

## Photo-physical characterization of Rhodamine B in liquid and solid solutions

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*SUMMARY. – Absorption, fluorescence, quantum yield and lifetime of rhodamine B in chloroform, methanol and dimethyl sulfoxide were measured. A comparison was done of these quantities with those for solid solutions, which are obtained by mixing constant volume proportions of dye at a concentration of  $1 \times 10^{-4} \text{M/l}$  with different volume proportions from the concentrated solution of polymer in chloroform and dimethyl sulfoxide. The results showed that the addition of polymer to liquid concentrated solutions ( $1 \times 10^{-4} \text{M/l}$ ) of rhodamine B dye from expecting, which leads to development of active medium for laser dye at high concentration, increase the spectra shift toward high energies, and the luminescence quantum yield but decreasing radiative lifetime.*

### 1. Introduction

Along the years dye lasers have demonstrated to be useful and versatile sources of tunable coherent radiation with wide applicability in many different fields (1). At present research on solid-state dye lasers is a very active field (2-9). Dye oscillators and amplifiers operate under intense optical excitation which results in significant population build up in the lowest excited singlet  $S_1$ . Absorption from  $S_1$  can produce a number of deleterious effects such as reduction of effective gain, interference with optical pumping, and introduction of an extra thermal load due to the energy released as heat in the subsequent relaxation back to  $S_1$ , as well as photochemical reaction. Thus knowledge of the spectral properties of  $S_1$  state would be necessary to design efficient dye lasers and to determine optimum pumping conditions. Organic dyes are doped in organic polymer (2-4). Good lasing performance has been achieved for rhodamine B doped PMMA polymer. The fluorescence quantum yield and lifetime are determined.

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## 2. Experimental

The following material were used: - rhodamine B ( $C_{28}H_{31}N_2O_3Cl$ ) {East-man Kodak Com.} whose molecular weight is 479.02 g/M, chloroform, methanol, dimethyl sulfoxide (all analytical grad, Fluka Com.) and PMMA beads (laboratory grade, ICI, Com.).

A series of solutions of RhB at concentrations varying from  $10^{-6}$  to  $10^{-4}$ M/l were prepared in chloroform, methanol, and dimethyl sulfoxide. The solid solutions were prepared by mixing a constant volume proportion from a concentrated of RhB ( $1 \times 10^{-4}$ M/l) with different volume proportions of concentrated solutions of the polymer in chloroform and dimethyl sulfoxide ( $V_{RhB}/V_{PMMA}$  = without polymer, 1/0.25, 1/4, 1/8).

The absorption and florescence spectra were measured by using a spectro-fluorimeter model RF-500, Shimadzu Com., as illustrated in Fig. 1.

The quantum efficiencies were measured by the comparative method (10) using as standard solutions (11) a solution of Rh6G in methanol which has a quantum efficiency of 94%.

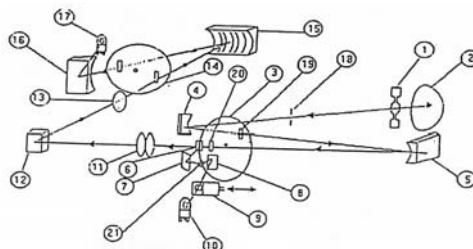


FIG. 1

Schematic of experimental apparatus.

- 1 - Xenon lamp. 2 - Condenser ellipsoidal mirror (SiO<sub>2</sub> coated). 3 - Excitation slit assembly. 4 - Concave mirror. 5 - Concave diffraction grating (for excitation).
- 6 - Beam splitter quartz plate. 7 - Teflon reflector No.1. 8 - Teflon reflector No.2.
- 9 - Optical attenuator. 10 - Monitor photomultiplier, R212-09. 11 - A couple of light-collecting lenses. 12 - Cell. 13 - Light- collecting lens. 14 - Emission slit assembly. 15 - Concave diffraction (for emission). 16 - Concave mirror. 17 - Photometric photomultiplier R452-01. 18 - Focus, 19 - Entrance slit. 20 - Exit slit. 21 - Light beam balancing aperture.

## 3. Results and discussion

In Figs. 2, 3, 4 we represent the absorption and the emission spectra (A, B, C, a, b, c) of RhB in chloroform, methanol, dimethyl sulfoxide for concentrations  $10^{-4}$ ,  $10^{-5}$ ,  $10^{-6}$  M/l. respectively. Absorption maxima, wave numbers, and lifetime are given in table 1.

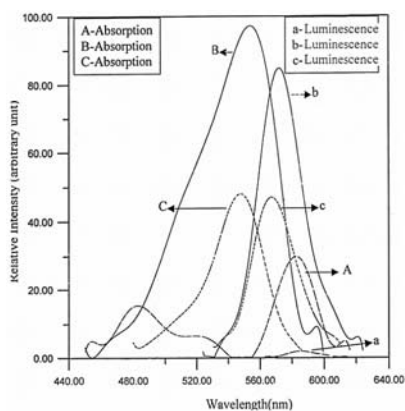


FIG. 2

Absorption, emission spectra (A, B, C, a, b, c) of RhB in chloroform for concentrations  $10^{-4}$ ,  $10^{-5}$ ,  $10^{-6}$ M/l.

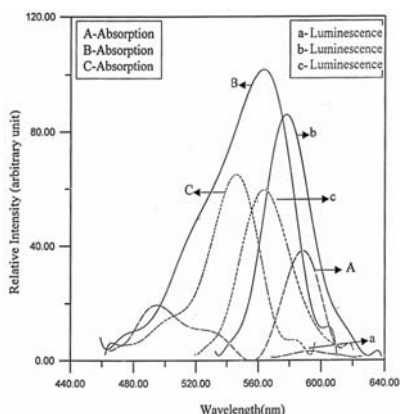


FIG. 3

Absorption, emission spectra (A, B, C, a, b, c) of RhB in methanol for concentrations  $10^{-4}$ ,  $10^{-5}$ ,  $10^{-6}$ M/l.

Emission maxima, wave numbers, and quantum efficiencies are given in table 2.

From these figures and tables we can see that there are shifts to the low energy (long wave length) as the concentration increases, while the quantum yield decreases and lifetime increases. The shift in spectra is toward long wave lengths as the concentration increases. These changes have been interpreted in two different ways. On the one hand they are considered as due to dimerization process (12-18). On the other, they are attributed to the change of RhB from its neutral form ( $\text{RhB}^+$ ) to the cationic one  $\text{RhBH}^+$  (19-22) (Fig. 5). This theory is based on the decreasing of PH produced when dye concentration increases.

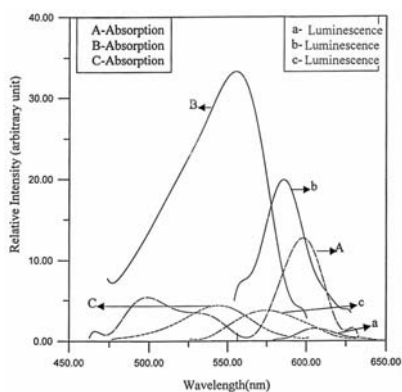


FIG. 4

Absorption, emission spectra (A, B, C, a, b,c) of RhB in dimethyl sulfoxide for concentrations  $10^{-4}$ ,  $10^{-5}$ ,  $10^{-6}$ M/l

**Table 1**

Mole concentration, absorption and emission maxima and life time of rhodamine B in chloroform, methanol, and dimethyl sulfoxid.

Rhodamin B						
Solvent	Concentration M/l	$\lambda_{Abs}$ (nm)	$\nu_{Abs}$ ( $cm^{-1}$ )	$\lambda_{Flu}$ (nm)	$\nu_{Flu}$ ( $cm^{-1}$ )	$\tau_{FM}$ (ns)
Chloroform	$1 \cdot 10^{-4}$	590.4	16937.66	595.15	16802.48	4.4
	$1 \cdot 10^{-5}$	563.8	17736.78	579	17271.15	3.1
	$1 \cdot 10^{-6}$	544	18382.35	563.8	17736.78	2.3
Methanol	$1 \cdot 10^{-4}$	584.7	17102.78	586.6	17047.39	4.7
	$1 \cdot 10^{-5}$	556.1	17982.37	573.3	17442.87	3.3
	$1 \cdot 10^{-6}$	546.1	18315.01	567.6	17618.04	2.4
Dimethyl Sulfoxide	$1 \cdot 10^{-4}$	598.6	16705.64	605.4	16518.01	5
	$1 \cdot 10^{-5}$	555.4	18005.04	586	17064.84	4.3
	$1 \cdot 10^{-6}$	548	18248.17	574.3	17412.5	3.2

**Table 2**

Mole concentration, life time, and quantum yeild of rhodamine B in chloroform methanol and dimethyl

Rhodamin B			
Solvent	Concentration M/l	$\tau_{FM}$ (ns)	Quantum Yield ( $Q_{FM}$ )
Chloroform	$1 \cdot 10^{-4}$	4.4	0.41
	$1 \cdot 10^{-5}$	3.1	0.45
Methanol	$1 \cdot 10^{-4}$	4.7	0.43
	$1 \cdot 10^{-5}$	3.3	0.48
Dimethyl Sulfoxide	$1 \cdot 10^{-4}$	5	0.4
	$1 \cdot 10^{-5}$	4.3	0.44

The decreasing of quantum yield as the concentration increases have been interpreted with dimer molecules which absorb the emission photons. This is due to the band energy of dimer molecules under the band energy of RhB molecules (monomer). These results are in agreement with those of Lopez Arbeloa, and his team.

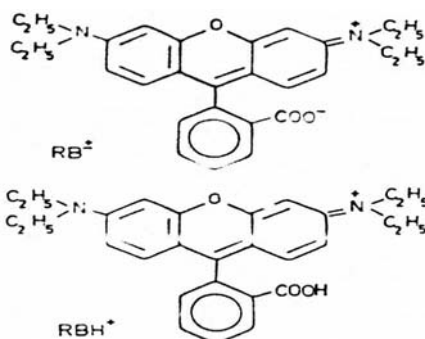


FIG. 5

Molecular structure of neutral ( $\text{RB}^+$ ) and cationic ( $\text{RBH}^+$ ) forms of rhodamine B.

Figures 6 represent the absorption spectra A, B of RhB in chloroform, and dimethyl sulfoxide of concentration  $10^{-4}\text{M/l}$ , when it is mixed with different proportions from the concentrated solution of polymer in chloroform and dimethyl sulfoxide respectively. The absorption maxima, FWHM and lifetime, are summarized in table 3.

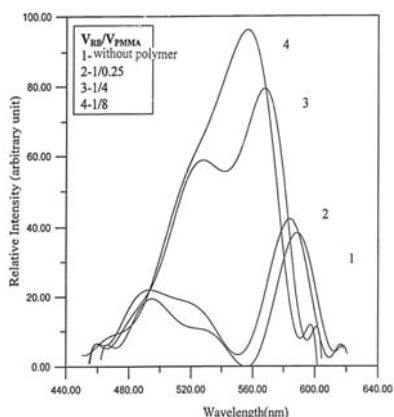


FIG. 6A

The absorption spectra of RhB in chloroform of concentration  $10^{-4}\text{M/l}$ , with different volume proportions of polymer.

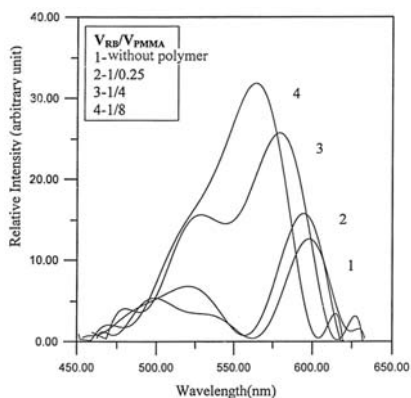


FIG. 6B

The absorption spectra of RhB in dimethyl sulfoxide of concentration  $10^{-4}$ M/l, with different volume proportions of polymer.

**Table 3**

Spectro parameters of absorption spectra of rhodamine B for concentration  $10^{-4}$ M/l in chloroform and dimethyl sulfoxide with different volume proportions of polymer.

Rhodamin B					
Solvent	$V_{RB}/V_{PMMA}$	$\lambda_{Abs}$ (nm)	$I_{(max.) Abs}$	$\Delta\lambda_{Abs. At}$ FWHM (nm)	$\tau_{FM}$ (ns)
Chloroform	Without polymer	590.4	38.69	573.68-601.71	4.4
	1/0.25	583.8	43.4	567.69-597.19	4
	1/4	556.8	83	507.78-583.51	3.1
	1/8	557.4	98.5	511.21-576.24	2.5
Dimethyl sulfoxide	Without polymer	598.6	12.78	613.51-613.51	5
	1/0.25	594.39	16.8	577.02-608.69	4.8
	1/4	578.95	27.6	515.44-598.25	4
	1/8	564.47	33	521.23-586.67	3.5

Figures 7 represent emission spectra (a, b) of RhB in chloroform and dimethyl sulfoxide of concentration  $1 \times 10^{-4}$ M/l when it is mixed with different proportions from the concentrated solution of polymer in chloroform and dimethyl sulfoxide respectively. Emission maxima, quantum yield of mixed RhB solution, and polymer solutions are summarized in table 4.

From these curves and tables we can get the effect of the addition of the polymer to concentrated solutions ( $10^{-4}$ M/l) of RhB; [from expecting that leading to development active medium for laser dye at high concentrations] where increasing spectra shift toward high energies increasing luminescence quantum yield and decreasing relative radiation lifetime, either in relation liquid solutions

that increasing concentration leading to increasing spectra shift toward low energies, decreasing luminescence quantum yield and increasing relative life-time. These results are agreement with (24-29).

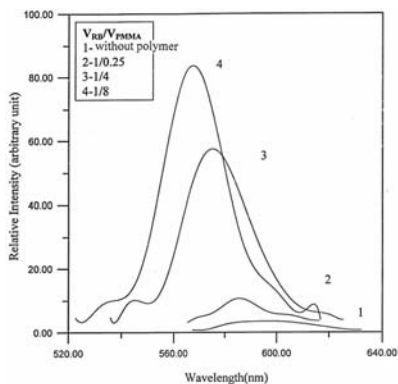


FIG. 7a

The emission spectra of RhB in chloroform of concentration  $10^{-4}$ M/l, with different volume proportions of polymer.

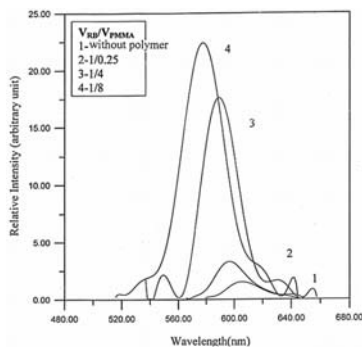


FIG. 7b

The emission spectra of RhB in dimethyl sulfoxide of concentration  $10^{-4}$ M/l, with different volume proportions of polymer.

**Table 4**

Spectro parameters of emission spectra of rhodamine B for concentration  $10^{-4}$ M/l in chloroform and dimethyl sulfoxide with different volume proportions of polymer.

Rhodamin B					
Solvent	$V_{RB}/V_{PMMA}$	$\lambda_{Flu}$ (nm)	$I_{max. Flu}$	$\Delta\lambda_{Flu}$ At FWHM (nm)	Quantum Yield ( $Q_{FM}$ )
Chloroform	Without polymer	595.15	3.18	576.24-619.48	0.41
	1/0.25	585.76	10.92	571.76-604.48	0.5
	1/4	575.68	57.79	561.12-593.6	0.61
	1/8	567.84	84.18	554.72-582.4	0.74
Dimethyl sulfoxide	Without polymer	605.4	1.62	592.76-621.84	0.4
	1/0.25	598	3.34	583.66-612.74	0.48
	1/4	590	17.94	574.56-604.55	0.59
	1/8	578.05	22.77	560-595.49	0.71

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