

studying the effect of Rhodamine b concentration on the spectral properties

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Abstract:

The effect of the molar concentration of Rhodamine B dye on optical absorption spectra and fluorescence spectra. The results show that the Absorption intensity increased and the fluorescence peaks are blue shifted as the dye molar concentration increased from 1 to 100 M. In addition, the results reveal an enhancement of the absorbance and fluorescence intensity quenching is observed. The obtained fluorescence quenching of the dye higher than 60 μ M has come from the collisional mechanism. The Beer-Lambert law governs absorbance at low concentrations. While the absorbance deviates from the Beer-Lambert law at high concentrations due to contributions from dimers and dye aggregation.

Key words: Organic dyes, Rhodamine B, Absorption, fluorescence, switching

Introduction:

Rhodamine B (Rh.B) dye is one type of xanathene family derivatives, which is represent a core of such group of dyes, and tends to be fluorescent[1].

Rh.B is a triphenylmethane dye, appears to be red-violet color, 479.02 g/mole molecular weight, molecular formula (C₂₈H₃₁N₂O₃), and figure (1) shows a molecular structure [2].

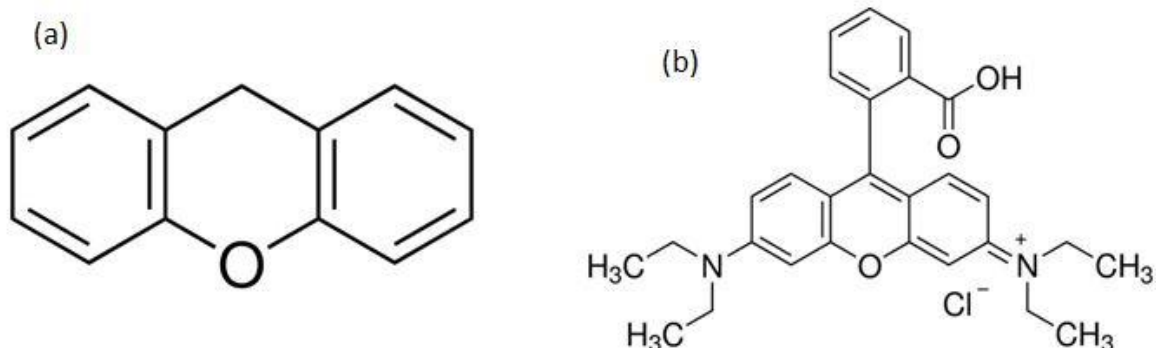


Figure (1): the molecular structure of Xanathine's (a), and (b) Rhodamine B dye [3].

In addition to dye sensitized solar cells as a prospective technical development in the field of solar cells, Fluorescence microscopy, flow cytometry, and fluorescence correlation spectroscopy are just a few of the biotechnology applications that use Rh. B dyes [4].

Organic dyes are well-known for fluorescence applications, such as active medium in liquid type lasers and a photonic switch (Q-switching), which is defined as an optical medium that absorbs a specific wavelength of the pumping source for a specified period and changes its spectral properties and characteristics based on its interaction with wavelength falling on it [5].

Several investigations on various types of dyes have been carried out. Barzan et al. explore the effect of concentration on the absorption and fluorescence properties of Rhodamine 6G dye [6], The impact of solvent type on the structural characteristics of Rhodamine 6G is investigated by Chapman et al [7], Ali et al. are a group of scholars who have developed a revolutionary method of [8], Ali et al. are a group of researchers who have collaborated on a variety of initiatives. [9], Zampini et al investigate the photophysical characteristics of dye doped silica particles. [10]. Dyes are extremely useful in a variety of applications, including liquid active media in tunable lasers [11], and fast passive Q-Switching element (saturable absorber) in solid state lasers [12], Beijaet al synthesized Rhodamine derivatives and demonstrated their utility as fluorescent probes [3], Al-Arab et.al create a random laser utilizing Fluorescein dye doped TiO₂ nanoparticles [13], and they also investigate a theoretical model to study the photophysical properties of Fluorescein Dye laser doped Ag nanoparticles [14], The present work focuses on the preparation of different concentrations of the Rh-B dye and studies the

effect of molar concentration on the photophysical properties (absorption & fluorescence).

Materials and methods:

Rh-B dye solution of (1, 10, 30, 60 and 100) μmol concentrations was made simply by dissolving the dye powder in of high purity (0.999) in ethanol and stirring the solution for 20 minutes at room temperature for each sample.

In order to examine the prepared samples, each sample was packed in a dark glass tube, the absorbance was tested using (UV/VIS Lasany), and then examined the fluorescence with (SHIMATDZU RF-5301pc) spectrofluorophotometer. The wavelength of maximum absorption peak was utilized as a wavelength of pumping source at the fluorescence experiment.

Results and discussion:

In order to verify the prepared Rh.B dye solutions, the fourier transform absorption in the infra-red region (FTIR) spectra were measured as shown in figure (2), the figure reveals the band observed at 3670 cm^{-1} is due to the OH group absorption in alcohol. The broad-band at 3317.5 cm^{-1} is assigned to OH-stretching of carboxylic acids, while the adsorption band at $2977\&2970\text{ cm}^{-1}$ are assigned to C-H asymmetric and symmetric stretching vibration respectively.

The band at 1485 cm^{-1} is due to C-H band in alkane, and the bands at $1319\ \&\ 1273\text{ cm}^{-1}$ are attributed to C-N stretch in aromatic amine.

The sharp band at 1041 cm^{-1} , due to C-O stretch in ether. The observed band at 879 cm^{-1} is assigned to aromatic ring, and the bands at $605\ \&\ 651\text{ cm}^{-1}$ is due to C-Cl stretch in halo-compounds.

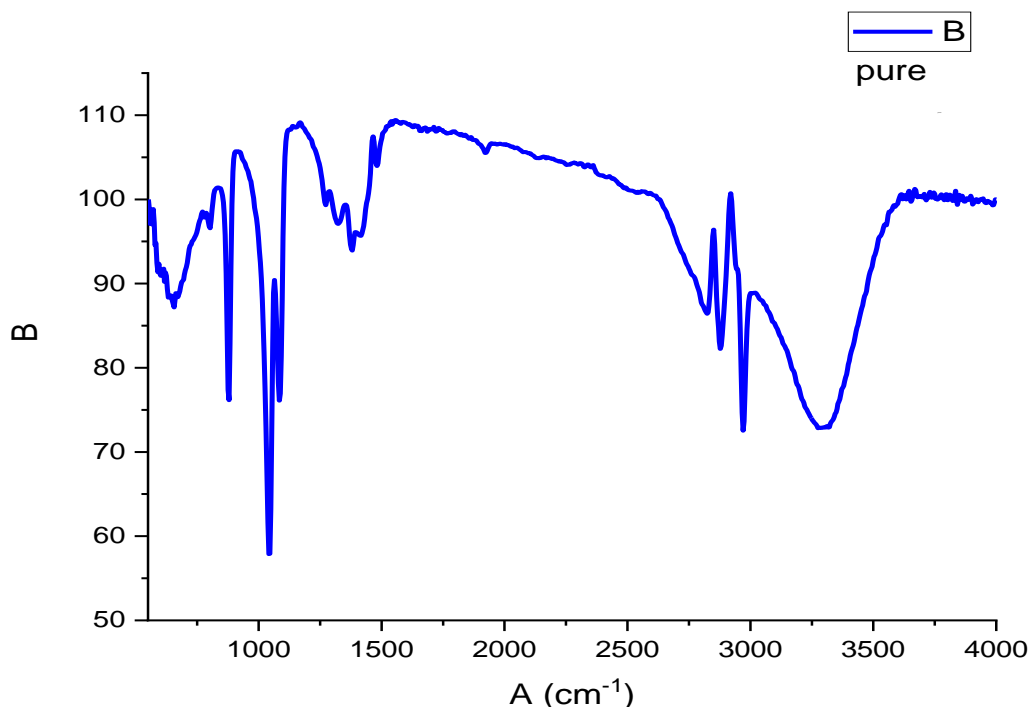


Figure (2): the FTIR spectrum of Rh.B dye solution

The absorption and fluorescence spectra varied with different concentrations, the synthesis of monomer and dimer, as well as aggregation, of Rh.B dye molecules, figure (3) depicts the optical absorption spectra of the Rh.B solution at various dye concentrations of (1, 10, 30, 60, and 100) μmol .

Figure (4a) shows that the peak absorption intensity increases as the molar concentration increase that is due to the increase of the absorption cross-section increase.

Up to 30 μmol Rh. B solution shows an absorption peak around 543 nm due mostly to monomer absorption corresponding to the S_0-S_1 electronic transition, and a shoulder around 580 nm due to the presence of dimers[15]. On the other hand, the molar concentration of 30 μmol dye solution, exhibits a complete dimerization process. Aggregation of the Rh. B dye occurs at 60 and 100 μM dye concentrations, When the absorption peak at 544 nm fades away. Figures (2 and 3) reveal that the dimerization tendency rises as dye concentration increases.

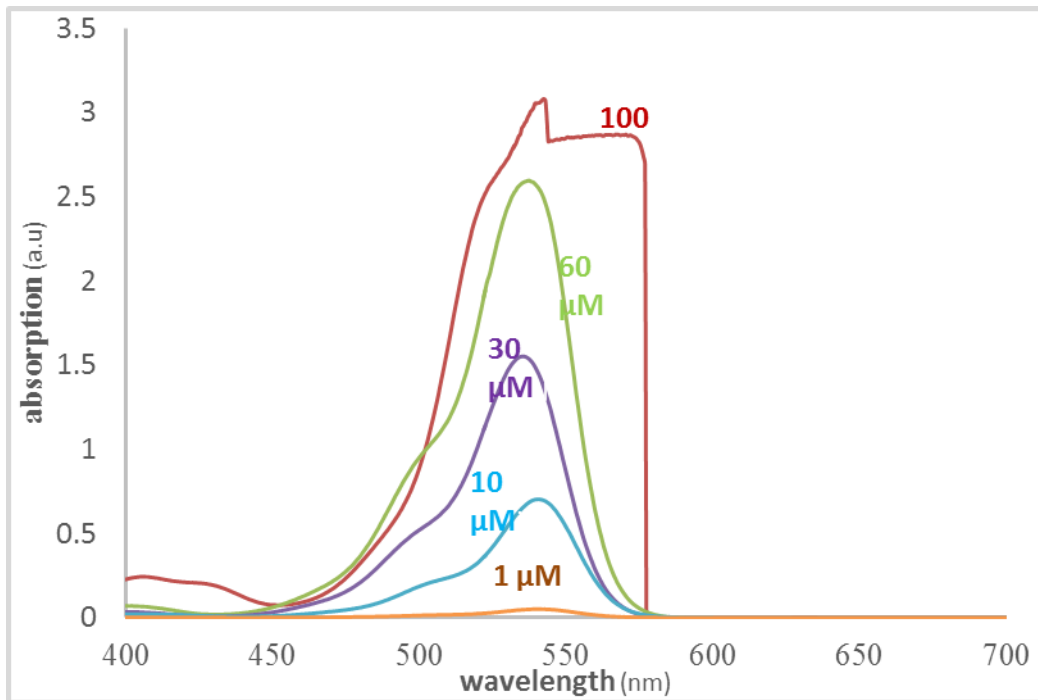


Figure 3: the absorption spectra of Rh.B with various molar concentrations.

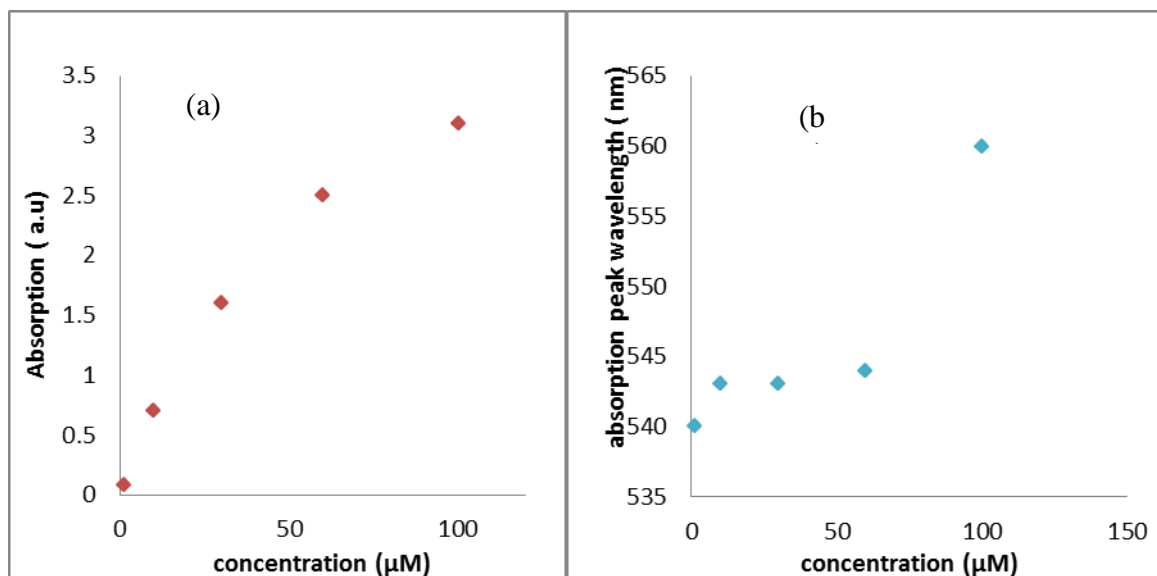


Figure (4): The absorbance vs. concentration relationship (a), and (b) the wavelength vs. concentration connection.

The absorption peak wavelength and absorbance as a function of dye concentration are presented in figure 4 (b and c) respectively, to more

quantitatively assess the absorption spectra of Rh-B dye. The significant absorption peak wavelength is essentially continuous at 544 nm below 30 μmol dye concentrations, indicating that the dye molecules are really separated. The peak wavelength then gradually rises to 568 nm at 100 μmol . The assembly makes a significant contribution to this concentration. Rh. B generates stable ground state dimers at greater concentrations in ethanol via the van der Waals dye-dye reaction or Rhodamine anti-ions interactions with ethanol [15]. The absorbance of the Rh.B solution grows linearly from 1 to 30 μmol , as shown in figure 3a, and is subject to the Beer-Lambert law, which states that absorption cross-sections are independent of concentration. The absorption spectrum contains contributions from monomers, dimers, and aggregation of Rh-B molecules beyond 30 μmol , resulting in concentration dependent absorption cross sections. As a result, the absorbance does not increase linearly and deviates from the Beer-Lambert's law.

Utilizing the Origin pro 8.1 graphic software, be one can calculate some useful physical parameters related to the absorption spectra curves for each sample, such as the area under the curve, which gives a more accurate view of the results, table (1) list of the most parameters.

Table (1): some physical parameter calculated from absorption spectra In Figure (3).

Concentration (M)	5×10^{-4}	1×10^{-4}	6×10^{-5}	3×10^{-5}	1×10^{-5}	1×10^{-6}
Area under curve	266.113	62.35	22.571	13.514	7.43	4.899
Curve Area	710.3	467.7	213.85	120.38	56.538	7.812
Row Index	105	69	51	52	74	53
Beginning x	200	213	212.5	211.5	212.5	208.5
Ending x	291.5	244	244	244.5	245	437
FWHM	91	30.5	31	32.5	32	35.75
Left-Half Width	52	11	12.5	14	14	17.5
Right-Half Width	39	19.5	18.5	18.5	18	18.25
Centre	252	224	225	225.5	226.5	226
Height	3.166	2.215	0.779	0.449	0.246	0.095
Centroid	245.98	228.08	228.16	228.12	228.49	254.13

The energy band-gaps of the Rh.B were determined utilizing the optical absorption spectra taking the advantage of the following relationship[16]:

$$\alpha h\nu = A(h\nu - E_g)^2 \dots\dots\dots (1)$$

Where: α denotes the absorption coefficient, h is Planck's constant, ν is the frequency, A is a transition probability-dependent constant, E_g is the energy band-gap and the gradient (n) depends on the type of transformation, (E_g refers to the energy distance between the absorption and the fluorescence peaks).

The following figures also refers to plotting $(\alpha h\nu)^2$ as a function of $(h\nu)$ where the energy bandgap was obtained by extracting it from the straight line of the curve $(\alpha h\nu)^2$ versus $h\nu$ to intercept the horizontal axis, where it was found that it is equal to ($E_g=4.54$ eV) and is approximately the same for all dye concentrations as shown in figure (5).

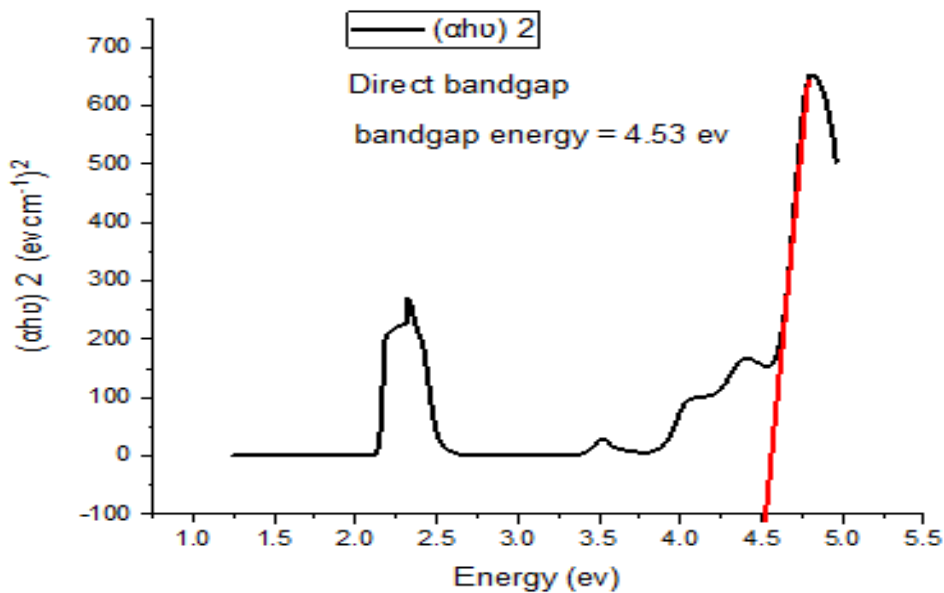


Figure (5): The Energy gap calculation from the absorption spectra.

Figure (6) shows the fluorescence emission spectra of Rh.B solution at various dye concentrations ranging from 1 to 100 μ M. At 542 nm, the emission spectrum exhibits a relatively narrow bandwidth, indicating that dye solution excitation occurs at this wavelength.

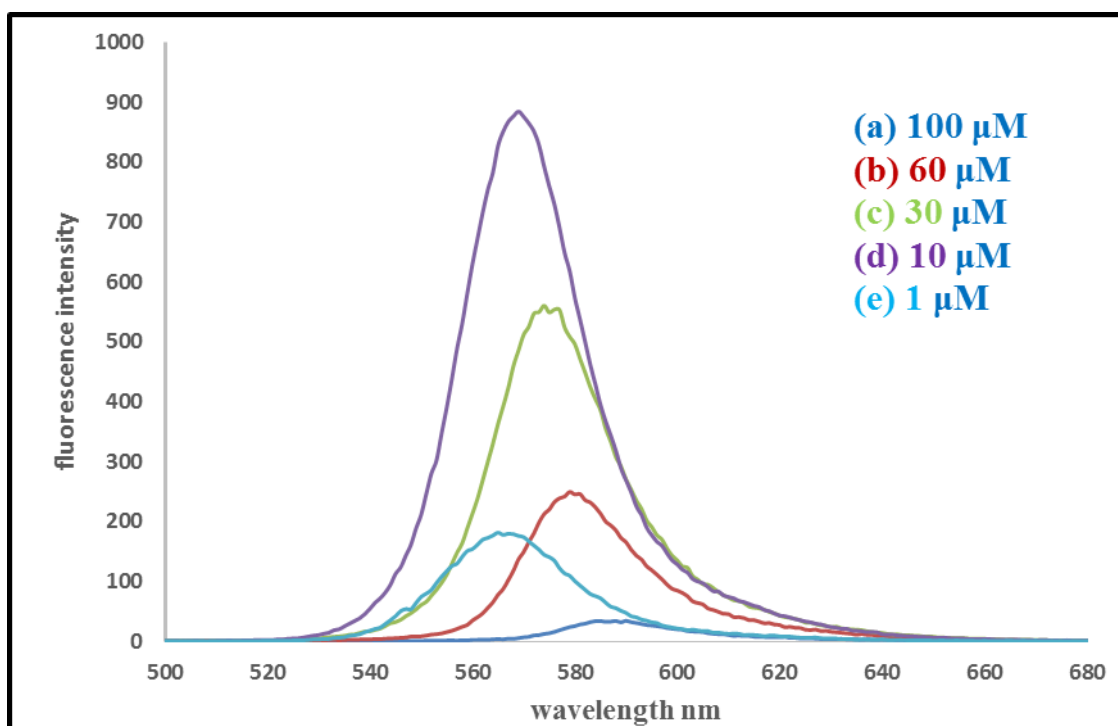


Figure (6): The fluorescence spectra of pure dye with various molecular concentrations.

Figures (7) (a and b) shows the fluorescence peak wavelength and fluorescence intensity of Rh.B as a function of dye concentration. The 1 μmol dye concentration solution emits at a peak wavelength of roughly 594 nm, as shown in figure 5 (a), and the fluorescence peak wavelength is significantly red shifted with increasing dye concentration. A red spectral shift is detected due to spectral overlap between the fluorescence spectrum of Rh.B dye and the low energy tail of its absorption band, which leads to re-absorption effects [17]. As shown in figure 5 (b), the dye's fluorescence intensity decreases significantly with increasing concentration for each sample, with the exception of certain limits where the fluorescence intensity is strongly quenched due to collisions of excited dye molecules with those in the ground state, which causes dimerization and aggregation processes[18].

The molecules form sandwich shapes, such as H-type and J-type dimers or bigger aggregates, with greater concentrations of Rh-B dye. The absorption spectra of a type I dimer changes to blue, and the 3-ring systems of two molecules are aligned in parallel, as seen in figure 1. The type II absorption spectrum is red shifted because these molecules are orthogonal to each other. Experiments showing a blue change in the absorption spectra of the Rh. B

dye with increasing dye concentration clearly demonstrate that H-type aggregates occur in our study, This blue shift occurs at the molecular level due to the substantial splitting of the single electron state generated by strong interactions between nearby molecules via strong electron pairing [18].

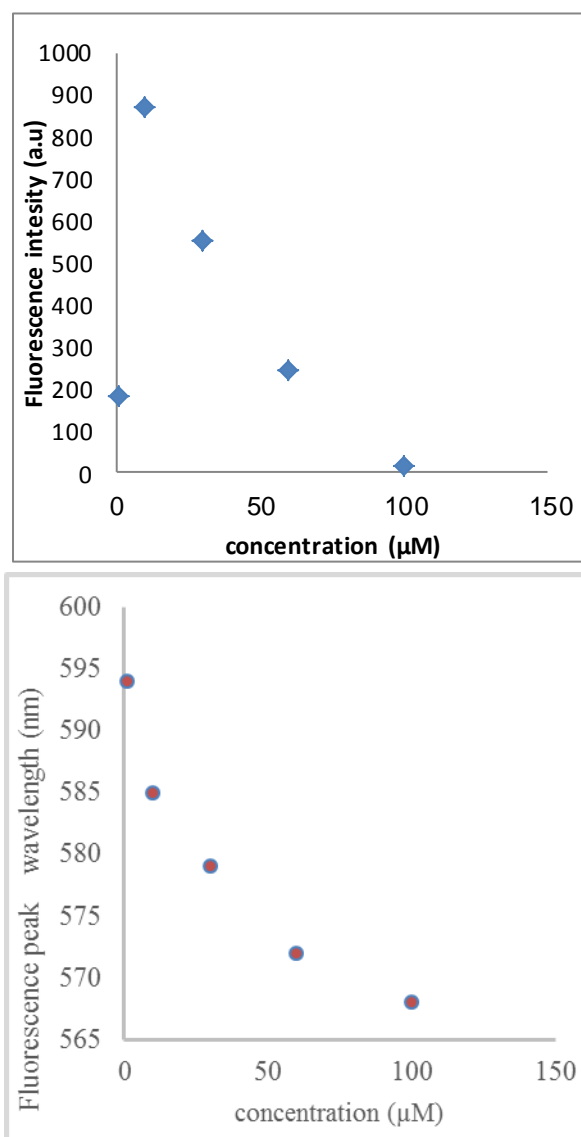


Figure (7): Fluorescence as a function of concentration (a), and (b) the relationship of peak wavelength with concentration

The results obtained for the absorption and fluorescence spectra can also be summarized in Table no.1

Table (2): Conclude the obtained results for absorbance and fluorescence.

Molar Concentration (M)	Absorbency (a.u.)	Wavelength (nm)	fluorescence	Wavelength (nm)
1×10^{-4}	3	559	10	568
6×10^{-5}	2.5	544	242	572
3×10^{-5}	1.5	543	550	579
1×10^{-5}	0.7	543	870	585
1×10^{-6}	0.2	540	180	594

Conclusion:

In this research, a comprehensive study was study and comparison of dye concentrations to help the selection of an appropriate concentration for a particular application. Several concentrations of Rh- B dye were taken (1 to 100 μmol). The absorption and fluorescence spectra were studied, and it was found that by increasing the molar concentration, the absorbance increased according to Beer-Lambert's law. As for the fluorescence, it was suppressed by increasing the concentration due to the many collisions between the excited state particles and the ground state.

Acknowledgments:

The authors would like to express their gratitude to the University of Mustansiriyah (www.uomustansiriyah.edu.iq), Bagdad, Iraq, for their support of this study, as well as the Ministry of Science and Technology.

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على الخواص الطيفية "b" دراسة تأثير تركيز رودامين

مستخلص البحث:

في هذا البحث تم دراسة تأثير التركيز المولاري لصبغة الرودامين b المذاب في الكحول الأيثيلي على الخواص الطيفية (الامتصاصية والفلورة). وأظهرت النتائج زيادة في قمم الامتصاصية وإزاحة قمم الفلورة للأطوال الموجية الأقصر مع زيادة التركيز المولاري (1-100) مايكرو مول، كذلك بينت النتائج تحسين في قمم الامتصاص والفلورة مع زيادة التركيز المولاري. إن ظاهرة الخمود في قمة الفلورة عند تراكيز أكبر من (60) والناجمة من ميكانيكية التصادم. ولوحظ أن قانون بير-لامبرت هو السائد في التراكيز الواطئة، ولكنها تحيد عن هذه القاعدة في التراكيز العالية نتيجة مساهمة الجزيئات الثنائية وتجمعات الكتل الصبغية.

الكلمات المفتاحية: صبغة الرودامين b، الامتصاصية، الفلورة، المفاتيح الضوئية.