

## Study the spectroscopic characteristics of Rhodamine B Dye in Ethanol and Methanol mixture and Calculation the Quantum Efficiency

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### Abstract:

The effect of ethanol and methanol solvent, and their mixture has been studied on the absorption and fluorescence spectra of laser dye Rhodamine B at concentration of ( $10^{-4}$ ) Molar at room temperature. The molar absorption coefficient has been determined for mixture which was (3.223) at wave number ( $18181.8 \text{ cm}^{-1}$ ), Also the Quantum Efficiency of the two solvents (ethanol and methanol) and their mixture have been calculated, which was for mixture spectrum (38.94%) and it was larger comparing with other and solvents. The characteristics of spectrum has been determined by calculating ( $\Delta\lambda$ ) of absorption spectrum for the solvents and its mixture at maximum wave number ( $\bar{\nu}$ )  $\text{cm}^{-1}$  depending on solvent polarity and the transitions between molecular energy levels in each solvent of Rhodamine B dye.

**Key words: Rhodamine B, Quantum Efficiency, laser dye, ethanol and methanol.**

### Introduction:

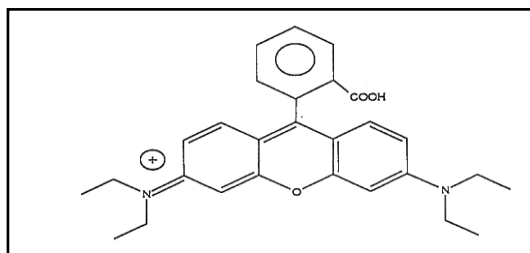
In the past decade we have made some surface photochemical studies of several dyes, including Rhodamines, absorbed onto a scarcely used absorbent powdered microcrystalline cellulose [1-6]. From these studies, a large amount of information concerning room-temperature fluorescence and phosphorescence [1-4] triplet-triplet energy transfer, 3 electron and hydrogen transfer and the nature of the absorption process [5]. As studied in field in the Rhodamine B and related xanthene dyes have been extensively in solution [7-10]. Both molecular structure and solvent play a very important role in the nonradiative pathway of deactivation of the first excited state of these dyes. The cationic forms of Rhodamine B and Rhodamine 101 in acidic ethanol present different [11]. The amino groups in Rhodamine B are fully ethylated, while in Rhodamine 101 the

amino groups are rigidly attached to the xanthenes ring by methylenic bridges. The precise interpretation of the mechanism of internal conversion appears not to be completely stable Rhodamine 101. It also shows a monoexponential decay in ethanol ( $\tau_F$  in ethanol is 4.3 ns and in water is 4.2 ns), while that absorbed on glass with distorted adsorption sites shows a marked decrease in the lifetime [10]. This fact is indicative of the formation of nonplanar conformers.

The most important distinguishing characteristic of reactive dyes is that they form covalent bonds with the substrate that is to Rhodamine B xanthene dye [12]. Upon excitation, there is a change in its dipole moment associated with the internal twisting of the diethylamino group about the CN bond (see figure 1), A twisted-intramolecular-charge-transfer (TICT) state that it formed by the internal

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twisting and characterized by charge transfer from a donor to an acceptor. For rhodamine B, the donor is the amino group and the acceptor is the xantheno ring with the carboxyphenyl group [12(b)].



**Fig (1) : structure of Rhodamine B types.**

The polarity of fluorescence of Molecules in solution has been reported to depend upon various factor ; viscosity of the solvent [13] .migration of the excited state energy from the originally excited molecule ;shape and size of the fluorescent molecule , temperature ,etc. In the present report the effect of dipole moment of the solvent as an extrinsic cause of depolarization has been dealt with [14]. Rhodamine B isothiocyanate was a reactive single anchor dye that can easily be chemically bound to cellulose in the presence of a base [15]. Been in several studies on the changing spectrum absorption of dye is different, in this research we studied the effect of polar nature of the spectrum dye Rhodamine B and prove a nice dye have a higher efficiency in the case of solvents were mixed, so you must specify the purpose of this study the effect of the solvent is different in polar and be higher value has mixture.

#### **Theoretical part:-**

Let us consider a collimated beam of monochromatic radiation passing through an absorbing medium, and let us assume that the absorption is due to only one electron transition (that is , power flowing across unit area unit area ) of the beam

as it propagates is given by  $\Delta I(x) = I(x+\Delta x) - I(x)$  [16], and If the medium is homogeneous  $\Delta I$  is proportional to the distance travelled  $\Delta x$  and to the irradiance  $I(x)$ .

The process of absorption was the main factor and the amount of light absorbed depends on the severity of the incident radiation ( $I_0$ ) and plant uptake, which depends on the physical nature of the material, along the path of light absorbed ( $I$ ) and can express this relationship also sports the following formula [17]:

$$I(x) = I_0 e^{-\epsilon c x} \dots (1)$$

Where:-

$I_0$ : is the intensity of incident radiation

$I(x)$ : is the intensity of transmitted radiation

$\epsilon$ : is the absorption coefficient

$c$ : molar concentration

$x$ : path length

The negative sign in this equation indicates a reduction in beam with distance [16, 17].

Particle exposure to the electromagnetic beam, according to the rules, the transfer test (singlet-singlet (f), triple-triple), allowed while the transfer window (singlet - triple (f), triple -singlet) was forbidden for the article, the interactions of radiation Particle Electromagnetic filed to lift one of the levels vibration ( $S_1$ ) in determining the severity of a package to put out the absorption coefficient in terms of molecules (K) which defines the relationship as follows [15]:

$$K = 1/c \ln \frac{I_0}{I} \dots (2)$$

#### **Quantum Efficiency**

The Quantum Efficiency of fluoridation ( $q_{FM}$ ) Known as the ratio between the numbers of photons emitted from the system by molecular fluorescence to the number of photons of irritability by the absorption and is

calculated from the following relationship:

$$q_{FM} = \int_0^{\infty} F(\bar{\nu}) d\bar{\nu} \dots\dots\dots (3)$$

Where:-

$F(\bar{\nu})$  :Molecular fluorescence spectrum

$\bar{\nu}$  : wave number

### The practical part

Spectrofluorophotometer has been used bilateral package of the type[ CECILCE7200] for the purpose of measuring the absorption spectrum of the dye laser which used as a device on one of light Deuterium lamp package gives wavelengths nm (322.5 -190), while the other is to provide Lamp Tungsten Lamp light wavelengths ranging between wavelengths' (322.5-800) nm and a measurement system based on the ratio between the two radiations is dissolved in the solvent with the known (Sample) and the beam and the other is in the solvent alone, which is called (Reference) is recorded by the spectrum (Recorder unit).

Used in the This research used in the Rhodamine B dye and the molecular weight ( $\text{gm/cm}^3$  479.02) and the chemical formula ( $\text{C}_{28}\text{H}_{31}\text{N}_2\text{O}_3\text{C}_1$ ) as in Figure (1) and processed by the company (Lambda physic) German, is the scientific name:9-(2-carboxyphenyl)-6-diethylamino-3-xanthenylidene]-diethylammonium chloride .

### Solvent:

Two organic solvents have been used in present work from (Riedel-Detlanen) company with purity 99.8%, Ethanol (Ethyl Alcohol) its molecular formula is  $\text{C}_2\text{H}_5\text{OH}$  and molecular weight 46.04 gm /mol , and methanol solvent (Methyl Alcohol) its molecular  $\text{CH}_3\text{OH}$  and molecular weight is 32.04 gm/mol [18].

### Solutions preparation:

Dissolve specific weight of (Rhodamine B) dye in specific volume of solvent and prepare solution with concentration  $10^{-4}$  molar according to relation:

$$W = c \times v \times M.w / 1000$$

Where :-

W: weight of dye

c: molar concentration mole/l

M.w: molecular weight

v: volume of solvent

The area under the curve has been measured by computer program (Table curve 2D V 5.01)

### Results and Discussion:

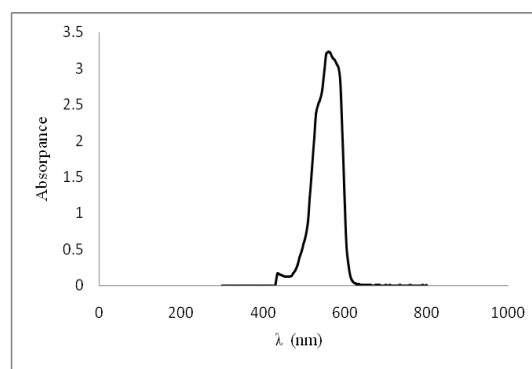
Fig. (2) illustrates (Rhodamine B) absorption spectrum in Ethanol solvent at room temperature the absorption spectrum peak was at wavelength (560 nm) and intensity 3.228 and in fig (3) observe the max. value for  $\sigma$  it  $3.192 \times 10^4$  du to that low polarity of ethanol and the intramolecular proton-transfer reaction is given by the Mannich base (4), which can be considered as an analogue of the corresponding intermolecular complexes between phenols and amines and in UV/V spectroscopic measurements show that this proton-transfer equilibrium is shifted to the right-hand with increasing solvent polarity . Fig (5) illustrates (Rhodamine B) absorption spectrum in methanol solvent where the absorption spectrum peak was at wavelength (563 nm) and intensity 3.20, it was observed that the methanol polarity is larger than Ethanol solvent so absorption spectrum shifts to the short wavelength in Ethanol solvent (Blue shift), and not in Fig.(6) observe the max. value for  $\sigma$  it  $3.22 \times 10^4$  the large shift compared with value for  $\sigma$  in Ethanol spectrum peak , This indicates that the increase in the polarity of the solvent displacement occurs towards the longer wavelengths.

from Fig (8) , it was observed a shift in absorption spectrum of mixture from methanol and ethanol solvent shifts towards (550 nm) wavelength (Blue shift) that mean the mixture of ethanol and methanol have a polarity larger than methanol and Ethanol solvent alone as shown in Table (1), and that increasing solvent polarity shifts the equilibrium towards the pyridone-form. This form is more dipolar than the hydroxy-form due to the contribution of the charge-separated. The hydrogen-bonding ability of the solvent plays an important role since hydrogen-bond donors tend to stabilize the oxo-form, whereas hydrogen-bond acceptors stabilize the hydrogen-form. Fig. (4) represents fluorescence spectrum for dye in ethanol solvent where the peak of fluorescence spectrum at wavelength (600 nm) and intensity 82.6 and in methanol (605 nm) and intensity 81.8 depending on the polarity of solvent as show that in Fig.(7) to explain the Excitation & Fluorescence of Rhodamine B in Methanol and table (2). Through Fig.(9) and Fig. (10) The fluorescence and absorption spectrum have been observed decreasing the overlap between absorption spectrum and fluorescence spectrum in the mixture of solvents from Ethanol and methanol solvent, which means decreasing the self absorption in the mixture and increasing the laser efficiency. In Table (3) it was observed the variation in quantum efficiency depends on solvent polarity in mixture it is larger than every solvent alone where is 38.94% ,from eq. (7) it has obtained the variation in molar Absorption coefficient ( $\epsilon$ ) with acceptor of solvent polarity that caused strong bond between the dye and high polarity solvents as illustrated in mixture to increasing the bonding force when mix two solvents with the dye to consist

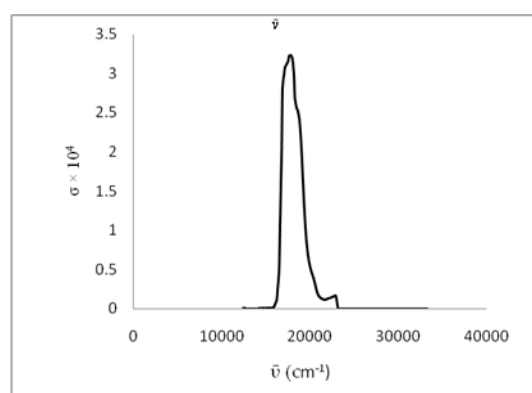
this bond which its value is  $(3.23 \times 10^{-4} \text{ l/mole.cm})$ .

### Conclusions:

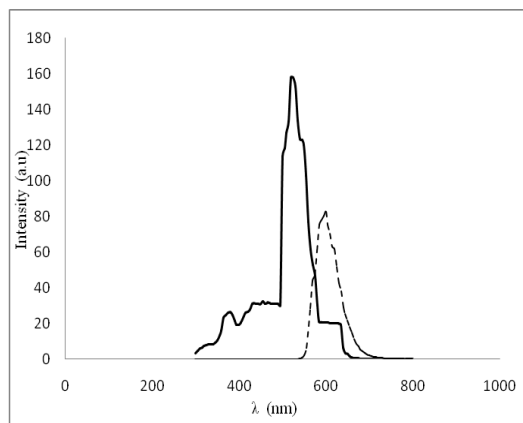
- 1- The values of wave number and molar absorption coefficient in the mixture (ethanol+methanol) are larger than its value in Ethanol and methanol alone.
- 2- The variation in quantum efficiency value as a function of increasing in solvent polarity and smallness area under the curve as in methanol and forming a strong bond where is the methanol and forming a strong bond where is the methanol polarity is larger then Ethanol polarity.



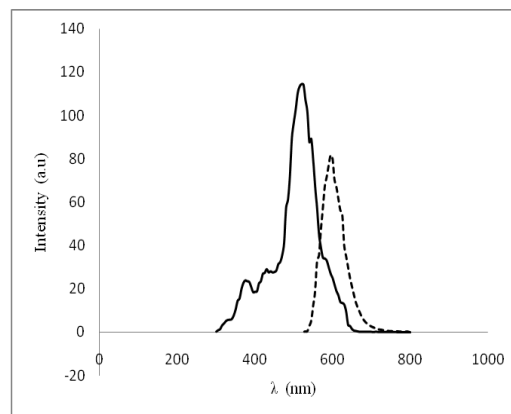
**Fig (2): absorption spectrum of Rhodamine B in Ethanol at  $(10^{-4}$  molar).**



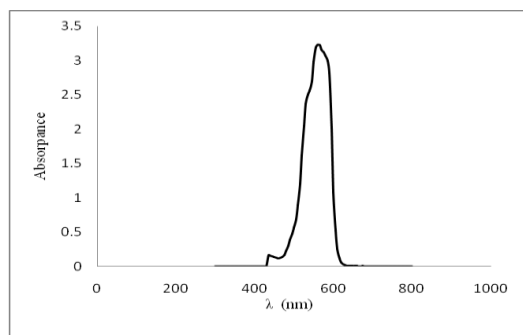
**Fig (3): Rhodamine B in ethanol solvent ( $\sigma$ ) at  $(10^{-4}$  molar).**



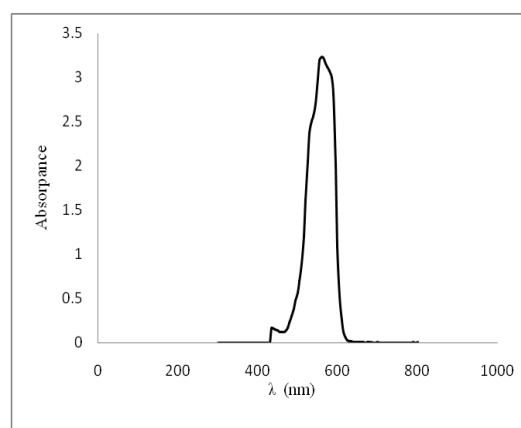
**Fig (4):** Excitation (—) & Fluorescence (--) spectra of Rhodamine B in ethanol ( $10^{-4}$  molar).



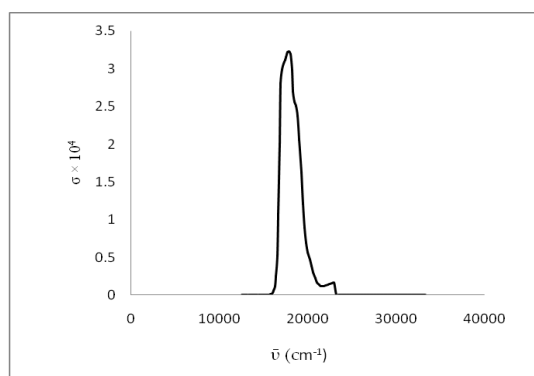
**Fig (7):** Excitation (—) & Fluorescence (----) of Rhodamine B in Methanol at ( $10^{-4}$  molar).



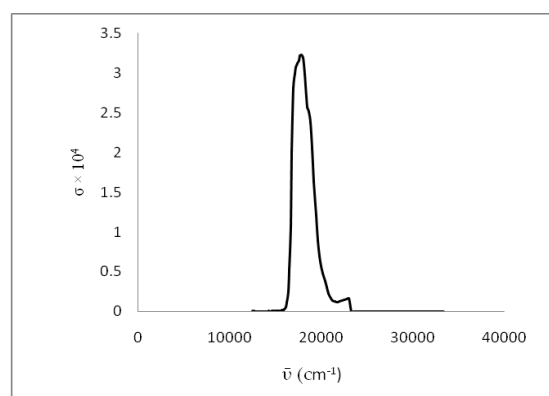
**Fig (5):** absorption spectrum of Rhodamine B in methanol ( $10^{-4}$  molar).



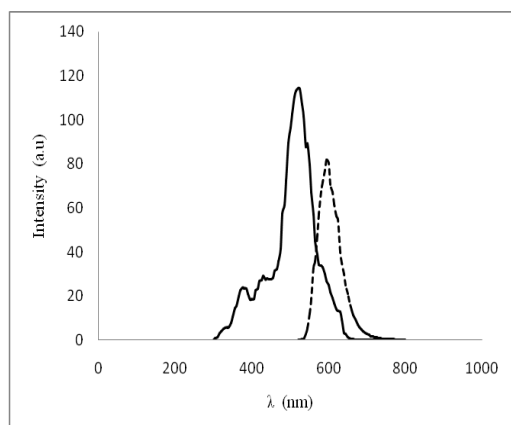
**Fig (8):** absorption spectrum of mixture at ( $10^{-4}$  molar).



**Fig (6):** Rhodamine B in methanol solvent ( $\sigma$ ) in ( $10^{-4}$  molar).



**Fig (9):** Mixture [ethanol+ methanol] solvent ( $\sigma$ ) at ( $10^{-4}$  molar) .



**Fig (10):**Excitation ( — ) & Fluorescence (-----) of Rhodamine B Mixture ( $10^{-4}$  molar).

**Table (1):** Absorption spectrum of dye Rhodamine B solvent in methanol & Ethanol & Methanol+ Ethanol (mixture) in  $10^{-4}$  concentration (molar).

solvent	Relative intensity	Absorption spectrum $\lambda_{\max}$ (nm)	$\bar{\nu}$ ( $\text{cm}^{-1}$ )
methanol	3.20	563	17761.9
ethanol	3.228	560	17857.1
mixture	3.230	550	18181.8

**Table (2):** Fluorescence spectrum of dye Rhodamine B solvent in methanol & Ethanol & Methanol+ Ethanol (mixture) in  $10^{-4}$  concentration (molar)

solvent	Relative intensity	Fluorescence's spectrum $\lambda_{\max}$ (nm)	$\bar{\nu}$ ( $\text{cm}^{-1}$ )
methanol	81.8	605	16528.9
ethanol	82.6	600	16666.6
mixture	109.6	595	16806.7

**Table (3):** illustrates increasing in Quantum efficiency as depending solvent type and polarity and Band width and molar absorption coefficient

solvent	Band width $\Delta\lambda$ (nm)	Band width at (F.W.H.M.) $\Delta\lambda$ (nm)	$\epsilon$ (l/mol.cm)	Quantum Efficiency (Q)
methanol	490-610	80	$3.2 \times 10^{-4}$	36.96%
Ethanol	440-640	85	$3.228 \times 10^{-4}$	37.2%
mixture	480-600	90	$3.230 \times 10^{-4}$	38.94%

## References:

- Netto-Ferreira. J. C.; Vieira Ferreira, L. F.; Costa, S.M.B. 1996. Quím. Nova. 19, pp(230-232).
- Oliveira. A. S.; Vieira Ferreira, L. F.; Wilkinson, F.; Worrall. 1996. D. R. J. Chem. Soc., Faraday Trans, 92, pp(4809-4814).
- Vieira. F., L. F.; Oliveira, A. S.; Khmelinskii, I. V.; Costa, S.M.B. 1994. J. Lumin. 60 & 61, pp(485-488).
- Vieira. F., L. F.; Netto-Ferreira, J. C.; Costa, S.M.B. 1995. Spectrochim. Acta, 51, pp(1385-1388).
- Levin. P.P.; Vieira Ferreira, L.F.; Costa, S. M.B. Langmuir. 1993. 9, pp(1001-1008).
- Ilharco. L. R.; Garcia, A. R.; Lopes da Silva, J.; Vieira Ferreira, L. F. Langmuir. 1997. 13, pp(4126-4132).
- Blackwell. J.; Marchessault, Bikales, N.M., Segal, L.L. 1971. Eds.; R.H. In Cellulose & Cellulose Derivatives. Wiley-Interscience: New York, Vol. IV, Chapter 13, p(1).
- Drexhage. K. H. J. Res. 1976. Nat. Bur. Stand. A. Phys. Chem. 80, pp(421-428).
- Arden, J.; Deltan, G.; Huth, V.; Kringed, U.; Peros, D.; Drexhage, K. H. 1991. J. Lumin. 48 & 49, pp(352-358).
- Vogel. M.; Rettig, W.; Sens, R.; Drexhage, K.H. 1988. Chem. Phys. Lett. 147, pp(461-465).
- Lopez A., T.; Estevez, M. J.; Lopez Arbeloa, F.; Urretxa Aguirresacona, I.; Lopez Arbeloa, I. 1991. J. Lumin. 48 & 49, pp(400-404).
- Casey, K. G.; Onganer, Y.; Quitevis, E.L. 1992. J. Photochem. Photobio. A: Chem. 64, pp(307-

- 314). (b)Casey, K.G.; Quitevis, K.E.1988. J.Phys. Chem., 92&2, pp(6590-6594).
13. Kemnitz, K.; Tamai, N.; Yamazaki, I.; Nakashima, N.; Yoshihara. K. 1987. J. Phys. Chem, 91&1, pp (1423-1430).
14. Taffe, H.; Helmling, W.; Miischk, P.; Rebsmen, K.; Reiner,U.; Russ, W.; Schlafer, L.; Vermehren. 1993. P. Reactive Dyes. In Ullman's Encyclopedia of Industrial Chemistry; VCH Publishers: Deerfield Beach, FL; Vol. A22, pp(651).
15. Siegel. E.; Schundehutte, K. H.; Hildebrand. 1972. D. Reactive Dyes. In The Chemistry of Synthetic Dyes; Venkataraman,K., Ed.; Academic Press: New York, London, Vol. 6, pp(327).
16. Wilson .J.; Hawkes. J.F.B. 1987. "Laser principles and Application" prentice Hall International (UK)ltd.
17. Offenartz. P. 1992. "MOLSPEC Version 2.3," Laser Photonics Inc.
18. Schfer. F.p. 1977.(Dye laser ) Topic sin Applied physics 2<sup>nd</sup> Ed springer-Berlin.

### دراسة الخواص الطيفية لصبغة Rhodamine B في مذيب الايثانول والميثانول ومزيجهما وحساب كفاءتها الكمية

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#### الخلاصة:

تمت دراسة تأثير كل من مذيب الايثانول والميثانول ومزيجهما على اطياف الامتصاص والفلورة لصبغة الليزر Rhodamine B بتركيز ( $10^{-4}$ ) مولاري بدرجة حرارة الغرفة . وتم حساب معامل الامتصاص المولاري في حالة المزيج والتي كانت (3.223) عند العدد الموجي  $18181.8 \text{ cm}^{-1}$  ، كذلك تم حساب الكفاءة الكمية لكل من المذيبين ( الايثانول والميثانول) ومزيجيهما و التي كانت قيمتها اكبر بمقدار (38.94%) عند طيف المزيج بالمقارنة مع طيف الايثانول والميثانول. وتم تحديد خواص الطيف من خلال حساب قيمة ( $\Delta\lambda$ ) لطيف الامتصاص للمزيج والمذيبين عند اعظم قيمة للعدد الموجي  $18181.8 \text{ cm}^{-1}$  (  $\bar{\nu}$  ) بالاعتماد على قطبية المذيب والانتقالات بين مستويات الطاقة للجزيئة في كل مذيب لـ Rhodamine B .