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The Spectroscopic Behaviour of Rhodamine 6G in Liquid and Solid Solutions

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Abstract:

Absorption, fluorescence, quantum yield and lifetime of rhodamine 6G in chloroform, methanol and dimethyl sulfoxide were measured. From a comparison of these quantities, with those for solid solutions (solid solutions are obtained by mixing constant volume proportions of dye at a concentration of $1*10^{-4}$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 ($1*10^{-4}$M/l)of rhodamine 6G dye from expecting [which leading to development active medium for laser dye at high concentration] increase the spectra shift toward high energies, and the luminescence quantum yield but decreasing radiative lifetime.

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]. 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 the spectral properties of S_1 state would be necessary to design efficient dye lasers and to determine optimum pumping conditions [2-9].

In this paper we have study the absorption, emission spectra with a different solvents, and, concentrations of Rh6G, firstly as a solution, and secondly as a solid solution when it mixed with PMMA at a different volume.

Experimental:

The following materials were used: - rhodamine 6G ($C_{28}H_{31}N_2O_3Cl$) {Eastman Kodak Com.} which molecular weight is 479.02 g/M as shown the molecular structure in Fig. (1). chloroform, methanol, dimethyl sulfoxide (all analytical grad, Fluka Com.) and PMMA beads (laboratory grade, ICI, Com.).

A series of solutions of Rh6G at concentrations varying from [10^{-6}- 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 Rh6G ($1*10^{-4}$M/l) with different volume proportions for 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 spectrofluorimeter model RF-500, Shimadzu Com. Which illustrated in Fig. (2).

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

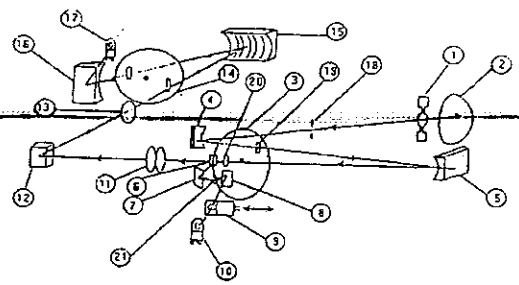

Fig. (1):- Schematic of experimental apparatus.

1- Xenon lamp, 2- Condensor ellipsoidal mirror,(Sio2 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 coupl of light-collecting lenses, 12- Cell, 13- Light-collecting lens, 14- Emission slit assembly, 15-Concave diffraction(for emission), 16- Concave mirror, 17- Photometric photomuliplier, R452-01, 18-Focus, 19- Entrance slit, 20-Exit slit, 21-Light beam balancing aperture

Results and Discussion:

In figures (2, 3, 4) which represents the absorption, emission spectra (A,B,C,a,b,c respectively) of Rh6G in chloroform, methanol, dimethyl sulfoxide for concentrations (10^{-4}, 10^{-5}, 10^{-6} M/l). Absorption maxima, wave numbers, and, lifetime are measured in table (1) [12]. Emission maxima, wave numbers, and, quantum efficiencies were measured in table (2). From this figures and tables we can see that there are shift to the low energy (long wave length) as the concentration increases, while the quantum yield decreases and lifetime increases. The shift in spectra toward long wave length as the concentration is increases. These changes have been interpreted in two different ways. On the one hand there are considered as due to dimerization process [13-19]. On the other, they are attributed to the change of RhB from its neutral form ($Rh6G^+$) to the cationic one $Rh6GH^+$ [20-23] Fig. (5).

This theory is based on the decreasing of PH produced when dye concentration increases.

The decreasing of quantum yield as the concentration increases, have been interpreted by dimmer 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 agreement with Lopez Arbeloa, and, his team[24].

The decreasing of quantum yield as the concentration increases, have been interpreted by dimmer molecules which absorb the emission photons. This is due to the band energy of dimer molecules under the band energy of Rh6G molecules (monomer). These results are agreement with Lopez Arbeloa, and, his team.

Fig.(6) represent the absorption spectra (A, B) of Rh6G in chloroform, and, dimethyl sulfoxide of concentration 10^{-4}M/l, where it 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. (7) represents emission spectra (a, b) of Rh6G in chloroform and dimethyl sulfoxide of concentration 10^{-4}M/l when it mixed with different proportions from the concentrated solution of polymer in chloroform and dimethyl sulfoxide respectively. Emission maxima, quantum yield of mixed Rh6G solution, and, polymer solutions are summarized in table (4).

From these curves and tables we can get that the addition of the polymer to

concentrated solutions (10^{-4}M/l)of Rh6G; [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 lifetime. These results are agreement with [25-30].

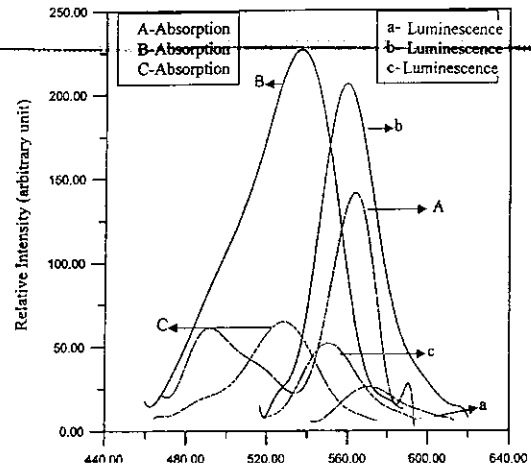

Fig.(2) :- Absorption, emission spectra (A, B, C, a, b, c) of Rh6G in chloroform for concentration (10^{-4}, 10^{-5}, 10^{-6} M/l)

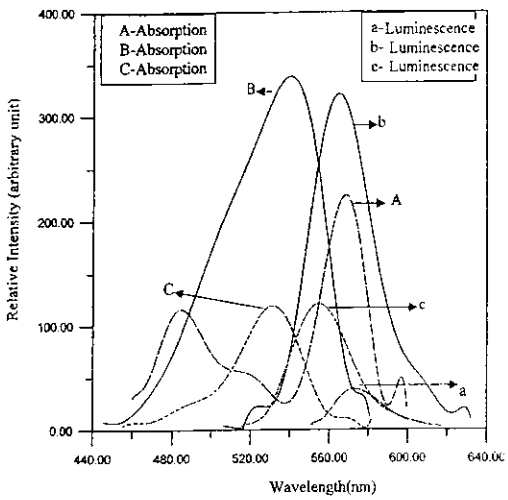

Fig. (3):- Absorption, emission spectra (A, B, C, a, b, c) of Rh6G in methanol for concentration (10^{-4}, 10^{-5}, 10^{-6} M/l).

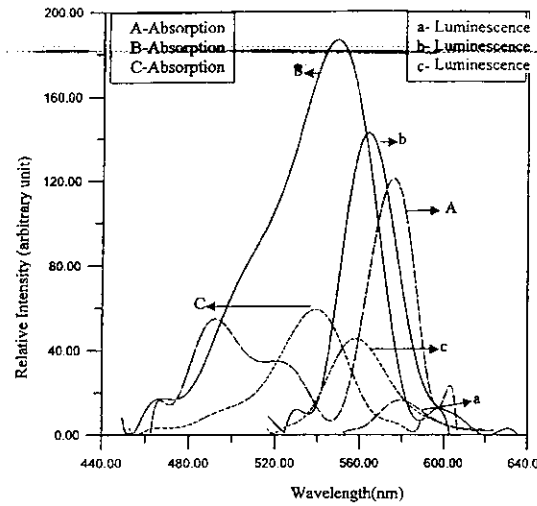

Fig. (4):- Absorption, emission spectra (A, B, C, a, b,c) of Rh6G in dimethyl sulfoxide for concentration (10^{-4}, 10^{-5}, 10^{-6} M/l).

Table 1: Mole concentration, absorption and emission maxima, and, life time of rhodamine 6G in chloroform, methanol, and, dimethyl sulfoxid.

Rhodamine 6G						
Solvent	Concentration M/L	$\lambda_{Abs.}$ (nm)	$\bar{\nu}_{Abs.}$ (cm^{-1})	λ_{Flu} (nm)	$\bar{\nu}_{Flu}$ (cm^{-1})	τ_{FM} (ns)
Chloroform	$1*10^{-4}$	563.8	17736.78	574	17421.6	5.2
	$1*10^{-5}$	536.15	18651.49	559.9	17860.33	4.1
	$1*10^{-6}$	531	18832.39	553	18083.18	3.4
Methanol	$1*10^{-4}$	567.6	17618.04	573.3	17442.87	5.5
	$1*10^{-5}$	540	18518.51	564.75	17706.94	3.9
	$1*10^{-6}$	529	18903.59	551	18148.82	3.6
Dimethyl Sulfoxide	$1*10^{-4}$	576.8	17337.03	580.8	17217.63	6.3
	$1*10^{-5}$	550.4	18168.6	564	17730.49	4.5
	$1*10^{-6}$	539.2	18545.99	558.4	17908.3	3.8

Table 2: Mole concentration, life time, and, quantum yeild of rhodamine 6G in chloroform, methanol, and, dimethyl sulfoxid.

Rhodamin 6G			
Solvent	Concentration M/l	τ_{FM} (ns)	Quantum Yield (Q_{FM})
Chloroform	$1*10^{-4}$	5.2	0.66
	$1*10^{-5}$	4.1	0.7
Methnol	$1*10^{-4}$	5.5	0.79
	$1*10^{-5}$	4.2	0.94
Dimethyl sulfoxide	$1*10^{-4}$	6.3	0.5
	$1*10^{-5}$	4.5	0.56

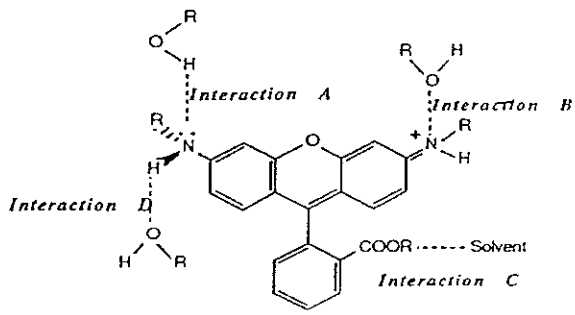

Fig. (5) Molecular structure of neutral ($R6G^{+}$) and catonic ($R6GH^{+}$) forms of rhodamine B.

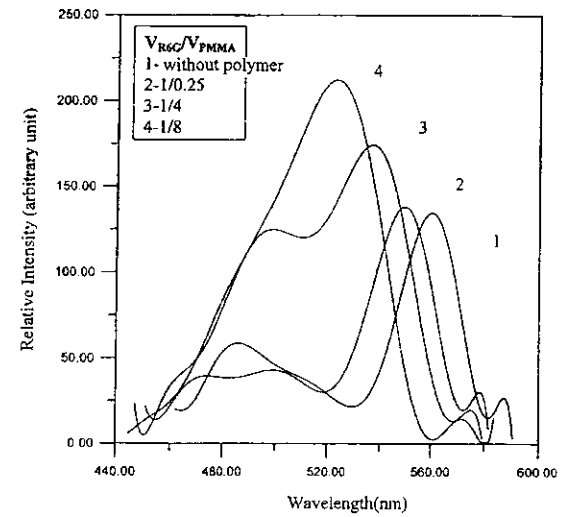

Fig. (6A):-The absorption spectra of Rh6G in chloroform of concentration 10-4M/l, with different volume proportions polymer.

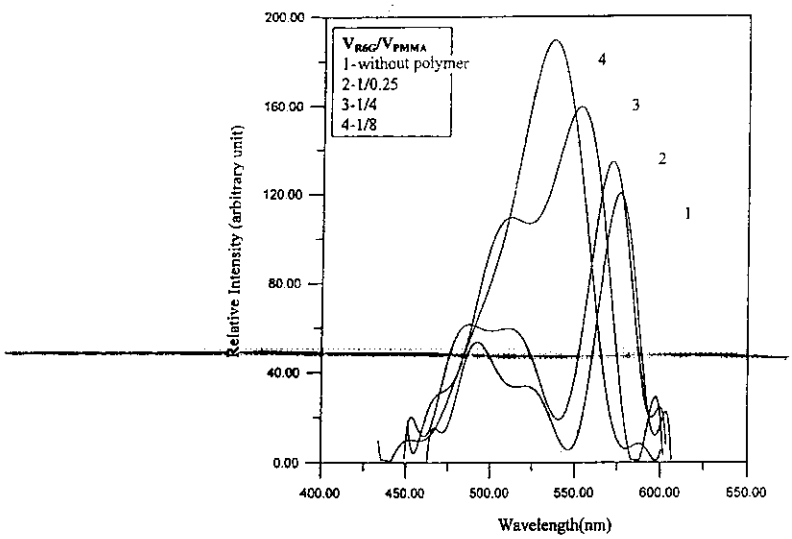

Fig. (6B):-The absorption spectra of Rh6G in dimethyl sulfoxide of concentration 10-4M/l with different volume proportions polymer.

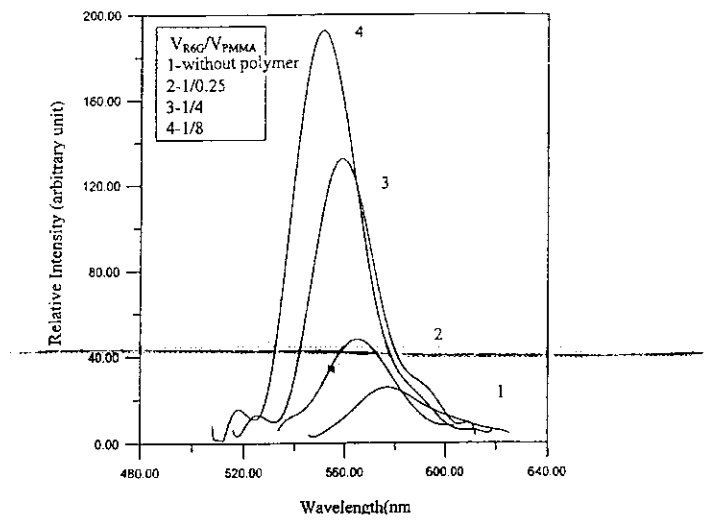

Fig. (7A):-The emission spectra of Rh6Gin chloroform of concentration 10-4M/l, with different volume proportionsof polymer.

Table 3: Spectro parameters of absorption spectra of rhodamine 6G for concentration 10-4 M/l in chloroform , and, dimethyl sulfoxide with different volume proportions of polymer.

Rhodamin 6G					
Solvent	V_{RB}/V_{PMMA}	λ_{Abs} (nm)	$I_{(max)Abs}$	$\Delta\lambda_{Abs}$ At FHWM (nm)	τ_{FM} (ns)
Chloroform	Without polymer	563.8	139.5	(572.24-545.92)	5.2
	1/0.25	551.5	144.9	(533.68-562.88)	5
	1/4	538	182.85	(482.16-553.84)	4.2
	1/8	523	221.95	(487.92-543.04)	3.7
Dimethyl sulfoxide	Without polymer	576.8	121.56	-587.41) (562.3	6.3
	1/0.25	571	136.12	(555.13-585.36)	6
	1/4	552.1	161.54	(493.56-570.5)	5.1
	1/8	537.8	191.88	(505.13-558.2)	4

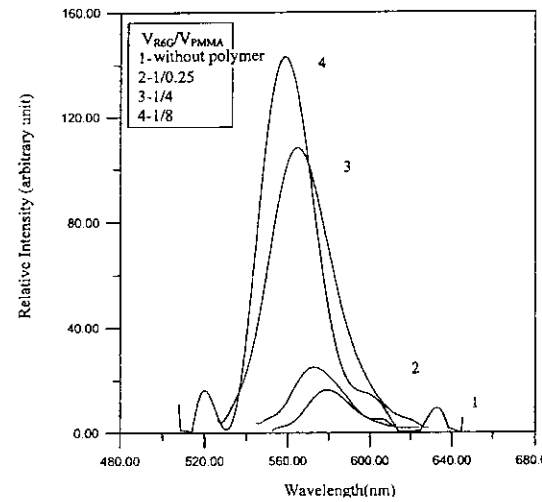

Fig. (7B):-The emission spectra of RhB in dimethyl sulfoxide of concentration 10-4M/l, with different volume proportionsof polymer.

Table 4: Spectro parameters of emission spectra of rhodamine 6Gfor concentration 10-4 M/l in chloroform , and, dimethyl sulfoxide with different volume proportions of polymer.

Rhodamin 6G					
Solvent	V_{RB}/V_{PMMA}	$(nm)\lambda_{Flu.}$	$I_{(max.)\,Flu.}$	$\lambda_{Flu.}\Delta$ At FHWM (nm)	Quantum Yield (Q_{FM})
	Without polymer	574	26.45	(561.44-598.88)	0.11
Chloroform	1/0.25	565.25	48.6	(549.52-582.32)	0.7
	1/4	558.5	133.2	(545.92-574.4)	0.78
	1/8	551.5	192.6	(537.28-567.2)	0.85
Dimethyl sulfoxide	Without polymer	580.8	16.16	(567.84-593.81)	0.5
	1/0.25	574	25.2	(560-589.89)	0.57
	1/4	565	110.6	(548.91-584.01)	0.18
	1/8	558	145.6	(544.01-575.68)	0.74

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دراسة الخصائص الفيزيائية الضوئية لصبغة رودامين 6G للمحاليل السائلة والصلدة

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*جامعة بغداد / كلية العلوم / قسم الفيزياء/ بغداد/ عراق

الخلاصة:

تضمن هذا البحث دراسة الخواص الفيزيائية الضوئية (الأمتصاص، التألق، والناتج الكمي وزمن العمر) للمحاليل السائلة والصلدة لصبغة رودامين 6G حيث تضمنت المحاليل السائلة التراكيز المختلفة للمذيبات الكلوروفورم، الميثانول وثنائي مثيل أوكسيد الكبريت، أما المحاليل الصلدة فهي تتضمن مزج نسبة حجمية ثابتة من المحلول المركز للصبغة ($1x10^{-4}$ mole/liter) مع نسب حجمية مختلفة من المحلول المركز للبوليمر في الكلوروفورم وثنائي مثيل أوكسيد الكبريت.

أظهرت النتائج أن أضافة البوليمر الى المحاليل المركزة السائلة ($1x10^{-4}$ mole/liter) لصبغة رودامين 6G من المتوقع أن تؤدي الى تحسين الوسط الفعال لليزر الصبغة عند التراكيز العالية حيث تزداد ازاحة الأطياف بأتجاه الطاقات العالية كما يزداد الناتج الكمي للتألق ويقل زمن العمر الأشعاعي نسبيا.