77

Analysis of the Effect of the Concentration of Rhodamine B in Ethanol on the Fluorescence Spectrum Using the "Gauss Mod" Function

Mahasin F. Al-Kadhemy[*], Israa F. Alsharuee and Ali Abid D. Al-Zuky

Physics Department, College of Science, Al-Mustansiriyah University, Iraq

*Corresponding author: drmahasinf@yahoo.com

Abstract: *The effect of varying concentrations on the photophysical properties of the laser dye Rhodamine B (RB) in ethanol was studied both experimentally and theoretically. The fluorescence spectrum of these concentrations (1×10^{-2}, 1×10^{-3}, 1×10^{-4} and 1×10^{-5} mol/litre) was taken experimentally. Pure tuning of RB in ethanol was obtained. Red shifting of about 20 nm to longer wavelengths was achieved by varying the concentration from 1×10^{-5} mol/litre to 1×10^{-2} mol/litre. The theoretical modelling equation for the effect of concentration on the fluorescence spectrum of RB solution in ethanol was achieved using the program Table Curve 2D, version 5.01. The best theoretical equation for the concentration profile was the Gauss mod function reported in the following equation:*

$$y = a + b * \exp\left(-0.5 * {\left(^{|x-c|}/_d\right)}^e\right)$$

The equation was applied to two concentration profiles, 0.5×10^{-3} and 0.5×10^{-4} mol/litre. The experimental fluorescence spectrum of RB in ethanol was plotted against the theoretical fluorescence spectrum. There is good consistency between the behaviour of the experimental and theoretical fluorescence spectra, specifically for intensity and wavelength fluorescence. This equation allows us to plot the fluorescence spectrum for any concentration of RB in ethanol that was not measured experimentally.

Keywords: fluorescence spectrum, Rhodamine B, laser dye, concentration effect, theoretical model

1.   INTRODUCTION

The optical excitation of a molecule and its subsequent emission of spontaneous luminescence or stimulated radiation results in a series of intermolecular processes, such as orientation or translational, which occur in both the ground and excited states.[1] The orientation relaxation processes have a substantial effect not only on the spontaneous luminescence spectrum but also on the stimulated emission spectrum of the solution.[2] Since a variety of fluorescent dyes adsorb to biological macromolecules, it is of interest to know information

about the dye environment the fluorescence can provide. Of all the dye molecules, the spectroscopic properties of those with electron donor and acceptor moieties have received considerable attention due to popularity of fluorescence probes.[3] Dyes, either as solution or vapours, are the active medium in pulsed and continuous wave dye lasers.[4]

The fluorescent dyes themselves can be used to quantify fluid mixing in aqueous solution. The general technique involves rationing optically separable fluorescence from two fluorescent dyes. Fluorescence intensity ratios can be used to measure the inherent variation in the dyes' temperature fields.[5] The Rhodamine dyes are self-associated in different liquid crystal (Anisotropic solvent) host materials like ethanol (isotropic solvent), which is very important in display and electronic technologies.[6]

Rhodamine dyes are used as the active medium of tunable laser radiation in the visible region of the light spectrum.[7] They appear red to violet in colour. The molecular formula of Rhodamine B (RB) is $C_{28}H_{31}ClN_2O_3$ with molecular weight of 479.02 gm/mol. It is often used as a tracer dye in water to determine the rate and direction of flow and transport. Rhodamine dyes are used extensively in biotechnology applications such as fluorescence microscopy, flow cytometry, fluorescence correlation spectroscopy and ELISA.[8] RB is tunable around 610 nm when used as a laser dye.[9] Its luminescence quantum yield is 0.65 in basic ethanol,[10] 0.49 in ethanol[11] and 1.0[12] and 0.68 in 94% ethanol.[13] The fluorescence yield is temperature dependent.[14] In addition, Bindhu et al.[15] used the dual beam thermal lens (DTL) technique as a quantitative method to determine absolute fluorescence quantum yield and the effect of the concentration of RB in different solvents. They investigated the absolute fluorescence quantum yield of RB excited by a CW argon ion laser at 514 nm and a pulsed Q-switched Nd:YAG laser at 532 nm. The chemical structure of Rhodamine B is reported in Figure 1.
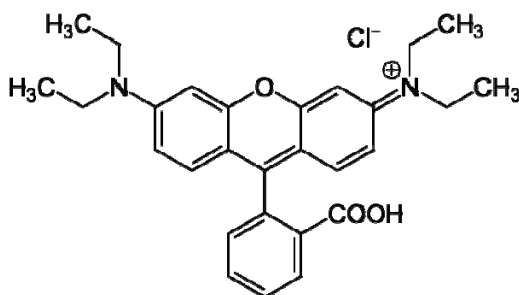

Figure 1: Chemical structure of Rhodamine B.[16]

2. EXPERIMENTAL

In this study, we took fluorescence spectra of RB in ethanol solution at room temperature at concentrations of 1×10^{-2}, 1×10^{-3}, 1×10^{-4} and 1×10^{-5} mol/litre. We report a theoretical model for studying the effects of varying concentration on the fluorescence spectrum of RB in ethanol solution. We compare our theoretical data with experimental fluorescence profiles.

We prepared the dye solution of these concentrations using the relation reported in Equation 1. In this relation, the variables are defined as follows: m is the mass of dye reported in grams (g); C is the final concentration reported in moles/litre (mol/L); V is the volume of the solvent, ethanol, and is reported in litre (L); and M is the molecular weight of the dye reported in grams/mole (g/mol).

$$m = C * V * M \qquad (1)$$

We recorded the fluorescence spectrum emitted from RB in ethanol by Jarrell Ash 82-4b monochromator grating, fitted to a one meter Czerny-Turner spectrometer spectrograph. Fitting curves for the fluorescence spectrum were determined using the program Table curve 2D, version 5.01.

3. RESULTS AND DISCUSSION

Experimental fluorescence spectrum curves for RB in ethanol at concentrations 1×10^{-2}, 1×10^{-3}, 1×10^{-4} and 1×10^{-5} mol/litre are illustrated in Figure 2.
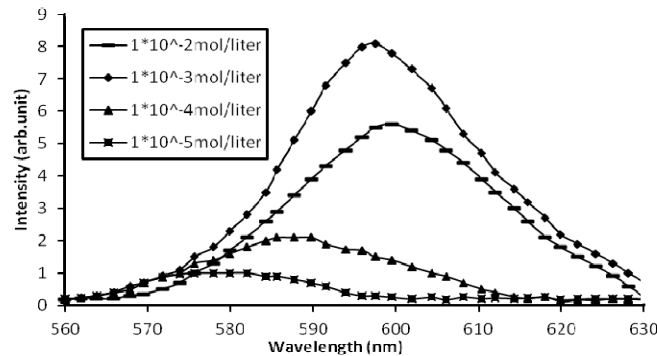

Figure 2: Fluorescence spectrum of RB in ethanol recorded at different concentrations.

The maximum wavelength and intensity of the fluorescence spectrum was clearly shown to be dependent on the concentration of the dye solution, as shown in Figure 2. At dilute concentrations of dye, 1×10^{-5} mol/litre, the fluorescence intensity appears to be low, and the maximum fluorescence wavelength is found at 580 nm. Increasing the concentration of the dye solution resulted in red shifting of the fluorescence wavelength to higher wavelengths. It shifts to 600 nm at a concentration of 1×10^{-2} mol/litre. We observe a wavelength shift of about 20 nm, which indicates the laser dye action has transferred to another wavelength. The intensity of the fluorescence spectrum increased with the increasing concentration of the dye solution. Fluorescence increased until 1.0×10^{-2} mol/litre, where formation of dimers was observed, resulting in a decrease in intensity.

Based on these experimental results, we created a theoretical model for the effect of varying concentration on the fluorescence spectrum of RB solution in ethanol. The theoretical model could be used to obtain any fluorescence spectrum at any concentration that was not specifically measured experimentally. Figure 3(a, b, c and d) show the fitting curve of the fluorescence spectrum of RB solution in ethanol for each concentration separately. The Gauss mod function was the equation that best fit the experimental data and is reported in Equation 2. The values for the parameters a, b, c, d, and e are reported in Table 1 for each concentration investigated.
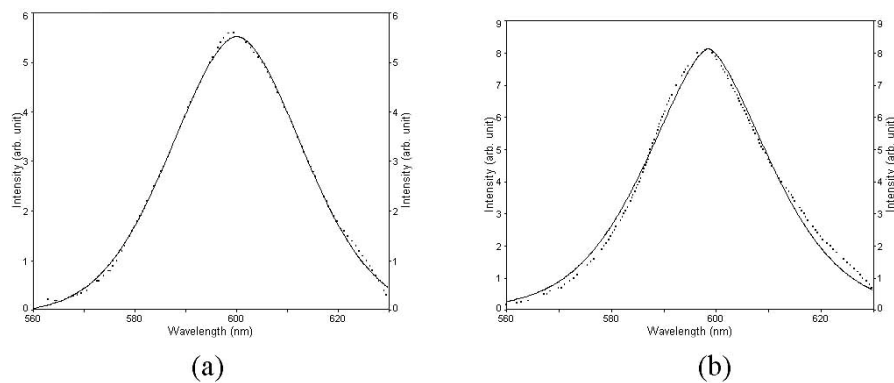
$$y = a + b * exp \left(-0.5 * \left(^{|x-c|}/_d\right)^e\right) \tag{2}$$

(a)   (b)

Figure 3: Fitting curve of the fluorescence spectrum of RB in ethanol at (a) 1×10^{-2}, (b) 1×10^{-3}, (c) 1×10^{-4} and (d) 1×10^{-5} mol/litre. *(continued on next page).*

Figure 3: *(continued)*

(c)   (d)
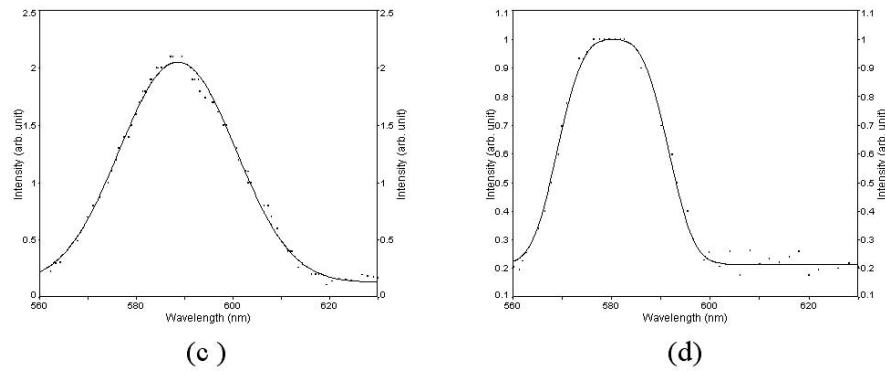
Table 1: The parameters of the Gauss mod equation for each concentration.

Parameter	C=1 × 10⁻² mol/litre	C=1 × 10⁻³ mol/litre	C=1 × 10⁻⁴ mol/litre	C=1 × 10⁻⁵ mol/litre
a	–0.054438971	0.067293696	0.12817566	0.21559128
b	5.5799233	8.0669675	1.9224015	0.78256198
c	600.12748	598.52283	588.63964	580.34502
d	12.669771	10.921908	11.99557	10.242903
e	1.824412	1.584004	2.0686971	3.2003081

Figures 4 to 8 describe the variation of each parameter with concentration. We determined the theoretical curve for each one, using the equation reported above each figure. Each fitting curve used a different fitting equation for the parameters.

Fitting equation :

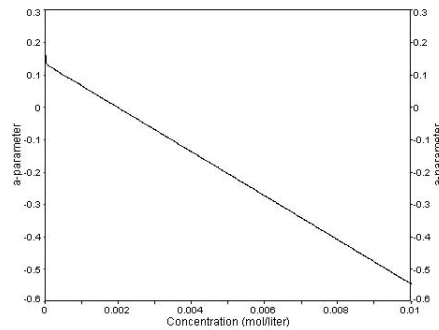$$y = 67.688219 - 67,553655 e^{x} - 7.0964181 e^{-13} \ln \frac{x}{x^{2}}$$

Figure 4: The relation between a-parameter and concentration.

Fitting equation :

$$\frac{1}{y} = -0.24776824 - 0.789464 \quad 0.5 \ln x + 0.\frac{0063092655}{} \times^0 .5$$
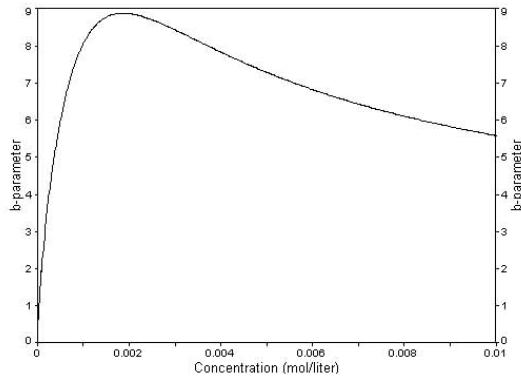

Figure 5: The relation between b-parameter and concentration.

Fitting equation :

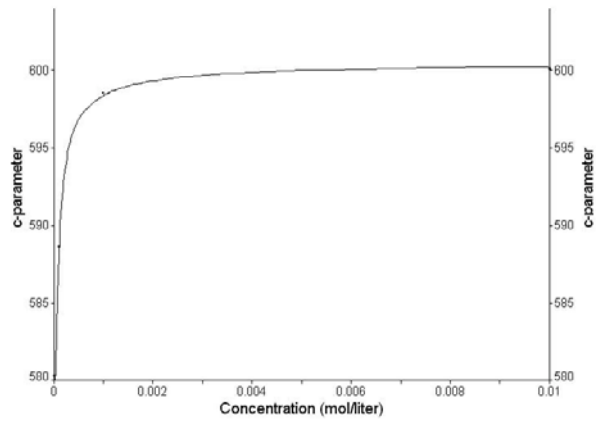$$y \quad -600.56027 - 0.000248835 \ln \frac{x}{x} \quad -\frac{0.005139344}{x}$$

Figure 6: The relation between c-parameter and concentration.

Fitting equation :

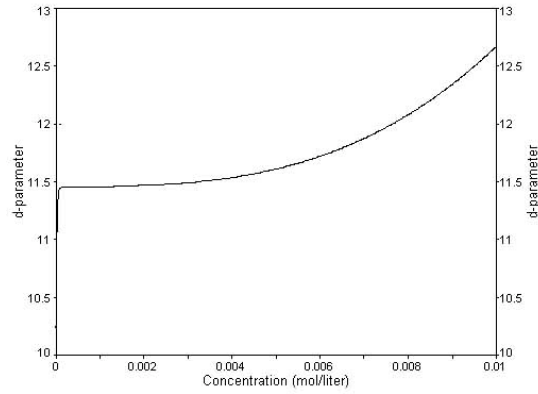$$y = \frac{-11.461136 + 1208095.7x^3 + 1.0543908e^{-11}\ln x}{x^2}$$

Figure 7: The relation between d-parameter and concentration.

Fitting equation :

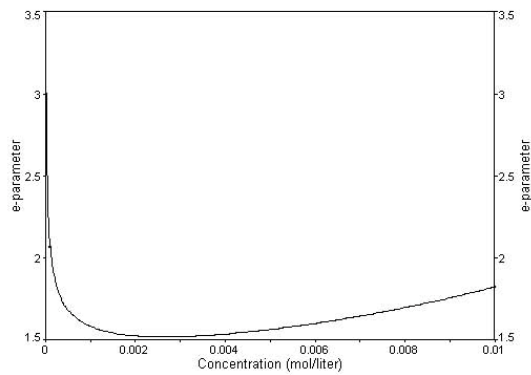$$\frac{1}{y} = 29.54278 - 28.362665e^x + 0.075338047\ln x$$

Figure 8: The relation between e-parameter and concentration.

Using the fitting equation above, we calculated the final parameters to determine the estimated theoretical equation for the fluorescence spectrum of RB solution in ethanol. We used two sample concentrations to verify this equation.

The first equation was fit to the fluorescence profile for the concentration of 0.5×10^{-3} mol/litre. The theoretical equation determined for this concentration is reported in Equation 3.

$$y = 0.10080032 + 5.932287 * \exp\left(0.5_* \left(^{|x - 596.80066|}/_{11.460966}\right)^{1.6855068}\right) \quad (3)$$

The second equation was fit to the fluorescence profile for a concentration of 0.5×10^{-4} mol/litre. The theoretical equation determined for this concentration is reported in Equation 4.

$$y = 0.13399742 + 1.42990177 * \exp\left(-0.5_* \left(^{|x - 582.7128|}/_{11.419368}\right)^{23116698}\right) \quad (4)$$

Then, the theoretical fluorescence spectrum for these two sample concentrations was plotted against the experimental fluorescence spectrum, as illustrated in Figure 9. In these two theoretical fluorescence spectra, the intensity and wavelength were increased with increasing concentration. These effects were also found in the experimental results. There is a good symmetry between the behaviour of the experimental and theoretical results.
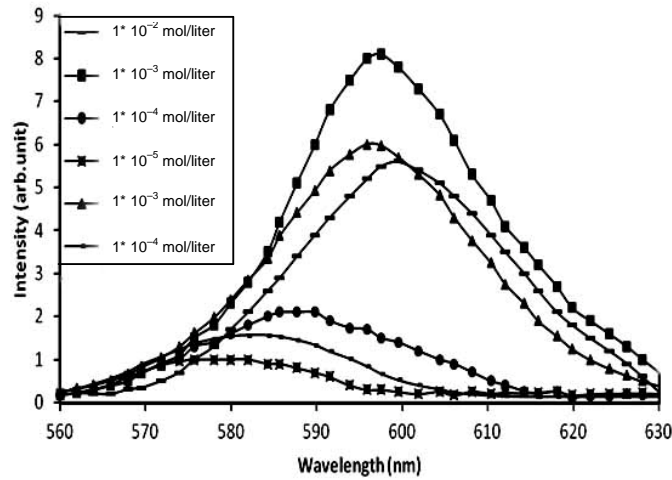

Figure 9: Theoretical and experimental fluorescence spectrum of RB in ethanol.

4.   CONCLUSION

Based on our analysis of the effect of concentration on the fluorescence spectrum, we can conclude that the ability to obtain a pure tuning dye laser (RB in ethanol) varies with the concentration of dye in solution. We observe an approximately 20 nm wavelength red shift through variation of the RB in ethanol concentration over the concentration range of 1×10^{-5} to 1×10^{-2} mol/litre.

Also, by using the data treatment program Table Curve 2D, version 5.01, we were able to determine the theoretical modelling equation for the effect of concentration on the fluorescence spectrum for RB solution in ethanol. The equation that best fit the experimental data was the Gauss mod function and is reported in the following relation.

$$y = a + b * \exp\left(-0.5*\left(^{|x-c|}/_d\right)^e\right)$$

Using the Gauss mod function, we can determine the fluorescence spectrum for RB in ethanol theoretically without the need to measure it experimentally.

5.   REFERENCES

1.   Ali, M. A., Moghaddasi, J. & Ahmed, S. A. (1991). Temperature effects in Rhodamine B dyes and improvement in CW dye laser performance. *Laser Chem.*, 11, 31–38.
2.   Alekseev, V. A. et al. (1979). A system of active energy and wavelength stabilization in flashlamp pumped dye lasers. *J. Appl. Spectrosc*., 46(4), 346–349.
3.   Chang, T. L. & Borst, W. L. (1990). Effect of solvent polarity on a rotational isomerization mechanism of rhodamine-B in normal alcohols. *J. Chem. Phys.*, 93(7), 4724–4729.
4.   Aldag, H. R. (2005). Flashlamp-pumped liquid dye lasers to diode-pumped solid state dye lasers. Proc. SPIE 5707, 194.
5.   Coppeta, J. R. & Rogers, C. B. (1995). A quantitative mixing analysis using fluorescent dyes. AIAA paper number 0539. American Institute of Aeronautics and Astronautics.
6.   Ghanadzadeh, A. & Zakerhamidi, M. S. (2004). Absorption anisotropy and molecular association of some ionic dyes in liquid crystalline solution. *J. Mol. Liq.*, 109(3), 149–154.
7.   Steven, P. L., Lee, L. M. & Mangel, W. F. (1983). Rhodamine-based compounds as fluorogenic substrates for serine proteases. *Biochem. J.*, 209, 299–307.

8.   Yang, F. (2006). Preparation of uniform Rhodamine B-doped SiO2/ TiO2 composite microspheres. *J. Solid State Chem.*, 179, 457–463.

9.   Du, H., Fuh, R. A., Corkan, J., Li, A. & Lindsey, J. S. (1998). PhotochemCAD: A computer-aided design and research tool in photochemistry. *Photochem. Photobiol.*, 68, 141–142.

10.   Kubin, R. F. & Fletcher, A. N. (1982). Fluorescence quantum yields of some rhodamine dyes. *J. Lumin.*, 27, 455–462.

11.   Casey, K. G. & Quitevis, E. L. (1988). Effect of solvent polarity on nonradiative processes in xanthene dyes: Rhodamine B in normal alcohols. *J. Phys. Chem.,* 92(23), 6590–6594.

12.   Kellogg, R. E. & Bennett, R. G. (1964). Radiationless intermolecular energy transfer. III. Determination of phosphorescence efficiencies. *J. Chem. Phys.*, 41, 3042–3045.

13.   Snare, M. J., Treloar, F. E., Ghiggino, K. P. & Thistlethwaite, P. J. (1982). The photophysics of rhodamine B. *J. Photochem.*, 18, 335–346.

14.   Karstens, T. and Kobs, K. (1980). Rhodamine B and Rhodamine 101 as reference substances for fluorescence quantum yield measurements. *J. Phys. Chem.*, 84, 1871–1872.

15.   Bindhu, C. V. & Harilal, S. S. (2001). Effect of excitation source on the quantum yield measurements of rhodamine B using thermal lens technique. *Anal Sci.*, 17, 141–144.

16.   Fikry, M., Omar, M. M. & Lotfi, Z. I., (2009). Effect of host medium on the fluorescence emission intensity of Rhodamine B in liquid and solid phase. *J. Fluores.,* 19, 741–746.