, Rhodamine B (Rh B) is used for many applications like studies of biological systems, sensors and are especially useful as biomarkers [2]. (Polyvinyl alcohol) (PVOH, PVA, or PVAI) its chemical formula \([CH_2CH(OH)]\) is a synthetic polymer that is water-soluble [3]. This dye is a promising material for applications in biological stains,
electrochemical luminescence collector, media for tunable lasers and water tracing agents [4-6]. The solubility of Rh B in a solution of acetic acid (30% vol) and water is about (15) g/L and (400) g/L, respectively. However its solubility in ethanol is (1.5) g/100 mL [7,8]. This compound has been misused in food industry since it can make the chili powder becomes red and therefore this compound has been banned and controlled by food safety regulators [9]. Optical properties of Rhodamine B were investigated for various dye solution doping ratios by using spectrophotometric measurement of absorption and transmission for the wavelength range (200-900) nm [10]. The optical constants and energy gap (Eg) calculated for these films.

The researcher R. M Ahmed studied the spectral properties of absorption and fluoride using different concentrations of rhodamine b dye for the region from (325 – 800) nm and studied the effect of focusing on the optical properties of the samples and the effect of thickness on the optical properties, where it was found that by increasing the thickness the absorption increases and reaches the best quantitative product at concentration 5×10⁻⁵ of dye rhodamine [11].

In 2018, the researcher was able to study the optical properties of dyeing rhodamine and applying them to sensitive sensors and studied the most important factors on which this sensor relies upon the concentration of 5×10⁻⁵ and the dye was dissolved in green aqueous media and not organic solvents. Study the effect of dye concentration on the fluorescence spectrum as well as the pH. The synthesis was fast, simple and inexpensive [12]. The prepared samples were investigated by UV-visible spectroscopy in the range from (300 to 900) nm of wavelength, fluorescence spectroscopy in the range from (550 to 800) nm of wavelength. The displacement in potential surface that lays between zero ground state and the first excited state can be determined by calculating the Stokes shift between these two states. Study the Optical and Structural Properties of polyvinyl alcohol doped silver (PVA:Ag) film [13]. (Rh) B is used in the field of biology as a pigmentation fluorescent dye, sometimes, as the auramine-rhodamine stain to demonstrate acid-fast organisms, notably Mycobacterium, and also (Rh) B dyes are used widely in many applications of biotechnology such as flow cytometry, fluorescence microscopy, fluorescence correlation spectroscopy and The enzyme-linked immunosorbent assay (ELISA). By applying gold nanorods (Au NRs) as catalysts in Rhodamine B-reaction, the enzyme-linked immunosorbent assay and a novel enhanced chemiluminescence system was developed.
2. Optical Properties

The absorption coefficient computed by [14]:

\[ \alpha = \frac{1}{t} \ln \frac{1}{T} \] \hspace{1cm} (1)

Where (T): transmission and (t): thickness.

The refractive index (n) can be calculated by equation below [15]:

\[ n = \frac{(1+R^{1/2})}{(1-R^{1/2})} \] \hspace{1cm} (2)

computed the extinction coefficient (k) by formula [16]:

\[ k = \frac{\alpha \lambda}{4\pi} \] \hspace{1cm} (3)

(\lambda): wavelength of incident ray. The relation between Absorbance, Transmittance and Reflectance is calculated by [17]:

\[ R = 1 - A - T \] \hspace{1cm} (5)

The real and imaginary complex dielectric constants (\( \varepsilon_r \) and \( \varepsilon_i \)) can be computed by equation (6) and (7) [18,19]:

\[ \varepsilon_r = n^2 - k^2 \] \hspace{1cm} (6)

\[ \varepsilon_i = 2nk \] \hspace{1cm} (7)

The optical energy gap computed using equation [20,21].

\[ (\alpha \ hv) = B(hv - E_g)^r \] \hspace{1cm} (8)

where (h): Planck’s constant, (hv): energy of incident photo, (E_g) is the optical energy band gap, (B) is a constant, (r) is the power coefficient.

3. Quantum yield

The photon emitted from molecules after direct excitation is known as the luminescence quantum yield and it is one of the most important keys to
the photophysical quantities which is symbolized by the symbol (Qf), where it measures the rate of non-radioactive transfers that compete with the emission of light. The absolute value of luminescence quantum yield of the organic dye lasers is important in calculating the threshold for the laser action and that the measurements used on the thermal photothermal effects are able to give absolute fluorescence yields of high fluorescent solutions with high accuracy and reproducibility. For the purpose of assessing absolute quantum efficiency, we must consider both the radiative and non-radiative processes to take place in the medium. Because of the contribution of non-radiative processes, quantum yield isn’t measured directly by using conventional optical detection methods, but by spectroscopic methods such as photoacoustic (PA) and thermal lenses (TL) have been adopted. The quantum yield values are influenced by various parameters, such as the dye concentration in the solution, the environmental effects, and the type of exciter (pulsed or cw laser). [22,23]

\[ \phi_f = \frac{\int F(v')dv'}{\int g(v')dv'} \]  

(9)

4. Fluorescence lifetime

The fluorescence of organic molecules is not only has characteristic lifetime, it has also characterized by the emission spectrum. The radiative decay rate is a characteristic property of a molecule and therefore may be used to contrast different chemical species, i.e., different fluorophore. The average decay time of the fluorescence emitted by a molecule after excitation with an ultra-short lamp (laser) pulse is fluorescence lifetime. It depends on the radiative and nonradiative decay rates of molecules in an excited state. [24]

\[ \tau_F = \frac{a \times \tau_{fRB}}{a_{RB}} \]  

(10)

\( \tau_{fRB} \) is the fluorescence lifetime of the standard compound, a is the area under the curve of the compound required in this work and a_{RB} area under the fluorescence curve of Rhodamine B.

5. Experimental Work

5.1. Sample preparation
Dissolve (2) g Rhodamine B in deionized water at room temperature after that prepare different concentration (1x10⁻³, 1x10⁻⁴, 1x10⁻⁵, 1x10⁻⁶ and 1x10⁻⁷ mole/liter) following relationship.

\[ W = \frac{M_w \cdot V \cdot C}{1000} \]  

\[ \text{(11)} \]

Where (W): weight of the dye in (gm), (Mw): molecular weight of the dye (393.95 g/mol), (V): volume of the solvent and (C): concentration of the dye (mol/l). The prepared solutions were diluted according to the following equation:

\[ C_1 \times V_1 = C_2 \times V_2 \]  

\[ \text{(12)} \]

\((C_1) \) and \((C_2)\): primary and new concentration, \((V_1)\) and \((V_2)\): the volume before and after dilution.

5.2. Fabrication of the film (Rhodamine B doped PVA)

Casting method was used to fabricate dye Rhodamine B doped (PVA) polymer films and the solution was produced by dissolving (1.5) g from (PVA) in (50) ml of water solvent at (30) °C. The final solution consisted mixed of (2:3) polymer solution dissolved in water and (1:3) Rhodamine B dye dissolved in water. The solution was thoroughly mixed using a magnetic hot plate stirrer to obtain a homogeneous mixture. The solution of (1x10⁻³) Ml concentration was poured at room temperature on glass slides with the dimensions (2.5×7.5) cm and left for (24) hours in order for the solution to solidify. The prepared films had different thickness \((t=2,3,4,5,6)\) µm.

6. Results and Discussions

6.1. Rhodamine B

After the dye was prepared with different concentrations (1x10⁻³, 1x10⁻⁴, 1x10⁻⁵, 1x10⁻⁶ and 1x10⁻⁷) mole/liter, it was placed in a spectrophotometer to measure the absorption spectrum as show in Fig. (2) Noting the absorption spectrum, we find that when reducing the dye concentration, it leads to a decrease in the absorption peak, as well as a decrease in bandwidth. Absorption was found in the range of wavelengths confined between (440—600) nm.
The changes (the displacement of the spectrum towards the lower energies) resulting in the absorption spectrum were explained by increasing the concentration in two different ways. On the first side, these changes were considered to be caused by the dimeration process, but on the other side, these changes were attributed to the change in the molecular structure of Rhodamine B from the basic structure to the acid composition, this theory was established on the basis of the resulting pH decrease with increasing the dye concentration. Therefore, the changes in the absorption spectrum are not only due to the increased dye concentration, but also from the change in pH. We also note that when the concentration increases, the intensity of the absorbance increases, due to the increase in the number of molecules, which in turn leads to an increased probability of absorption, and this absorption of the dyes is consistent with the Beer-Lambert Law. Thus, the best concentration of the dye is $1 \times 10^{-6}$ M. Using equations Nos. (1,3,5), linear optical properties were calculated from its permeability, absorption coefficient, and extinction coefficient as show in Table (1).

**Table (1): Show the optical properties of Rh B**

| Con. Ml | λ(nm) | absorption | T  | $\alpha$ (cm$^{-1}$) | $K \times 10^{-7}$ |
|---------|-------|------------|----|---------------------|------------------|
| $1 \times 10^{-3}$ | 530   | 0.680      | 0.17593 | 1.7376             | 73.59            |
| $1 \times 10^{-4}$ | 530   | 0.675      | 0.17947 | 1.7177             | 72.75            |
One of the modern applications of dye Rhodamine B is its use as a photo sensor so it became important to know its fluorescence quantum yield and Fluorescence lifetime dissolution by finding a fluorescence spectrum using a fluorescence Spectrophotometer device and the previous different concentrations were placed in the device and the fluorescence spectrum shown in the Fig. (3).

| Concentration | Wavelength (nm) | Relative Intensity | Quantum Yield | Fluorescence Lifetime |
|---------------|-----------------|--------------------|---------------|-----------------------|
| 1x10⁻³        | 550             | 0.670              | 0.18578       | 1.6831                | 71.29                |
| 1x10⁻⁶        | 550             | 0.660              | 0.19983       | 1.6102                | 68.202               |
| 1x10⁻⁷        | 550             | 0.630              | 0.24397       | 1.4107                | 59.75                |

![Fluorescence spectrum](image)

**Fig. (3): Fluorescence spectrum for different concentrations**

When observing Fig. (3), it shows the fluorescence spectra of Rhodamine B solution in water and for different concentrations from 1x10⁻³ to 1x10⁻⁷ molar. Water is a neutral solvent. It is observed through the fluorescence spectrum that this dye possesses a fluorescence spectrum with a wide range of wavelengths. It is clear that the effect of the concentration changes in determining the maximum wavelength of the fluorescence spectrum Was found at the concentration (1x10⁻³) molar (592) nm and then this peak was shifted towards the shorter wavelengths (blue shift).
specifically at (572 nm). When the concentration decreased to (1x10^{-4}) molar, then the peak site became at (550) nm for the lower concentration (1x10^{-5}) molar, and this is offset by a reduction in the spectral range as well. Increasing the concentration of the dye shifts the tip of the fluorescence towards long wavelengths (Red Shift) of low energies up to (40 nm), The explanation for this, is the increased concentration of the dye solution, as the local electric field present in the solution; It will be boosted, so charges will be re-arranged due to electronic partial transfers, Where the dipole of the excited state becomes larger than the ground state; This causes an increase in the polarity of the solution with more stability to the irritated state, which reduces the level of its energy, thus shifting the location of the peak of the fluorescence spectrum towards the long wavelength region (Red Shift).

Through the results of fluorescence spectra, it was possible to calculate the fluorescence lifetime (\( \tau_F \)) as well as the quantum output of the Quantum Yield fluorescence (\( \Phi_F \)), using relationships (9), (10), respectively. After calculating the area under the curve of the absorption and fluorescence curve using the computer program (GEUP 6), the results were as shown in the Table (2).

Table (2): fluorescence lifetime and quantum yield of Rhodamine B

| Concentration mol/L | \( F_{\text{max}} \) | \( \tau_F \) (ns) | %\( \Phi_F \) |
|---------------------|-----------------|-----------------|-------------|
| 1x10^{-7}           | 550             | 0.013           | 96%         |
| 1x10^{-6}           | 567             | 0.014           | 92%         |
| 1x10^{-5}           | 569             | 0.017           | 82%         |
| 1x10^{-4}           | 573             | 0.019           | 71%         |
| 1x10^{-3}           | 589             | 0.023           | 56%         |

From the note of the Table (2), we note the effect of the change of the dye concentration on the chronological age and the quantitative production of fluorescence, so the effect was that by increasing the concentration, the chronological lifetime of the fluorescence increases, and this can be attributed to polarity. The solvent thus reduces the area of the molecular diffusion of the dye and increases the rate of energy transfers, which leads to an increase in the quantitative output of the fluoridation, these results were close to what the scientist D.S. Elson [24]
6.2. Effect thickness film of optical properties

After studying the spectroscopy of absorption, fluorescence, and quantum yield, the concentration was chosen, fixed its \((1 \times 10^{-6})\) Ml, and different thickness (2µm, 3µm, 4µm, 5µm, 6µm) were taken from the film to study the effect of thickness on the optical properties. The concentration is one of most important parameters that has influence on the Rhodamine B dyes, where in a very dilute samples, dye dissolves completely into monomers. In such kind of dye solutions, the intrinsic absorption of the dye molecules is affected by interaction. Because of the large average distance between the dye molecules in dilute solution, dye interaction is negligible. By increasing dye concentration dimer or higher aggregates are formed.

Using equation (1), the absorption coefficient was calculated for different thickness as shown in the figure 4. When the thickness increases, the absorption coefficient decreases, it is possible to know the nature of electronic transfers that was Directly or Indirectly by the absorption coefficient values.

![Absorption coefficient as a function of photon energy](image)

**Fig. (4): Absorption coefficient as a function of the photon energy of the multiple thicknesses.**

Reflectivity was calculated from the absorption and permeability spectrum according to the law of energy conservation according to equation (5), and we notice from the form Fig. (5) that reflexivity increases with increasing energy for short wavelengths, while decreasing with increasing
energy at long wavelengths, and with increasing thickness the reflectivity decreases and that reflexivity depends a lot on surface nature.

Fig. (5): Reflectivities of different thickness films as a function of photon energy

The refractive index is calculated according to equation (2), and the refractive index is changed as a function of the photon energy in the form of (6). Note that the nature of the refractive index curve is almost the same as that of the curve reflexivity, due to the correlation of reflexivity with the refractive index, as in the previous equation. The values of the refractive index increase directly with energy of falling photons, these values range from (1.1-1.23).

Fig. (6): The refractive index as a function of the photon energy incident on thin films of different thicknesses.
The extinction coefficient was calculated from equation (3), and Fig. (7) shows the change of the extinction coefficient as a function of the energy of the incident photon. The nature of the damping factor curves is roughly similar to the thickness (3, 4, and 5) \( \mu m \). This change in the modulus of damping indicates the occurrence of rapid (electronic) transfers within the energies range between the valence and conduction bands, which led to a clear increase in the extinction coefficient to reach higher values at (2) \( \mu m \).

**Fig. (7): The extinction coefficient as a function of the photon energy incident on the thin film for various film thicknesses**

The dielectric constant was calculated with its real and imaginary parts respectively, according to equation (6,7) and Figure (8) shows (and the change in the real part of the dielectric constant) as a function of the falling photon energy. The real part of the dielectric is of a nature roughly similar to the refractive index curves, (This similarity results from the dependence of the calculation of the values of the real part on the refractive index more than the extinction coefficient, and upon observing the Fig. (9) we notice the change of the imaginary part as a function of the energy of the falling photon.
Fig. (8): The change of the real part of the dielectric constant as a function of the incident photon energy of different thicknesses.

Fig. (9): The change in the imaginary part of the dielectric constant as a function of the photon energy incident of various thicknesses.

The energy gap value was calculated using the absorption coefficient and knowing the type of transmission, and since the transition is direct according to an equation (8), it was drawn between($\alpha$hv)$^2$ and photon energy finding the energy gap through draw the tangent. The value of the energy gap was (2.138 Ev) at thickness(2µm), and the energy gap increased when the thickness increased it is agreement with experimental value [12], compute the energy gap is necessary to determine the type of transition.
Fig. (10): The energy gap of the allowed direct transmission as a function of photon energy incident of different thicknesses.

7. Conclusion

The purpose of this study lies in choosing an appropriate dye and studying the absorption and fluorescence spectra for it and then determining the possibility of its work as a suitable laser medium by studying the spectral properties of it at different concentrations. The fluorescence spectrum shifts to the region with long wavelengths and becomes increased in life time with a decrease in the quantum yield and when the concentration increases, this dye has shown absorption spectra of broad non-sharp beams. The linear optical properties of polyvinyl alcohol and Rhodamine B films were studied and the effect of thickness on these properties was studied, including the refractive index, whose amount can be controlled by selecting the appropriate thickness and thus obtaining an important insulation constant in the design of capacitors (increasing the value of the real insulation constant of the material after increasing the fish leads to an increase Polarization) The increase in thickness resulted in a decrease in the value of the absorption coefficient and the damping coefficient. The decrease in the extinction coefficient value means that the diaphragm has the ability to attenuate or suppress the falling wavelengths on it less.
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