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A Study of the Spectral Properties of Rhodamine (6G&B) Dyes Mixture Dissolved in Chloroform

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ABSTRACT

The spectral properties (absorption and fluorescence) of laser dyes (R6G& R B) mixture have been studied; this type of laser dye belongs to the Xanthenes family, and has been dissolved in chloroform to prepare ($1*10^{-5}$, $2*10^{-5}$, $5*10^{-5}$, $7*10^{-5}$, $1*10^{-4}$ M) at room temperature.

The achieved results pointed out to an increase in the absorption and fluorescence intensities with the increased concentration which are found in agreement with Beer – Lambert law. These results have been also showed an expansion in the spectral range of absorption and fluorescence with a noticed shift in the direction of longer wavelength.

The quantum efficiency of the dissolved Rhodamine mixture in chloroform has been calculated by using the same above concentration (96%, 91%, 80%, 71%, and 66%) respectively. The radiative life time (0.21 , 0.41,0.89,1.19 and 1.48) ns and fluorescent life time (0.20 , 0.37,0.71,0.84, and 0.97) ns respectively .

It has been determined that the resulting overlap between the absorption spectrum and fluorescence spectrum for(R 6G&RB) mixture is more than that shown for the every dye alone solution, therefore stock shift will be more.

Keywords: Xanthene dyes, Rhodamine, Laser dye, Rhodamine 6G, Rhodamine B.

دراسة الخواص الطيفية لمزيج من صبغة الرودامين (6G&B) مذابة في الكلوروفورم

الخلاصة

تمت دراسة الخواص الطيفية (الامتصاصية و الفلورة) لمزيج الصبغة الليزرية (رودامين 6G و رودامين B) ، تنتمي هذه الصبغات لعائلة الزانثين ، والمذابة في مذيب الكلوروفورم لتحضير($1*10^{-5}$, $2*10^{-5}$, $5*10^{-5}$, $7*10^{-5}$, $1*10^{-4}$) مولاري وبدرجة حرارة الغرفة.

أظهرت النتائج زيادة في شدة الامتصاصية و الفلورة مع زيادة التركيز والتي تتوافق مع قانون بيير -لامبرت .وكذلك توسيع المدى الطيفي للامتصاص و الفلورة وحدوث أزاحه لقمة طيف الامتصاص و الفلورة باتجاه الأطوال الموجية الأطول.

الكفاءة الكمية المحسوبة لصبغة الرودامين المذابة في مذيب الكلوروفورم باستعمال التراكيز السابقة فكانت كما يلي(96%،91%، 80% ،71%، و66%) على التوالي،وكذلك زمن العمر

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الإشعاعي(0.21،0.41،0.89،1.19،و1.48) على التوالي. كما تم حساب زمن عمر التألق وكما يلي(0.20،0.37،0.71 ،0.84،و0.97) على التوالي.

إن التداخل الحاصل بين طيف الامتصاص وطيف الفلورة لمـزيج (R6G&RB) أكثـر مـن التداخل الحاصل لمحلول كل صبغة منفردة ، لذلك فأن حيود الحزمة سيكون أكثر .

الكلمات المرشدة: صبغات الزانثين، الرودامين، صبغة ليزر، رودامين (6G)، (B) .

INTRODUCTION

Most dye lasers today operate with materials that belong to the class of xanthene dyes. They cover the wavelength region from 500-700nm and are generally very efficient [1]. Xanthene dyes are those containing the xanthylium as chromophore with amino or hydroxy groups meta to the oxygen as the usual auxochromes. Rhodamines are commercially the most important amino xanthenes**.** The organic dye laser has found many applications in scientific research because of its unusual flexibility [2].

There are large amount of data about laser dyes from many authors, Douglas Magde and co-workers studied fluorescence quantum yields and their relation to lifetimes of Rhodamine (6G) and fluorescence in nine solvent [3].

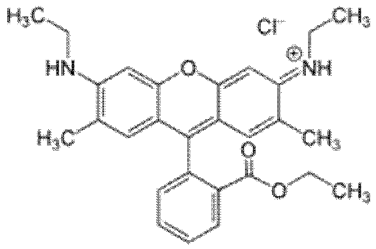
Annieta P. K. and co-workers studied photosensitivity of laser dye mixtures in polymer matrix, using Polymethyl methacrylate (PMMA) films doped with Rhodamine 6G -Rhodamine B dye system [4]. Kalif L.K. studied the quantum efficiency and radiative life-time of polymer PMMA dopped with Coumarin-47 dye laser[5]. Barka N. and co-workers studied the photocatalytic degradation of five dyes on dynamic solar pilot plant using non-woven fibers coated with TiO2 as photocatalyst [6]. Abd El Mongy S. studied the spectroscopic properties of Rhodamine 6G Doped in Polystyrene [7].

In this study we chose two kind of Rhodamine dye and studied the effect of blending them in different concentrations using chloroform as a solvent on spectral properties.

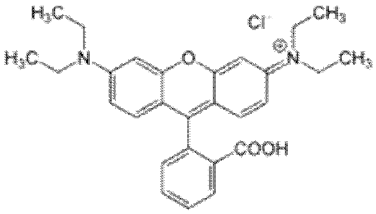
EXPERIMENTAL PART

Materials and Chemicals

This work has been carried out with dyes of xanthenes derivative, Rhodamine 6G chloride which has the structure:



Molecular formula $C_{28}H_{31}N_2O_3Cl$, molar mass 479.02 g/mole).
Rhodamine B, which has the structure:



Molecular formula $C_{28}H_{31}N_2O_3Cl$, molar mass 479.02 g/mole), HIMEDIA company, India. Chloroform was used as a solvent which purity is (99.5%), Analar company (England)**.** Electronic balance type (Denver Instrument).

Spectroscopic Measurement

The measurements of the absorption spectrum of the samples are taken by using a spectrophotometer (Metertech, SP8001, UV/VIS Spectrophotometer), and the emission spectrum taken by using (Spectrofluorometer-model SL174, Elico). Refractive index is taken by using refractometer (Bellingham and Stanley Ltd, Tunbridgewells, ABBE60, England).

Solvent(chloroform)

The study showed that there is no absorption and overlapping at the fluorescence spectrum range of chloroform and Rhodamine dye within wavelength range (400-700nm).

Preparation of dyes:

The powder of Rhodamine dyes are accurately weighted by using analytical balances (Denver instrument, TP-214, Germany).
Solutions of concentration ($1*10^{-5}$,$2*10^{-5}$, $5*10^{-5}$, $7*10^{-5}$,$1*10^{-4}$ M) of two dyes (R6G, RB) in chloroform solvent were prepared. Concentrations were prepared according to the following equation:-

$$W = \frac{M_W \times V \times C}{1000} \qquad \mathbf{K}(1)$$

Where: W weight of the dissolved dye (gm), M_W molecular weight of the dye (gm/mol), V the volume of the solvent (ml),C the dye concentration (mol/l).

The prepared solutions were diluted according to the following equation:-

$$C_1 V_1 = C_2 V_2 \qquad \ldots(2)$$

Where: C_1 primary concentration, C_2 new concentration, V_1 the volume before dilution, V_2 the volume after dilution.

Measuring of Quantum efficiency (q_{fm}):

Quantum efficiency is defined as the ratio between the number of quanta emitted and the number of quanta absorbed:

$$q_{fm} = \frac{Number\ \ Of\ \ Quanta\ \ Emitted}{NumberOfQu\ anta\ \ Absorbed} \qquad \mathbf{K}(3)$$

The spectrum of the molecular fluorescence F (ύ) gives the relative fluorescence intensity at wave-number (ύ); this is related to the quantum efficiency by the following equation**:**

$$q_{fm} = \int_0^{\infty} F(u')du' \qquad \mathbf{K}(4)$$

In order to evaluate absolute quantum efficiency, we have to consider both the radiative and non-radiative processes taking place in the medium, therefore

$$q_{fm} = \frac{K_{fm}}{K_{fm} + \Sigma K_d} = \frac{K_{fm}}{K_{fm} + K_{IC} + K_{ISC}} \qquad \mathbf{K}(5)$$

Since

$$Kfm = \frac{1}{t_{fm}} \qquad \mathbf{K}(6),$$

and

$$tf = \frac{1}{Kfm + \sum Kd} \qquad \mathbf{K}(7)$$

Where: K_{fm} is radiative emission probability, τ_{fm} is non-radiative life time, τ_f is fluorescence life time.

Therefore:

$$q_{fm} = \frac{t_f}{t_{fm}} = \int_0^{\infty} F(u')du' \qquad \mathbf{K}(8)$$

Radiative emission probability measurement (K_{fm})

The radiative emission probability (K_{fm}) can be determined from Bowen-wokes equation [8]:

$$Kfm = \frac{1}{tfm} = 2.88 \times 10^{-9} \times n^2 \times (\bar{u}^2) \int e(\bar{u}) d\bar{u} \qquad \mathbf{K}\ (9)$$

Where: n is refractive index, ε is molar absorption coefficient, ύ is wave number.

RESULTS AND DISCUSSION

Absorption and fluorescence spectrum

The absorption and fluorescence spectrum of R 6G, and R B before mixing at concentration ($1*10^{-5}$,$2*10^{-5}$, $5*10^{-5}$, $7*10^{-5}$ $1*10^{-4}$,M) are shown in figure (2),(3)respectively.

The absorption and fluorescence spectrum for mixtures of R 6G and R B at concentration ($1*10^{-5}$, $2*10^{-5}$, $5*10^{-5}$, $7*10^{-5}$ $1*10^{-4}$,M) are shown in figure (4).

From these figures we can observed that (R 6G, R B, and the mixture) solution absorption spectrum has a wide spectral range at wavelength range between (400-700nm).

It has also been showed that maximum absorption for R6G appears at higher concentration ($1*10^{-4}$M) at wavelength (514nm) and red shifted by approximately (57nm),while at lower concentration ($1*10^{-5}$ M) at wavelength (528nm) and red shifted by approximately (22nm).For RB the maximum absorption also appears at higher concentration ($1*10^{-4}$M) at wavelength (524.8nm) and red shifted by approximately (60nm) , while at lower concentration ($1*10^{-5}$ M) at wavelength (546.6nm) and red shifted by approximately (20nm). And for the mixture the maximum absorption also appears at higher concentration ($7*10^{-5}$M) at wavelength (528nm) and red shifted by approximately (56nm) , while at lower concentration ($1*10^{-5}$ M) at wavelength (531.75nm) and red shifted by approximately (26nm).

These behaviors are due to the increase in concentration which produces an increase in number of molecules in volumetric unit which effect in the energy state.

The wavelength at relative maximum intensity for absorption and fluorescence of R 6G, and R B at study stock concentration listed in table (1), (2).

The wavelength at relative maximum intensity for absorption and fluorescence of R 6G and R B mixtures at study stock concentration listed in table (3).

Quantum efficiency:

From the results of calculation by using computer model (Matlab 6.5), and equation (3), the result of fluorescence quantum efficiency yield is listed in table (1), (2) for each R 6G and R B, and in table (3) for the mixture at study stock concentration.

We observed that the quantum efficiency yield decrease with increasing the concentration of (R 6G, R B, and the mixture) solution. This is due to reduce self absorption process.

Radiative and fluorescence life time

From equation (9) radiative emission probability was calculated, radiative life time from equation (6) ,and fluorescence life time from equation (8),the result are listed in table (1), (2) for each R 6G and R B , and in table (3) for the mixture at study stock concentration. We observed that the radiative life time and fluorescence life time increase with increase in the concentration, and fluorescence life time less than radiative life time because of non radiative processes (Internal conversion ,Inter system crossing).

CONCLUSIONS

From the observations it can be concluded that:

- There is an increase in the relative intensity of fluorescence for R6G, RB, and (R6G, RB) mixture with increasing in the concentration.
- The stock shift of R6G, RB, and (R6G, RB) mixture increase with increasing the concentration.
- There is a reduction of quantum efficiency yield with increasing in the concentration.
- Quantum efficiency yield of the (R6G, RB) mixture is more than that of RB dye, but less that of R6G dye.
- Radiative emission probability of the (R6G,RB) mixture is more than that of RB dye, and approximate to that of R6G dye.
- Mixing R6G dye can be enhance the property of RB dye.

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Table (1): The wavelength at relative maximum intensity for absorption and fluorescence, quantum efficiency yield, radiative emission probability, radiative life time, and fluorescence life time for R6G dye.

C	ABS max.	$F._{max}$	Stock Shift	Quantum efficiency	K_{fm}	τ_{fm} sec.	τ_f sec.
$1*10^{-5}$	528	550	22	0.97	4.28269	0.2335	0.2264
$2*10^{-5}$	530	554.5	24.5	0.93	2.1944	0.4556	0.4237
$5*10^{-5}$	526	563.5	37.5	0.76	1.1923	0.8386	0.6373
$7*10^{-5}$	518	568	50	0.74	0.9876	1.0124	0.7492
$1*10^{-4}$	514	571.5	57.5	0.69	0.7962	1.2558	0.8665

Table (2): The wavelength at relative maximum intensity for absorption and fluorescence, quantum efficiency yield, radiative emission probability, radiative life time, and fluorescence life time for RB dye.

C	ABS max.	$F._{max}$	Stock Shift	Quantum efficiency	K_{fm}	τ_{fm} sec.	τ_f sec.
$1*10^{-5}$	546.6	567	20.4	0.81	2.6921	0.3714	0.3008
$2*10^{-5}$	547.2	574.5	27.3	0.83	1.4759	0.6775	0.5623
$5*10^{-5}$	539.5	580	40.5	0.70	0.9444	1.0588	0.7411
$7*10^{-5}$	533.2	581.5	48.3	0.63	0.7923	1.2620	0.7950
$1*10^{-4}$	524.8	585	60.2	0.58	0.6488	1.5411	0.8938

Table (3): The wavelength at relative maximum intensity for absorption and fluorescence, quantum efficiency yield, radiative emission probability, radiativelife time and fluorescence life time for R 6G and R B mixtures.

Conc.	ABS max.	F_{max}	Stock Shift	Quantum efficiency	K_{fm}	τ_{fm} nSec	τ_f nSec
$1*10^{-5}$	531.75	558.5	26.75	0.96	4.7210	0.2118	0.2033
$2*10^{-5}$	535.64	568	32.36	0.91	2.3951	0.4175	0.3799
$5*10^{-5}$	534.99	577.5	42.51	0.80	1.1190	0.8935	0.7148
$7*10^{-5}$	528.08	584.5	56.42	0.71	0.8388	1.1921	0.8463
$1*10^{-4}$	529.94	584.5	54.56	0.66	0.6742	1.4831	0.9788

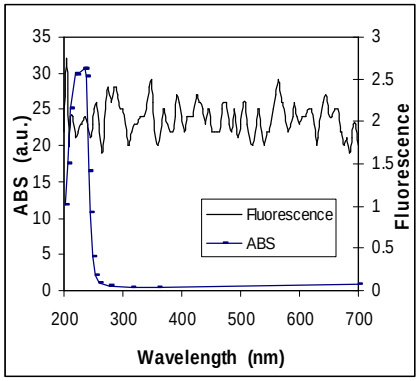
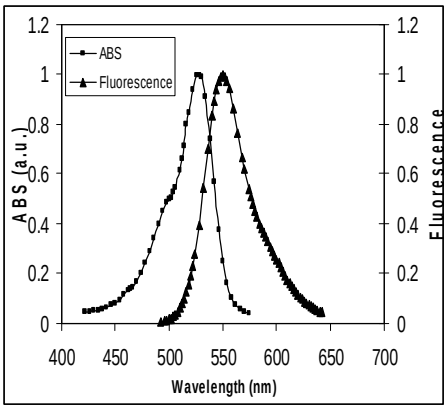
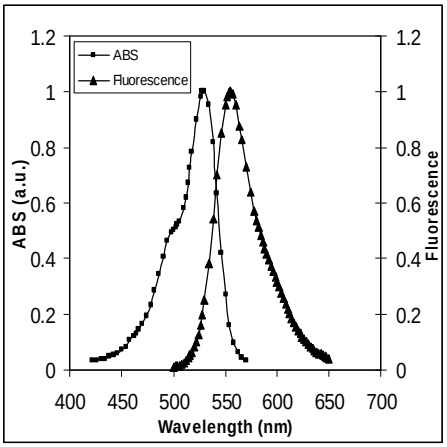


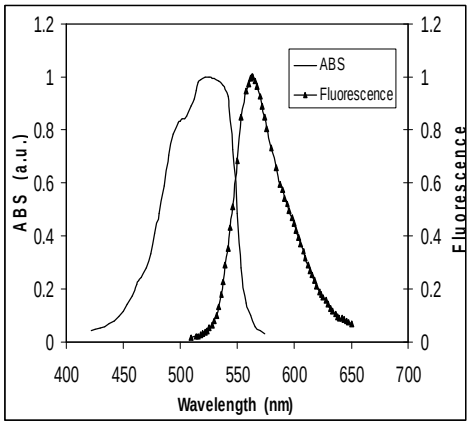
Figure (1): Absorption and fluorescence spectrum of chloroform.



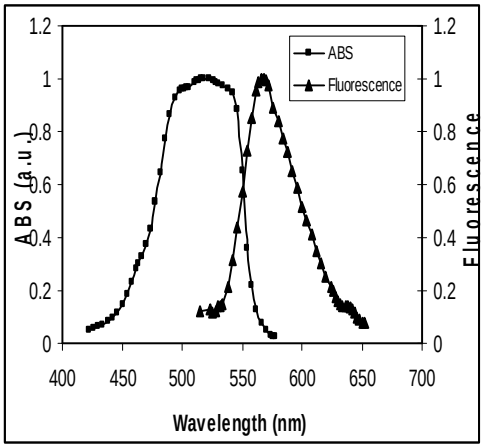
(2a) at ($1*10^{-5}$) M.



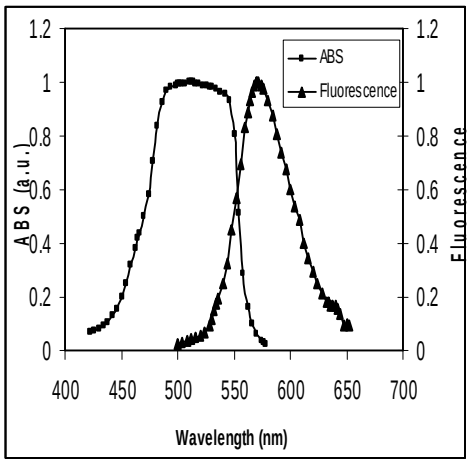
(2b) at ($2*10^{-5}$)M.



(2c) at ($5*10^{-5}$)M.

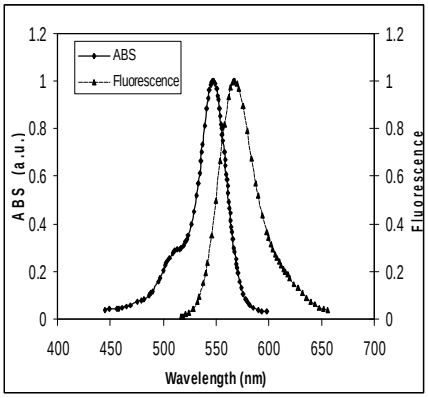


(2d) at ($7*10^{-5}$)M.

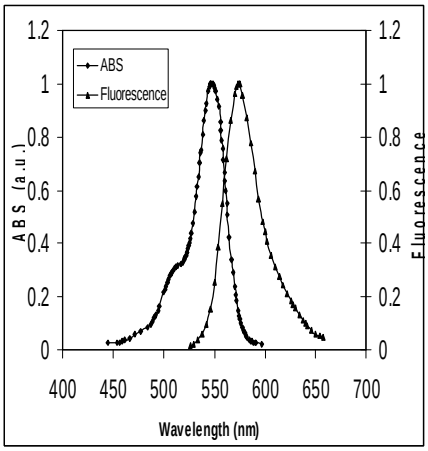


(2e) at ($1*10^{-4}$)M.

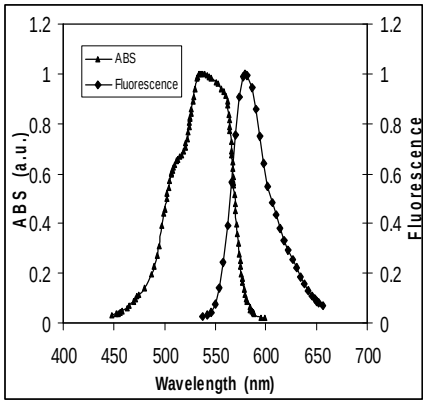
Figure (2): Absorption and fluorescence spectrum of R6G for various concentrations



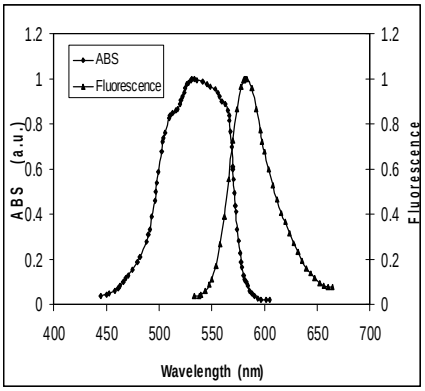
(3a) at $(1*10^{-5})$M.



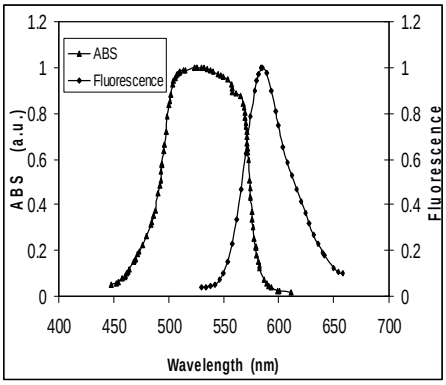
(3b) at $(2*10^{-5})$ M.



(3c) at $(5*10^{-5})$ M.

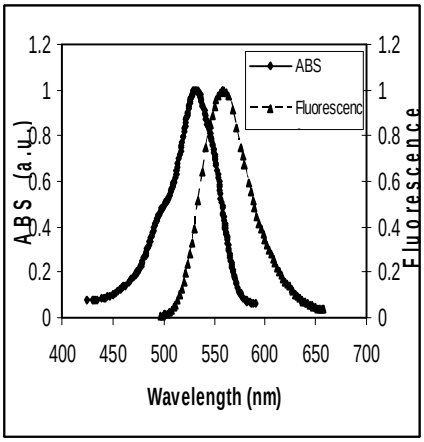


(3d) at ($7*10^{-5}$) M.

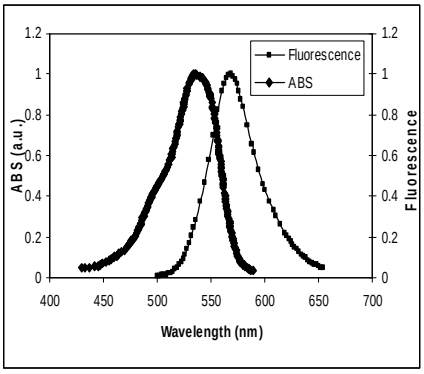


(3e) at ($1*10^{-4}$) M.

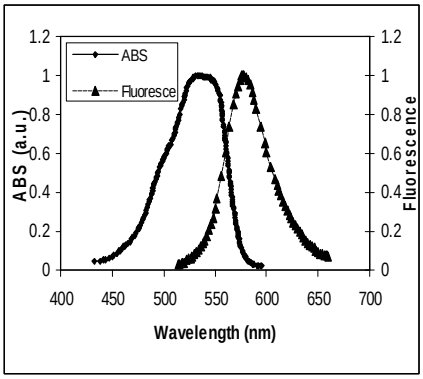
Figure (3): Absorption and fluorescence spectrum of RB for various concentrations



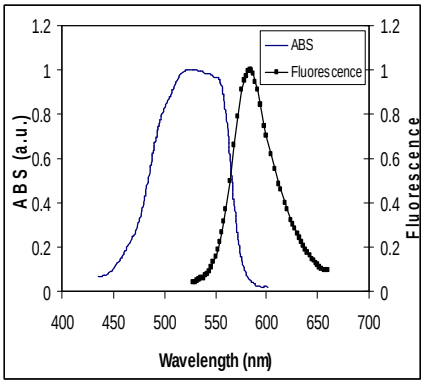
(4a) at $(1*10^{-5})$M.



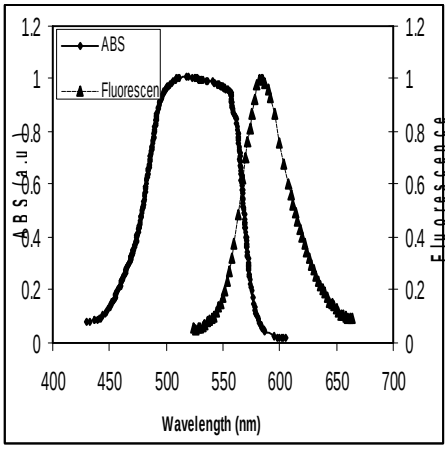
(4b) at $(2*10^{-5})$ M.



(4c) at $(5*10^{-5})$M.



(4d) at $(7*10^{-5})$M.



(4e) at $(1*10^{-4})$M

Figure (4): Absorption and fluorescence spectrum of R 6G and R B mixtures for various concentrations:-