Optical properties of Rhodamine B Dye mixed with Polyvinylpyrrolidone (PVP) as a matrix

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Abstract:

In the present work, the spin casting method has been utilized for preparing different concentrations of Rhodamine B (Rh B) (5%,10% and 15%) mixed with a transparent polymer Polyvinylpyrrolidone (PVP) as a matrix. The spectral characteristics of the prepared samples are studied by absorption, transmission, reflection (the wavelength region from 300 nm to 900 nm) and fluorescence spectroscopy (the wavelength region from 550 nm to 800 nm). The calculated Stokes shift between the absorption and emission of Rh.B reflects the displacement in potential surface between the ground and the excited states. The analysis of the spectral behavior of the absorption coefficient in the absorption region reveals an direct allowed transition with a band gap of 2.07 eV . The values of some important parameters (refractive index n and extinction coefficient K) of polymer thin film are determined from these spectra.

Keywords: Polyvinylpyrrolidone, Rhodamine B, optical properties, Stokes shift.

الخصائص البصرية لصبغة الرودامين بي الممزوجة مع البولي فينيل بايرودين المستخدم كقالب

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الخلاصة:

حضرت اغشية من البولي فينيل بايرودين الممزوجة بنسب مختلفة من صبغة الرودامين بي بطريقة الصب البرمي وبحثت الخصائص البصرية المتضمنة الامتصاصية والنفاذية والانعكاسية للمدى (300-900) نانومتر بالاضافة الى خصائص طيف الفلورة للمدى (550-800) نانومتر.تم حساب أزاحة ستوك وهي فرق المسافة بين قمة الامتصاص وقمة الانبعاث , وحساب فجوة الطاقة وكانت (2.07) الكترون.فولت وتم حساب بعض الثوابت البصرية مثل معامل الانكسار ومعامل الخمود.

الكلمات المفتاحية:.

1. Introduction

A great deal of interest has been concerned with the incorporation of organic dyes into solid matrices, owing to useful applications such as light concentrators in solar cells [1], optical waveguides[2], laser materials [3], sensors [4], and nonlinear optical materials [5].Polymers have become profitable for sensor technologies, because of their low

cost materials and their fabrication techniques being quite simple. In the past few decades significant interest has been shown in polymer-based sensing materials, which exhibit a change of their absorption and/or fluorescence characteristics in response to an external stimulus. Some examples of these stimuli include heat, deformation, chemicals, light, and others, which make the sensors useful for a wide range of technologies [6]. Polymer films containing luminescent dyes are widely used in sensors. To maximize the effectiveness of the sensor, one often chooses polymer-dye combinations in which the dye dissolves in the solvent of the polymer [7].

A Polyvinylpyrrolidone (PVP) has been widely used in many fields, because of its outstanding chemical stability, transparent optical property, low cost, high performance of the products and combined with the wide range of its properties. It has enormous technical and economic importance, even though its degradation at high temperature stills an intensively studied problem by many scientists [8]. It can incorporate dye molecules to become colorful and functional. Indeed, incorporating dyes into polymer supported matrices, such as PVP, could keep them far away from the disturbance of external environments, which remarkably influences the spectral properties of dyes [9].

Rhodamine B (Rh B) is one of the dyes that are most widely used as active media for tunable lasers, biological stains, water tracing agents, electrochemical luminescence collector and many others[10-12]. Rh B in aqueous solution was first studied by Holmes [13], who concluded that the absorption spectra could be explained by dynamic equilibrium between constitutional forms. Levshin and Gorskov [14] concluded that the dye absorption spectrum is pH independent. Permogorov et al.[15] attributed secondary maxima in the absorption spectrum to vibrational structure and disputed the existence of dimmers in ethanol solution. Selwyn and Steinfeld [16] treated the concentration dependence of the absorption of Rh B in aqueous and alcohol solutions on the basis of monomer dimer equilibrium only. Farah Al-Nuaimi [17] treated different concentration of Rh B doped Polymethylmethacrylate / Polycarbonate. Herein, we have been concerned with studying the optical properties including the absorbance, fluorescence, Stokes shift for samples of different concentrations of Rh B dye mixed in a transparent polymer host PVP.

2. Materials and Methods

Polyvinylpyrrolidone (PVP) obtained from (Sigma -Aldrich) were reported to have molecular weights of 29,000 $g.mol^{-1}$.N,N,N′,N′Tetraethylrhodamine chloride, known as Rhodamine B with molecular mass = 479.02 $g.\ mol^{-1}$ obtained from (Sigma -Aldrich), was used in this study without further purification. The molecular structure of Rhodamine B and Polyvinylpyrrolidone (PVP) are shown in Figure. l. The weight of host material Polyvinylpyrrolidone (PVP) to different weights ratios of Rh B (w/w)% are (5,10 and 15)%. In our experiment: Rh B and PVP are dissolved separately in distilled water and then the solution of Rh B and that of PVP are mixed, heated (up to 40°C) and stirred for 1 h; thus the mixed solutions of Rh B and PVP were obtained. After the solutions were filtrated, the films were prepared on a clean glass slide by spin-coating method(one layer), 1100 rpm for 1 minute, and dried at room

temperature for 48 h. The thickness of the film is about 0.7 μm and the film samples have good purity and uniform thickness . UV /Vis absorption spectra were taken using double beam spectrometer (Shimatzu 1800) and the Fluorescence spectra were carried out Fluorescence spectrometer (Perkin Elmer LS 3).

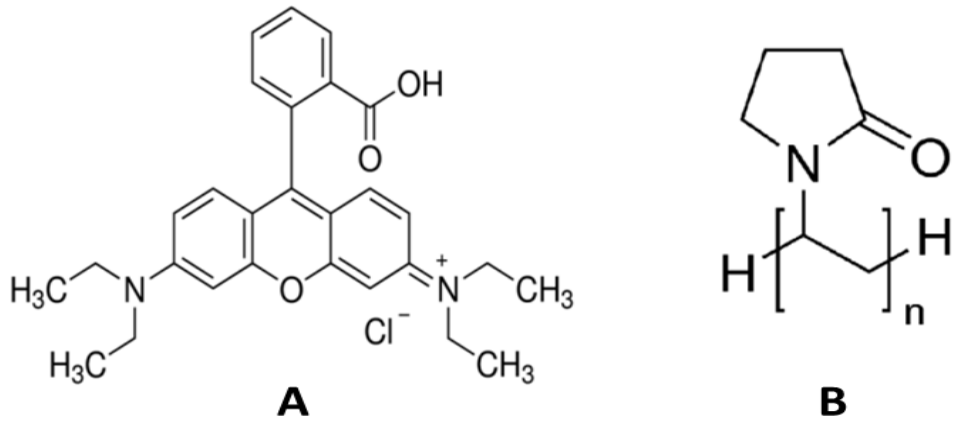

Figure 1: Chemical structure of **A**: Rhodamine B [10] and **B** Polyvinylpyrrolidone.[8]

3. Result and Discussion:

Figure 2 shows the absorption spectra at room temperature for PVP mixed with different concentrations of Rh-B (5, 10, 15)% measured in a range of wavelengths from (300 to 800) nm. It could be seen that there is an absorption band at (565) nm called Q-band, which originates from the π – π * (bonding and antibonding molecular orbital's) transitions from the binding HOMO (highest occupied molecular orbital) to the anti-binding LUMO (lowest unoccupied molecular orbital) along the longest dimension of the conjugated system. However, the shoulder around (525) nm is usually ascribed to the dimmer. The bands below 450 nm represent the transitions to the mesomeric limit structures with shorter conjugation units and originate from n– π* transitions from the NHOMO (next highest occupied molecular orbital) to the LUMO [15]. Moreover, as shown in the inset, the absorption peak values increased with increasing Rh-B content, due to the increase of the number of the absorbing species according to Beer's law [18,19].

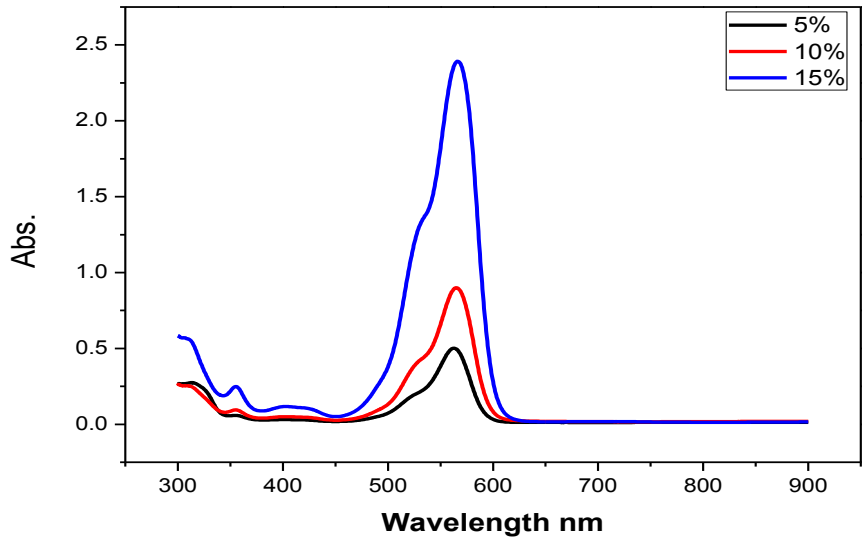

Figure 2 shows the absorption spectra at room temperature for PVP mixed with different concentrations of Rh-B (5, 10, 15)%.

Figures 3 & 4 illustrate the transmission and reflectance, respectively, for three samples measured in the range 300 to 900 nm they show high transmission and reflectivity in the range (λ > 600 nm) and low transmission and reflectivity in the range (450 -600) nm, known as absorption region.

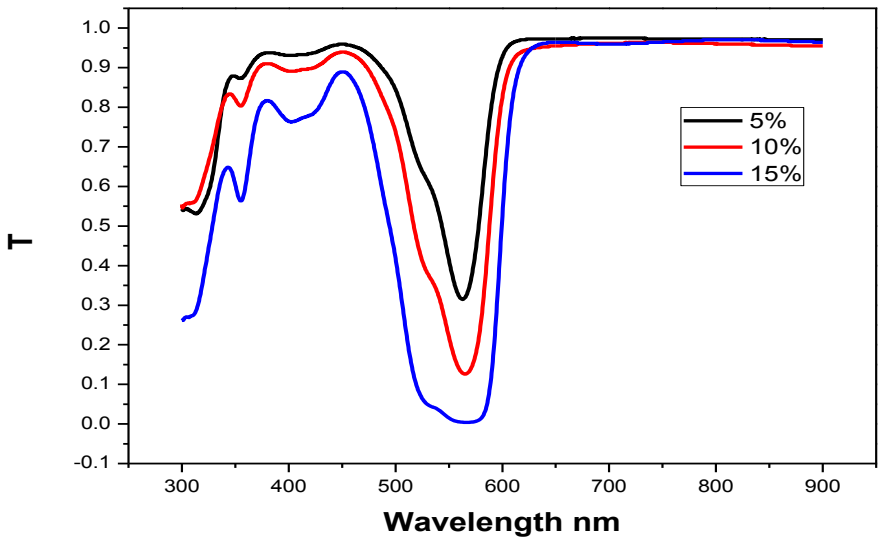

Figure 3 The transmission spectra at room temperature for PVP mixed with different concentrations of Rh-B (5, 10, 15)%.

The optical parameter (α) can be calculated from the absorption data using the following relation [20] :

$$\alpha = 2.303\ {}^{A}/_{d} \quad \text{.....(1)}$$

Where A and d are the absorption and thickness of samples respectively, then the extinction coefficient(k) can be calculated using the relation [21];

$$k = {\alpha\lambda}/{4\pi} \quad \text{.....(2)}$$

Where λ is the wavelength. The refractive index (n) was approximately calculated using the following equation [22]:

$$n = {1+\sqrt{R}}/{1-\sqrt{R}} \quad \text{.....(3)}$$

The spectral distribution of the extinction coefficient and refractive index versus wavelength for all samples can be shown in figure 5, k is very small at longer wavelengths, showing that the prepared films are highly transparent. Evaluation of the refractive indices of optical materials is considerably important for the applications in integrated optics devices, such as switches, filters and modulation, etc., in which the refractive index is a key parameter for the device design [23]. The refractive index n of Rh.B thin film shows anomalous dispersion in the spectral range 400 >λ< 600 nm and normal dispersion in the spectral range 900 > λ. This anomalous behavior is due to the resonance effect between the incident electromagnetic radiation and the electron's polarization, which leads to the coupling of electrons in Rh.B films to the oscillating electric field [24].

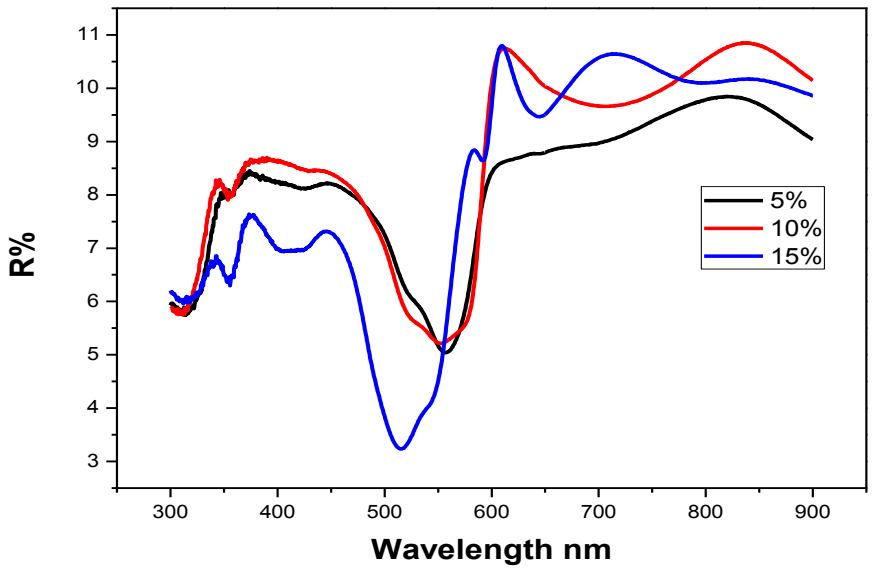

Figure 4 The reflectance spectra at room temperature for PVP mixed with different concentrations of Rh-B (5, 10, 15)%.

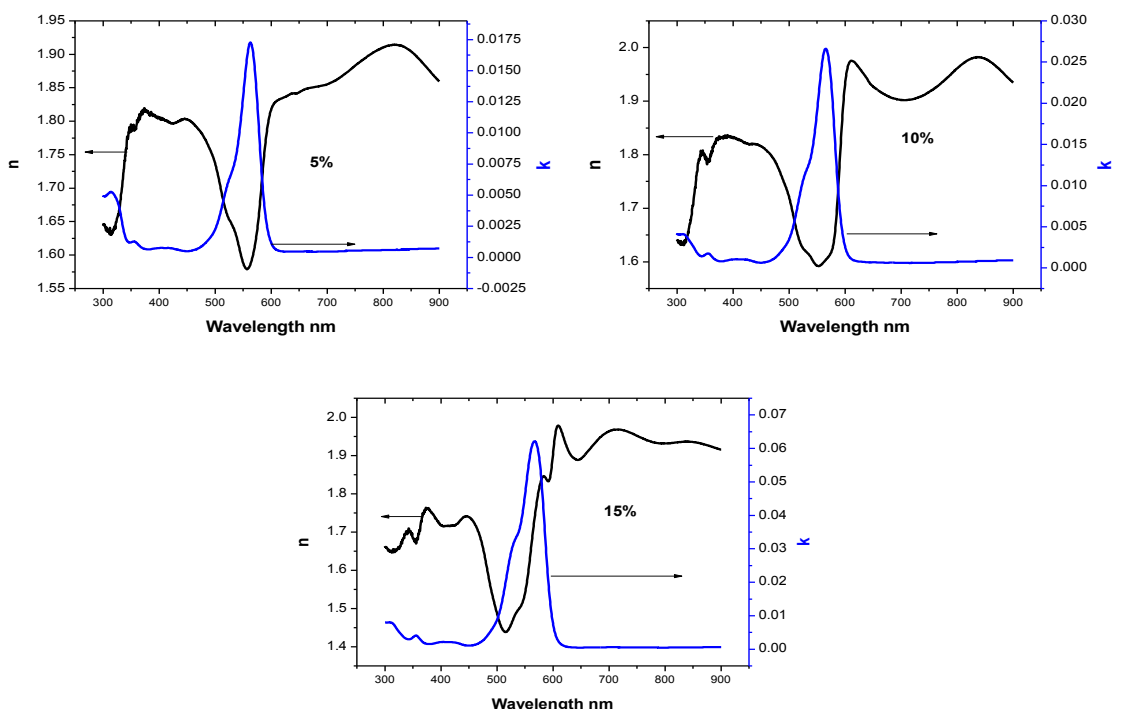

Figure 5 The refractive index (n) and extinction coefficient dependent on wave length PVP mixed with different concentrations of Rh-B (5, 10, 15)%.

The study of the spectrum of the absorption coefficient of the material in the fundamental edge provide valuable information about the energy band structure of the material. According to Tauc`s relation [25], the photon energy dependence of the absorption coefficient can be described by:

$$\alpha h\nu = C\,(h\nu - E_g^{opt})^n \ldots\ldots\ldots\ldots (4)$$

where *C* is a constant, *hν* is the photon energy, *Eg* is the bandgap and *n* is an integer that can take different values depending on the type of interband allowed/forbidden transitions. For example, *n* can be 1/2 (direct allowed) and 2 (indirect allowed) for allowed transitions. The position of the absorption edge is determined by extrapolating the linear portions of the curves to zero absorption value. The absorption coefficient for direct transition takes the values $\alpha \geq 10^4$ cm $^{-1}$, while the absorption coefficient for indirect transition take the values $\alpha \leq 10^4$ cm $^{-1}$ [26]. Figure 6 illustrate the spectral distribution of the absorption coefficient (α) , shows that the direct transition of all samples. Figure 7 shows the absorption coefficient in the form $(\alpha h\nu)^2$ versus (hν) for all samples, the intercepts of the straight lines with the photon energy axis yield the values of the direct energy gap (2.07 eV), indicating there is no change of Eg with increasing the ratio of the dye [27].

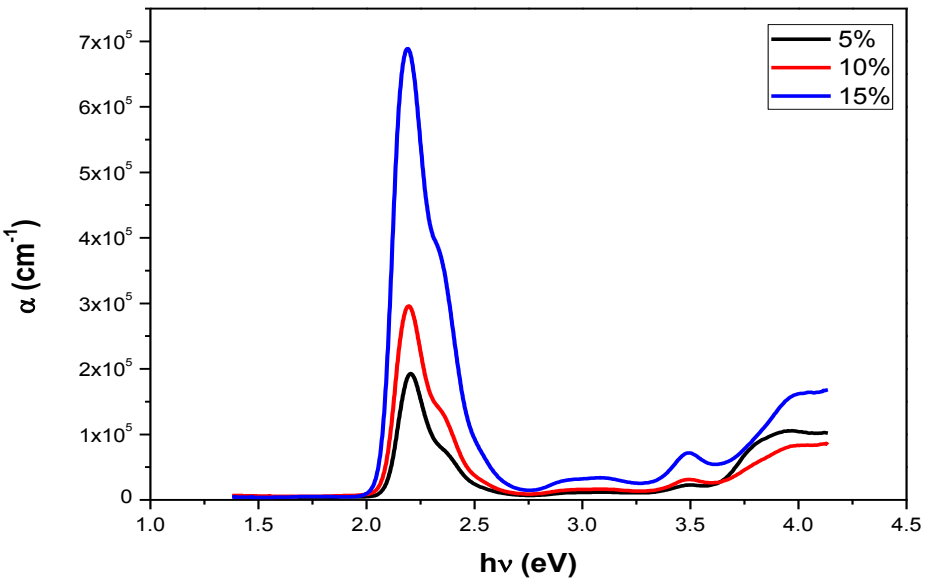

Figure 6. Dependence of α on the photon energy for PVP mixed with different concentrations of Rh-B (5, 10, 15)%.

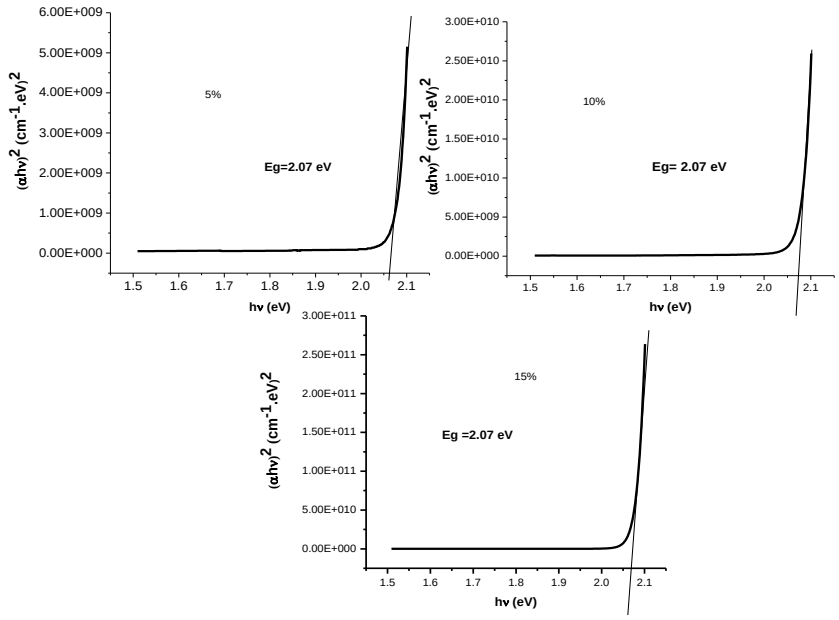

Figure 7. Plot $(\alpha h\nu)^2$ vs. photon energy for PVP mixed with different concentrations of Rh-B (5, 10, 15)%.

The fluorescence spectra of different concentrations of Rh-B mixed with PVP polymer are shown in figure 8. It is known that the fluorescence of a molecule depends on its structure and environment, such as the interaction with the solvent and other dissolved compounds in the matrix, the temperature, and the concentration of the fluorescing species. Herein, the fluorescence intensity increased with increasing Rh-B concentration. Hence, no concentration quenching effect was observed in the studied Rh-B concentration range as the dye–dye interaction is

negligible [28]. On the other hand, by increasing the concentration of Rh-B mixed PVP a red shift in wavelength from 607 to 609 nm (for first peak),and from 670 to 678 nm (for shoulder peak), was observed from the lowest to the highest concentration, respectively, this is mainly due to ground state absorption. Furthermore, the observed peak and shoulder for the highest concentration of Rh-B mixed PVP and its blend, respectively, at long wavelengths could be attributed to the existence of intermolecular interactions in the ground state in the PVP films [29].

One of the most important characteristics of the dye doped in solid matrix is the

Stokes shift $\Delta\mathbf{v}$, that indicates the difference in the dipole moments between the ground state S0 and the first excited state S1 of the dye molecules [30,31]. Furthermore, it is a measure of self-absorption of the emitted light; it was calculated from equation: [32]

$$\Delta v = v_f - v_a \quad \text{.....(5)}$$

Where ν_f and ν_a are the wavelengths at the fluorescence and absorbance maxima, respectively, the stokes shift for three samples were found to be (63, 64, 69) nm, respectively.

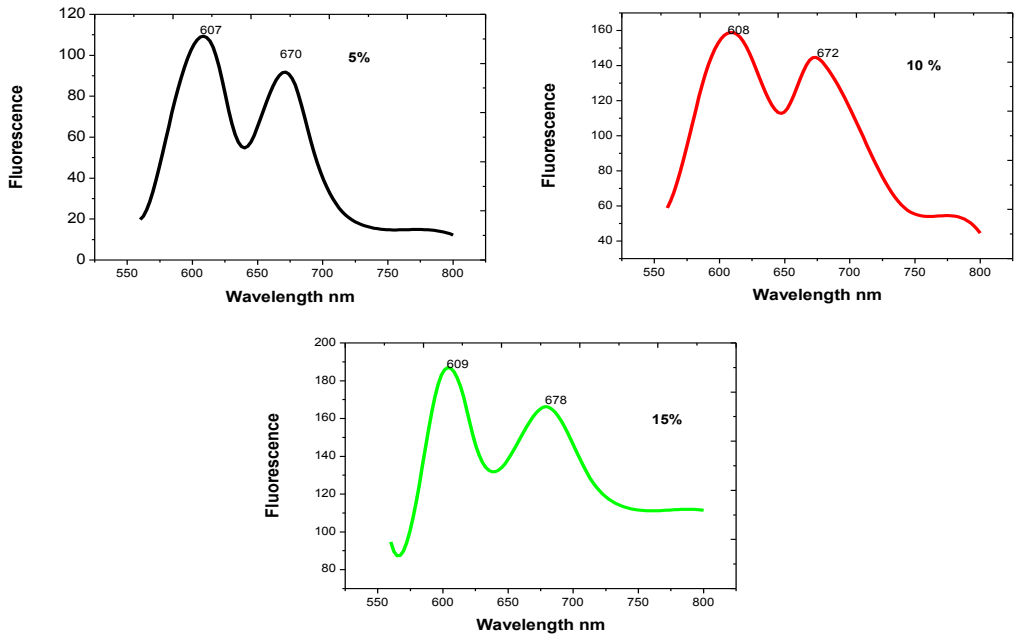

Figure 8.The fluorescence spectra at room temperature for PVP mixed with different concentrations of Rh-B (5, 10, 15)%

4. Conclusions

The values of the optical band gap Eg, of the films were determined from the optical absorption spectra using Tauc's method. The optical absorption measurements indicate that the absorption mechanism is due to allowed direct transitions. From reflectance and transmittance spectral curves the optical constants such as refractive index n, and extinction coefficient k of the all samples were calculated. The Stokes shift were calculated from the fluorescence and absorbance maxima.

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