

	<p>Journal Homepage: www.journalijar.com</p> <p>INTERNATIONAL JOURNAL OF ADVANCED RESEARCH (IJAR)</p> <p>Article DOI:10.21474/IJAR01/11655 DOI URL: http://dx.doi.org/10.21474/IJAR01/11655</p>	
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RESEARCH ARTICLE

INVESTIGATION IN SPECTROSCOPIC CHARACTERISTICS OF RHODAMINE C IN 1- BUTANOL

Slafa I. Ibrahim, M.K. Abood and K.S. Rida

Energy and Renewable Energies Technology Center, University of Technology, Baghdad, Iraq.

Manuscript Info

Manuscript History

Received: 10 July 2020

Final Accepted: 14 August 2020

Published: September 2020

Abstract

This research investigation is interesting to obtain information of absorption and fluorescence spectrum of the Rhodamine C dye in 1-butanol and the variations which happened in diverse concentration (1×10^{-5} , 2×10^{-5} , 4×10^{-5} , 6×10^{-5} , 8×10^{-5} and 1×10^{-4}) mole/l at ambient temperature. The outcomes obtained showed that there was a red shift with increasing concentration, the energy gaps decreasing from (2.168 to 2.1 eV) with increasing concentration. Also the extinction coefficient, real and imaginary dielectric constants are in agreement with resulted data.

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Introduction:-

Laser dyes are important because of their contributions to the fields of science and technology and its applications in the fields of optics, electronics, chemical dyes, communication networks as well as sensors [1]. One of the most significant kinds of fluorescent dyes is Xanthene dyes, which are characterized by spectrum variation and cumulating phenomena [2]. Rhodamine C (Rh C) is one of these dyes that utilized as "active media" for "tunable lasers" in the visible area of the light spectrum [2].

Rhodamine dyes are "self-associated" in diverse liquid crystal "Anisotropic solvent" host materials such as ethanol "isotropic solvent" and this is fundamental in the electronic technology [3].

The influence of solvents on the absorption spectrum and on the effectiveness of organic dyes was studied since the last century. As is known, the "photo-physical" behavior of a solved dye depends on the kind of its environment such as (intensity, shape). The solvent nature and "solvent- solute interactions" effects on the maximum wavelength of the dye absorption band. This influence is exceedingly related to the kind and degree of interactions between dye and solvent [4]. Therefore, Rhodamine dyes are sensitive to the conditions in which preparations are made and the nature of solutions used, whether acidic or alkaline [5].

Organic dyes dissolved in appropriate solvents have been widely used as laser media for many years. Which have contributed to a wide coverage of wavelength and the tunability in addition to the important fluorescence yield, but their applications have been limited (because of the toxicity, evaporation, inflammability, etc.) of some solvents, and some restrictions have been put on their use and make them in specific applications [6]. The spectroscopic properties of dyes with moieties electron donor and acceptor have received great attention due to solubility of fluorescence probes. Fluid mixing in aqueous solution can be quantified by used fluorescent dyes. Two fluorescent dyes can be separated optically using a general technique including fluorescence rationing [7].

The most effective Rhodamine derivatives are getting by replacing hydrogen of the Rhodamine dye skeleton by groups such as alkyls, amines, etc. This replacing will change the "ground state" and "excited state" dipole moments of exchanged Rhodamine molecules in addition to its "photo-physical" properties. Along with changes, influence of solvents in solutions play an important role in difference of "photo-physical" properties. The extent interactions

Corresponding Author:-Slafa I. Ibrahim

Address:-Energy and Renewable Energies Technology Center, University of Technology, Baghdad, Iraq.

between solute–solvent relied on solvent "relative permittivity" and "refractive index" in addition to the "dipole moment" for the solute [8].

This research is a continuation of the research series carried out by the team of researchers at the Center for Energy Technology and Renewable Energies at the University of Technology, Baghdad, Iraq [9-12].

Experimental Part

Materials & Devices

The Xanthene dye Rhodamine C, obtained from "HIMEDIA Company", India, with molecular formula " $C_{28}H_{31}N_2O_3Cl$ ", and molar mass (479.02 g/mole). This was dissolved in "1- Butanol" from "E. Merck AG, Darmstadt company", Germany, with refractive index (1.399685) at 20 °C, to prepare solutions with different concentrations (1×10^{-5} , 2×10^{-5} , 4×10^{-5} , 6×10^{-5} , 8×10^{-5} and 1×10^{-4}) mole/l.

The devices utilized in this research include "Refractometer" from (Bellingham and Stanley Ltd, Tunbridgewells, ABBE60, England), the excitation and emission spectrum were obtained from "Agilent Technologies Cary Eclipse Fluorescence Spectrophotometer (Malaysia)".

Estimation of optical properties values:

Radiative emission probability (K_{fm}) can be calculated from Bowen-wokese equation [13]:

$$K_{fm} = 2.88 \times 10^{-9} \times n^2 \times (\bar{\nu}^2) \int \epsilon(\bar{\nu}) d\bar{\nu} \quad \text{--- (1)}$$

Non-radiative life time (τ_{fm}) and fluorescence life time (τ_f) from:

$$\tau_{fm} = \frac{1}{K_{fm}} \quad \text{--- (2)}$$

$$\tau_f = q_f \times \tau_{fm} \quad \text{--- (3)}$$

Where quantum efficiency (q_{fm}) equal to:

$$q_{fm} = \frac{\text{Number Of Quanta Emitted}}{\text{Number Of Quanta Absorbed}} \quad \text{--- (4)}$$

The absorption coefficient (α), optical energy gap of Rhodamine dye, extinction coefficient (k), optical refractive index (n), real dielectric constant (ϵ_r), and imaginary dielectric constant (ϵ_i) can be calculated depending on the outcome of the optical properties from the following equations [14- 16]:

$$\alpha = \frac{2.303 A}{d} \quad \text{--- (5)}$$

Where: (α) absorption coefficient (cm^{-1}), (A): absorption at a specific wavelength.
(d): thickness.

$$\alpha_{hv} = A(h\nu - E_g)^2 \quad \text{--- (6)}$$

Where: (α) absorption coefficient (cm^{-1}), (A) constant depend on the transitions (h) Planck's constant, and (ν) photon frequency.

$$K = \frac{\alpha \lambda}{4\pi} \quad \text{--- (7)}$$

Where: (λ) is the wave length of the "incident photon".

$$n = \frac{1+R}{1-R} \sqrt{\frac{4R}{(1-R)^2} - K^2} \quad \text{--- (8)}$$

Where R is the reflection.

$$\sigma = \frac{\alpha n}{4} \text{ --- (9)}$$

$$\varepsilon_r = n^2 - K^2 \text{ --- (10)}$$

$$\varepsilon_i = 2nK \text{ --- (11)}$$

Result and Discussion:-

It is clear from the result obtained as shown in table (1) that the peak of absorption and fluorescence wavelength shows a (Red shift) with increasing concentration and this agreement with Beer – Lambert law.

Table (1):- The spectral parameters of Rhodamine C in 1-Butanol.

Conc.	Wavelength (ABSmax.) (nm)	FWHM (nm)	Wavelength (Fmax.) (nm)	Stock shift (nm)	Quantum efficiency %	K _{fm}	t _{fm} (nsec)	t _f (nsec)
1*10 ⁻⁵	548	49	569	21	62.662	30.6414	0.03263	0.02045
2*10 ⁻⁵	556	35	573	17	82.4178	10.548	0.0948	0.07813
4*10 ⁻⁵	564	27	575	11	92.2511	3.858	0.2592	0.2391
6*10 ⁻⁵	570	23	579	9	92.8439	2.9349	0.34072	0.31634
8*10 ⁻⁵	573.97	23	582.98	9	93.2289	1.5181	0.6587	0.6141
1*10 ⁻⁴	576	23	586	10	93.69	1.2133	0.8241	0.7721

Calculated spectral parameters; full width at half maximum (FWHM), Stock shift, quantum efficiency, radiative emission probability, Non-radiative life time and fluorescence life time of Rhodamine C are listed in table (1).

The "radiative life time" and "fluorescence life time" are increased with increasing in the concentration of Rhodamine C. The "fluorescence life time" was less than "radiative life time" because of "non radiative" processes.

It is also noted from the table that the value of (FWHM) was reduced due to the increase in the number of molecules that absorb active absorption by increasing the concentration of the dye.

Optical properties of Rhodamine C dye in 1- butanol in diverse concentration are shown in figure (1), (2), where figure (1) shows the absorption spectrum; and the internal figure shows the relation between (FWHM) and the absorption intensity with the dye concentration. Figure (2) shows the fluorescence spectrum; and the internal figure shows the relation between fluorescence intensity and concentration. Figure (3) shows the relation between stock shift and concentration of samples. And figure (4) shows the relation between absorption and fluorescence maximum wavelength and concentration.

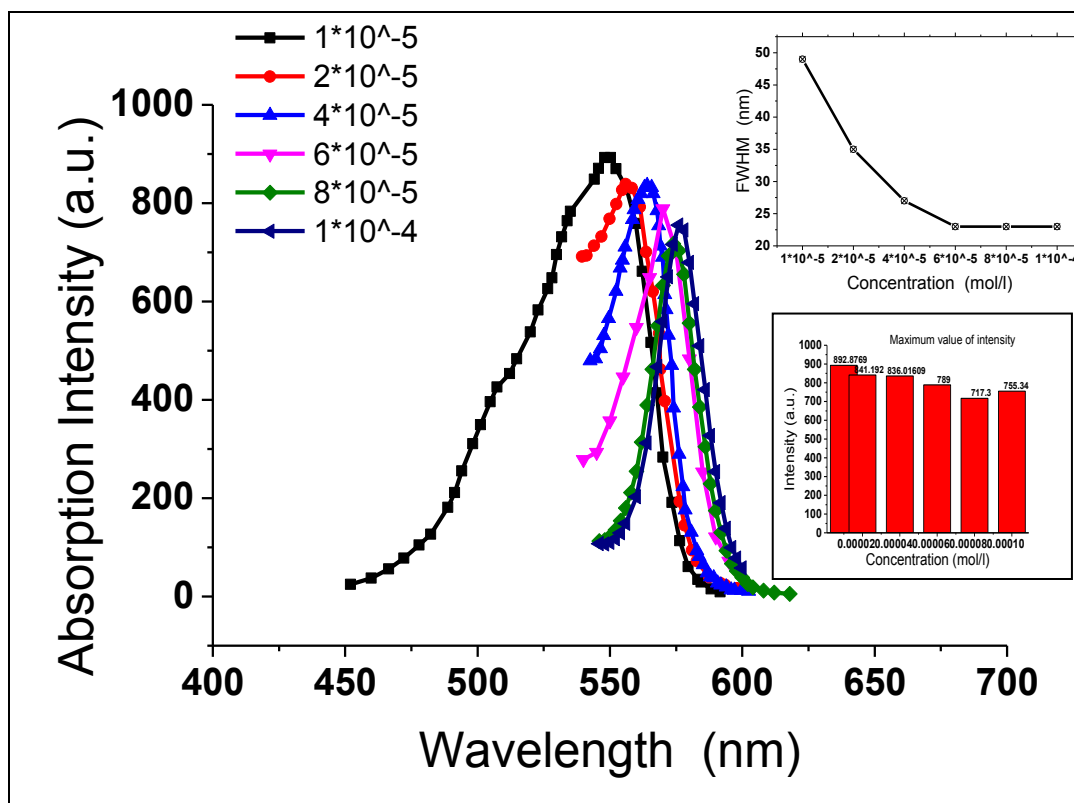


Figure (1):- The relation between wavelength and absorption spectrum of Rhodamine C in 1-Butanol with diverse concentration.

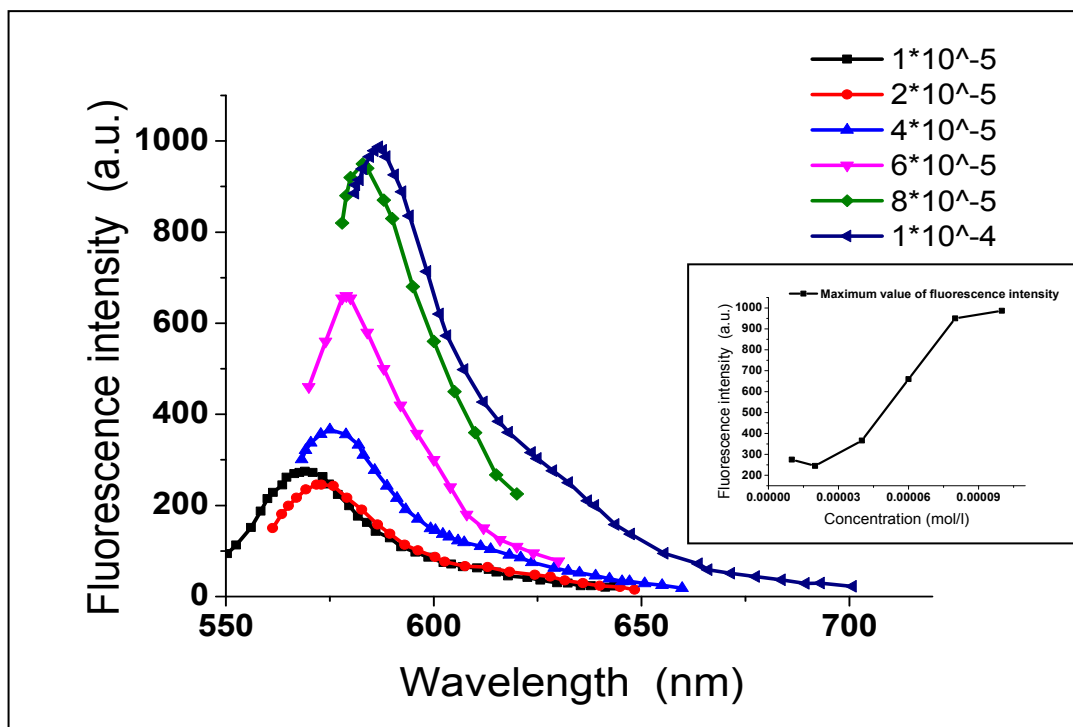


Figure (2):- The relation between wavelength and fluorescence spectrum of Rhodamine C in 1-Butanol with diverse concentration.

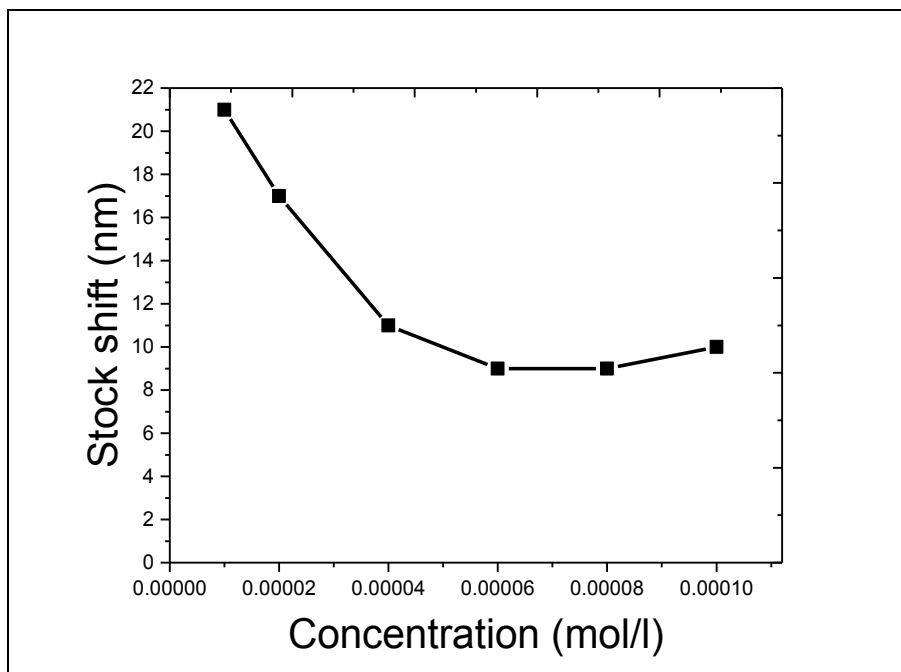


Figure (3):- The relation between stock shift and concentration of samples.

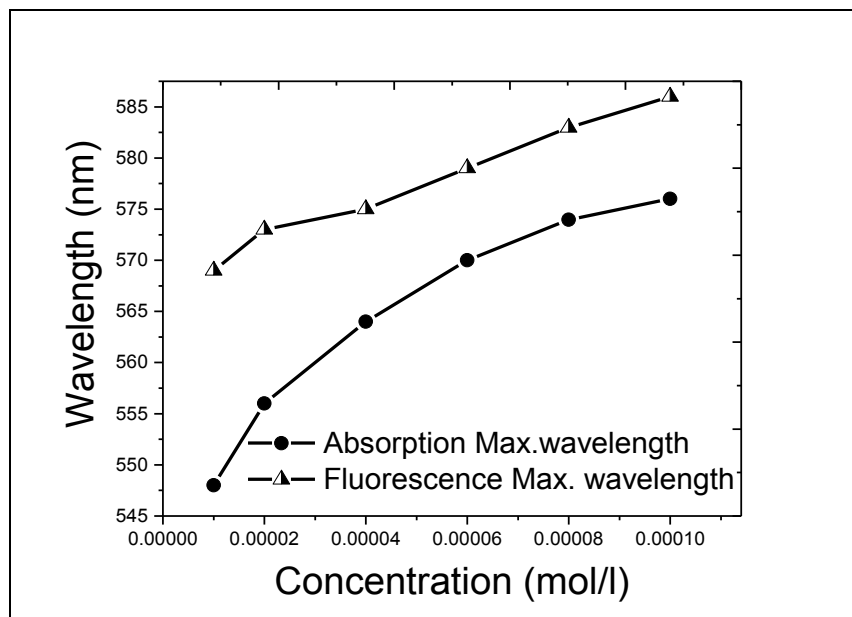


Figure (4):- The relationship between absorption and fluorescence maximum wavelength and concentration.

Another significant quantity is the optical energy gap (E_g) which estimated by using absorption spectrum of the diverse concentration of dye, and plot photon energy versus $(\alpha h\nu)^2$ [17], as shown in figure (5). This indicates a decrease in energy gap due to molecule distances variation with increasing the concentration.

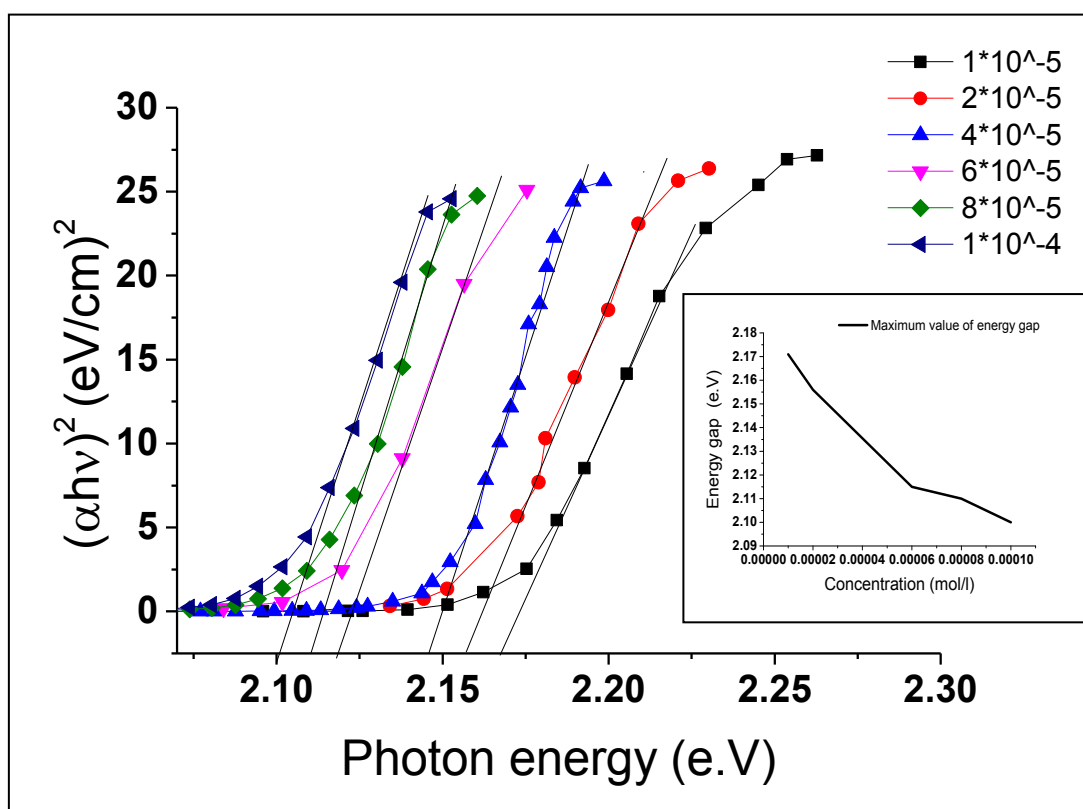


Figure (5):- Relationship between photon energy and $(\alpha h\nu)^2$.

The value of the changing optical refractive index (n) and optical conductivity is very slight and hardly feels, with increasing concentration, the reason for this is polarization of dye molecule [18], as shown in Table (2) and figure (6), (7).

Table (2):- Some optical properties of Rhodamine C in 1-Butanol.

concentration	Energy gap	K	n	conductivity	ϵ_r	ϵ_i
0.00001	2.168	1.00481E-05	2.181887	1.25622131	4.76063	4.38E-05
0.00002	2.157	1.01948E-05	2.181887	1.25622131	4.76063	4.45E-05
0.00004	2.146	1.03415E-05	2.181887	1.25622131	4.76063	4.51E-05
0.00006	2.118	1.04515E-05	2.181887	1.25622131	4.76063	4.56E-05
0.00008	2.11	1.05243E-05	2.181887	1.25622131	4.76063	4.59E-05
0.0001	2.1	1.05619E-05	2.181887	1.25622131	4.76063	4.61E-05

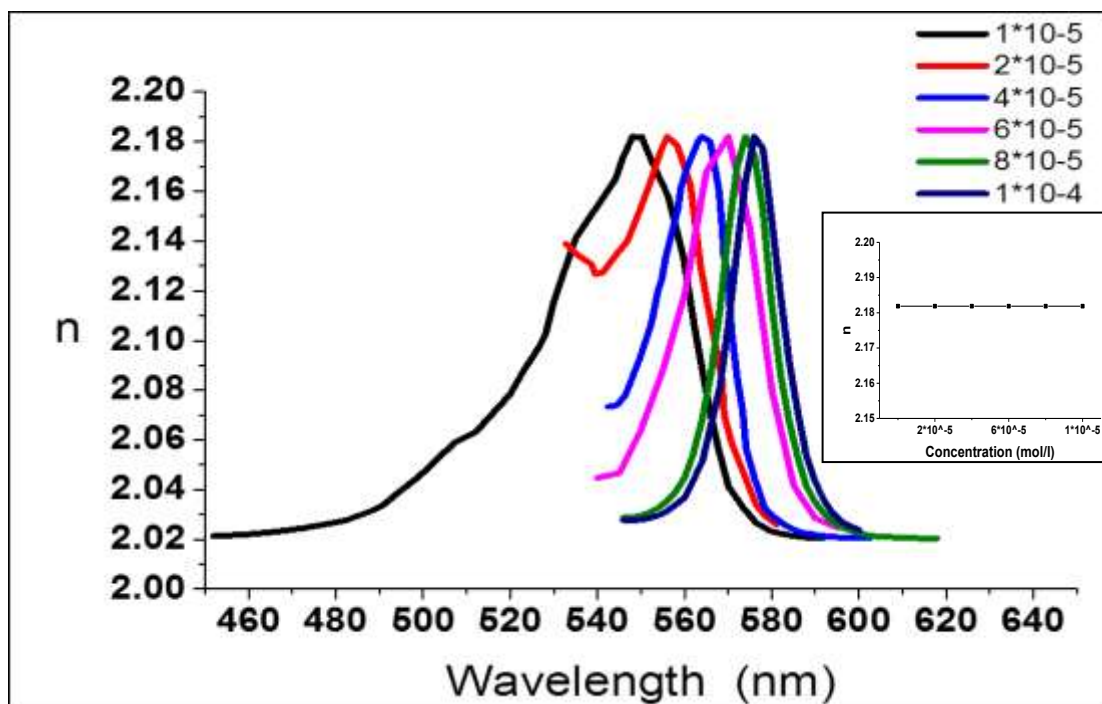


Figure (6):- Relation between wavelength and optical refractive index.

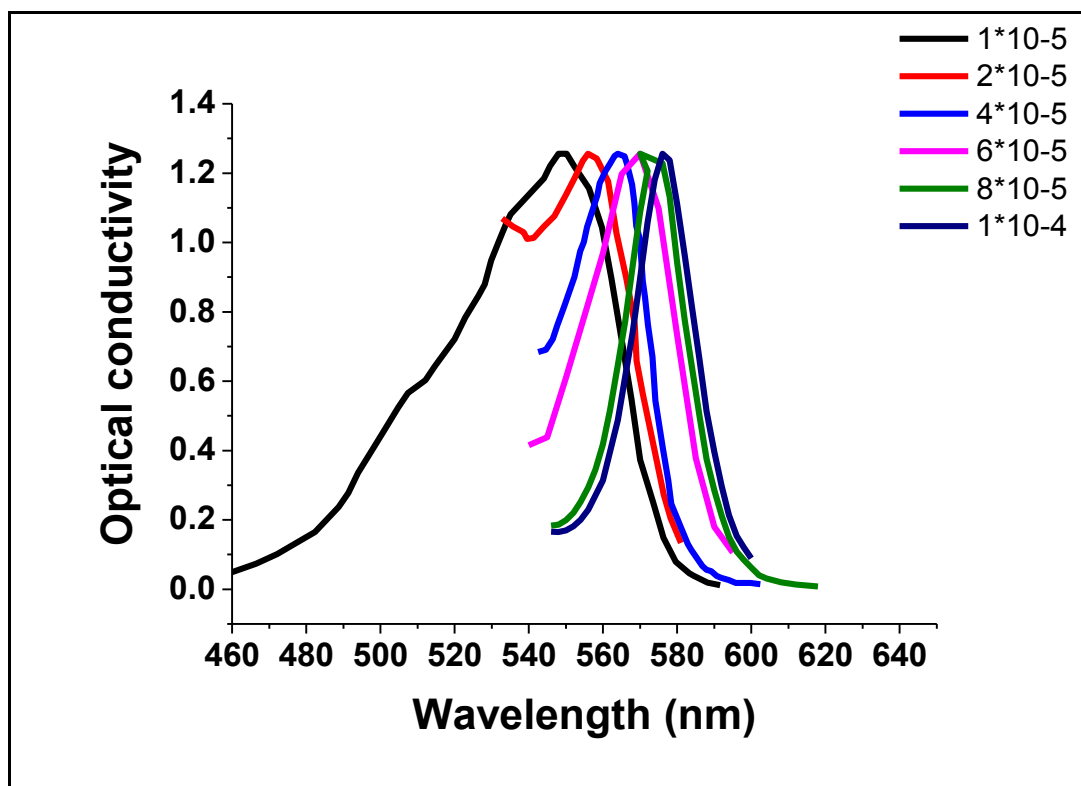


Figure (7):- Relation between wavelength and optical conductivity.

The extinction coefficient(k) is used in established the kind of the dye and it is a criterion of the dye content; and also it is indicate to how strongly a dye to absorb light at fixed wavelength, per molar concentration. Figure (8) illustrates the relation between wavelength and extinction coefficient where their value increases with wavelength and concentration.

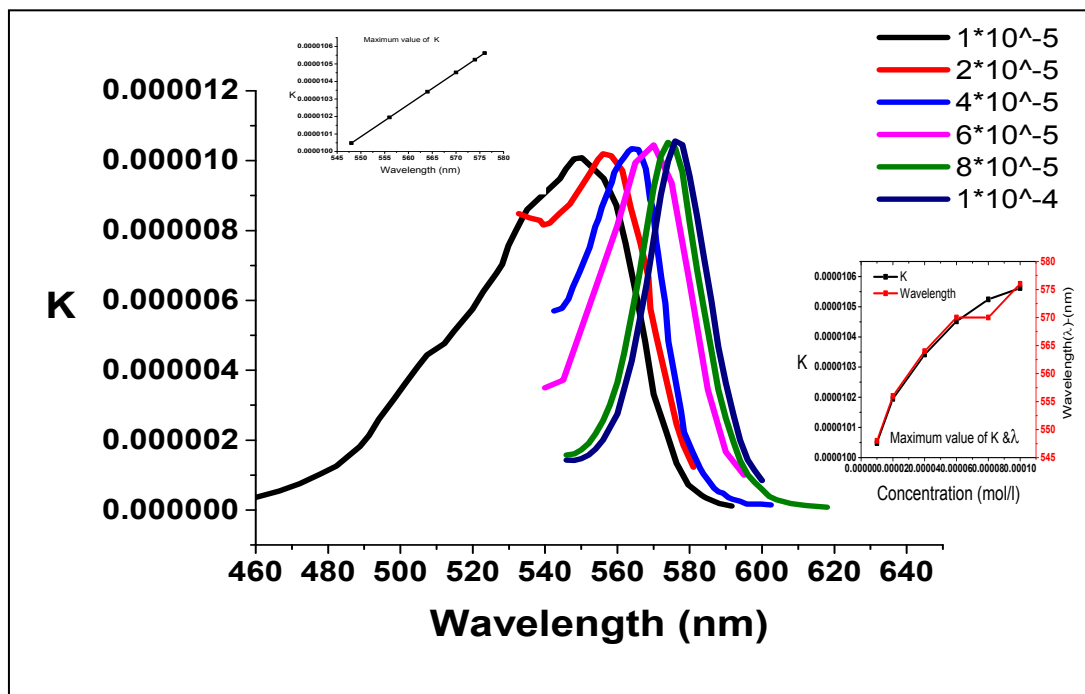


Figure (8):- Relation between wavelength and extinction coefficient (K).

The real dielectric constant value is higher than the imaginary dielectric constant.

Figure (9), (10) illustrates the relation between wavelength and real dielectric constant and imaginary dielectric constant respectively, it is seen that the real dielectric constant decrease with decreasing the photon energy. While imaginary dielectric constant increases with wavelength whose value depends on the (k) value.

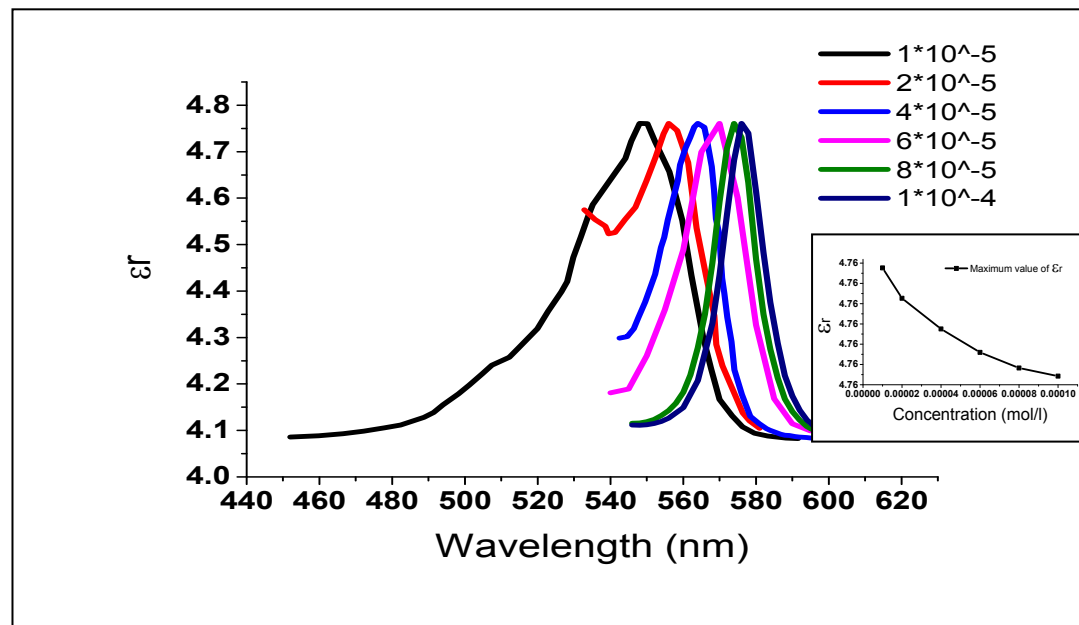


Figure (9):- Relationship between wavelength and real dielectric constant.

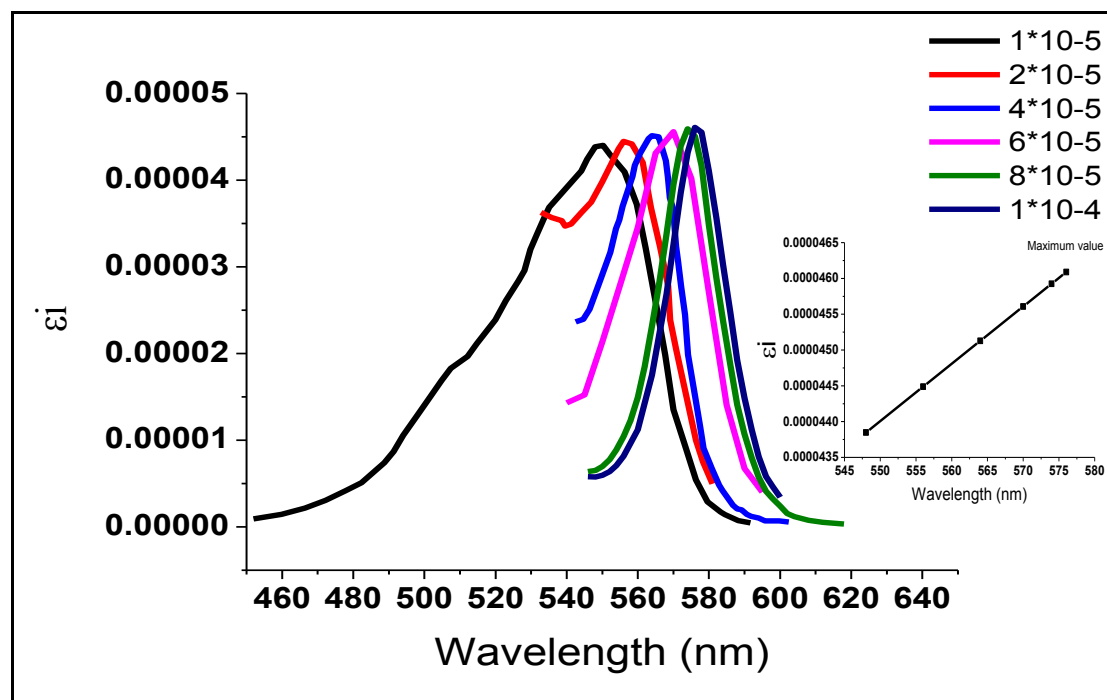


Figure (10):- Relationship between wavelength and imaginary dielectric constant.

Conclusions:-

From the result checking of optical properties it can be inferred that the quantum efficiency for Rhodamine C in 1-Butanol increased with increasing the concentration. While (FWHM) and stock shift and radiative emission probability decreased with increasing concentration. Also the result revealed a decrease in the energy gap with increasing the concentration of dye solution.

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