

Lyoluminescence of luminol in the presence of fluorescein and rhodamine-B dyes

V.M. RAUT, M.P. BHISE, R.P. PAWAR and D.P. GULWADE

Department of Chemistry, Government
Vidarbha Institute of Science & Humanities, Amravati (India).

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ABSTRACT

The lyoluminescence (LL) emission spectra of luminol, fluorescein & rhodamine-B (R-B) dyes have been recorded at optimum concentration of the activators in aqueous ethylamine. An enhancement of three & seven fold increases in LL intensity of luminol has been observed at 9×10^{-5} M concentration of fluorescein & 8×10^{-5} M concentration of R-B respectively, in the binary solution of luminol & dyes. The LL emission spectra of luminol-dye mixture are recorded at the concentration of enhancement in LL intensity of luminol. These spectra in resolution, should have four emission bands. The first two bands of 430 & 470 nm corresponds to LL of luminol & the other two bands of longer wavelength emission corresponds to LL of dye molecule. The observed enhancement of LL intensity is explained with the help of a mechanism based on the reactions of colour centers with activities.

Key words: Luminol, Fluorescein, Rhodamine-B, Lyoluminescence.

INTRODUCTION

The release of the stored energy from irradiated solids into solution resulting in emission of light known as lyoluminescence (LL)¹. This phenomenon was first reported by Wiedmann & Schmidt¹ in 1895. The solid substance which induced LL are termed as phosphores & they are classified into & inorganic solids^{2,3}. The organic luminescent phosphores have radicals while inorganic have trapping centers responsible for LL³. The most stable lyoluminescent inorganic phosphor which have been extensively studied for LL investigation in NaCl¹⁻³.

There are two important characteristics of LL glows. First it is very weak in intensity & second it exists for a very short interval of time. However, LL glow can be intensified by corresponding suitable activator such as thallium ions, fluorescent dyes & chemiluminescent material^{4,5}.

Fluorescent organic dyes are generally characterized by conjugated double bonds as in xanthenes^{6,7}. The dyes fluoresce^{8,9} in & rhodamine-B^{8,9} (R-B) belong to this class. They are not only fluorescent but lyoluminescent too in basic medium. Another popular activator extensively used in LL dosimetry is luminal^{14,10} (5-amino-2, 3-dihydro-1, 4-phthalhydrazine dione). Aqueous alkaline solution of luminal is chemiluminescent¹¹ as well as lyoluminescent^{12,13}. An enhancement of the order of 10^6 fold in intensity as compared to pure water has reported by Atari & Ettinger¹³ using NaCl as a phosphor. Therefore, it is of interest to study the LL intensity of luminal in the presence of xanthene dyes in an entirely different base. Present investigation deals with the measurements of LL intensities of both luminal & dye respectively at a fixed concentration of luminal & varying the concentration of dye in an aqueous solution of luminal-dye mixture. The LL emission spectra of luminal-dye mixture are recorded in aqueous ethylamine at the concentration in LL intensity.

EXPERIMENTAL

All the chemical used in the present investigations are analytical grade and luminol is procured from Koch-light laboratories (England).

Exactly 0.5g NaCl powder (40-50 mesh) is weighed in the glass envelopes sealed and wrapped in a black paper. The sample are irradiated to 30 Kgy gamma dose using ^{60}Co source. These samples are stored for four hours to allow room temperature luminescence (RTL) to decay completely. The irradiated salt is carefully added to a pyrex cell 10ml aqueous solution of the activator. The LL intensity is measured on a photomultiplier tube (IP-28) coupled to a faster scalar by keeping the cell closed to the detector. The LL intensity of the luminol and dye R are measured independently at a constant concentration of luminol ($3.5 \times 10^{-4}\text{M}$) and varying the concentration of dye in aqueous ethyl amine solution ($1.1 \times 10^{-3}\text{M}$) of luminol dye mixture. The LL intensity of luminol, fluorescent and R-B are measured by incorporating appropriate interference filters 430, 530 and 570 nm respectively.

The LL emission spectra

The LL emission spectra are recorded by continuous addition of γ -irradiated NaCl salt (200 mesh) to a Pyrex cell containing optimum

concentration of the activator or a binary mixture in front of the slit of a Fuses spectrography. All optical alignment is made before loading the Kodak film of 400 ASA. The exposure time varies from 8-11 hours depending on the light output of LL source. The standard lines from low-pressure mercury lamp are superimposed on the same film after the LL exposure is over. The film is developed, washed and dried. The spectral distribution is obtained with the help of Russian MÖ microdensitometer. The fluorescence (FL) spectra of fluorescein and Rhodamine-B (R-B) in aqueous ethyl amine ($1.1 \times 10^{-3}\text{M}$) while absorption spectra of these activators are recorded on Hitachi Spectrophotometer (Model 220).

RESULTS

It is well known that the luminescence intensity depends upon the concentration of the activator in solution. Kalkar *et.al.*^{14, 19} while studying the concentration dependence of luminol in aqueous amines observed an intense LL emission of luminol at $3.5 \times 10^{-4}\text{M}$ concentration. The concentration dependence of LL intensity of fluorescein and R-B in aqueous ethyl amine (pH=10.8) is shown in (fig. 1). The LL intensities of fluorescein and R-B are maximum at 2×10^{-5} & $5 \times 10^{-5}\text{M}$ concentration respectively.

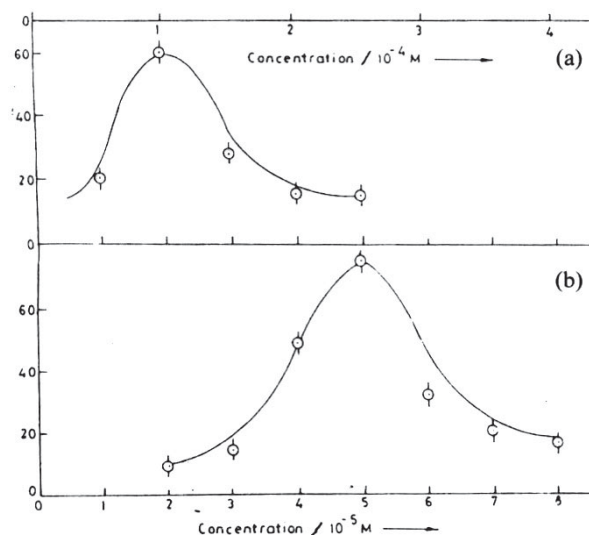


Fig. 1: Variation of relative LL intensity with concentration of (a) Fluorescein and (b) Rhodamin-B in aqueous ethyl amine solution

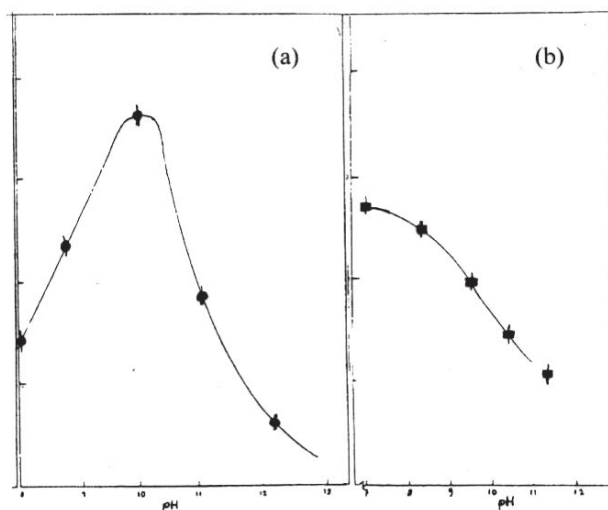


Fig. 2: pH dependence LL intensity of (a) Fluorescein and (b) Rhodamin-B

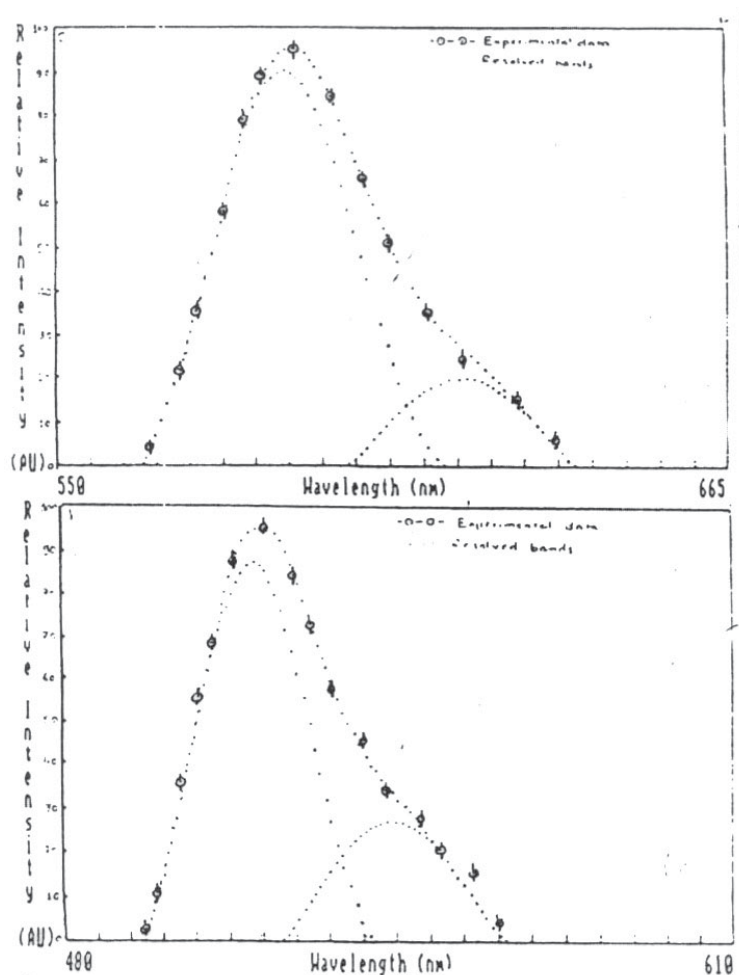


Fig. 3: The resolved fluorescence (FL) spectra of (a) fluorescein and (b) rhodamin-B

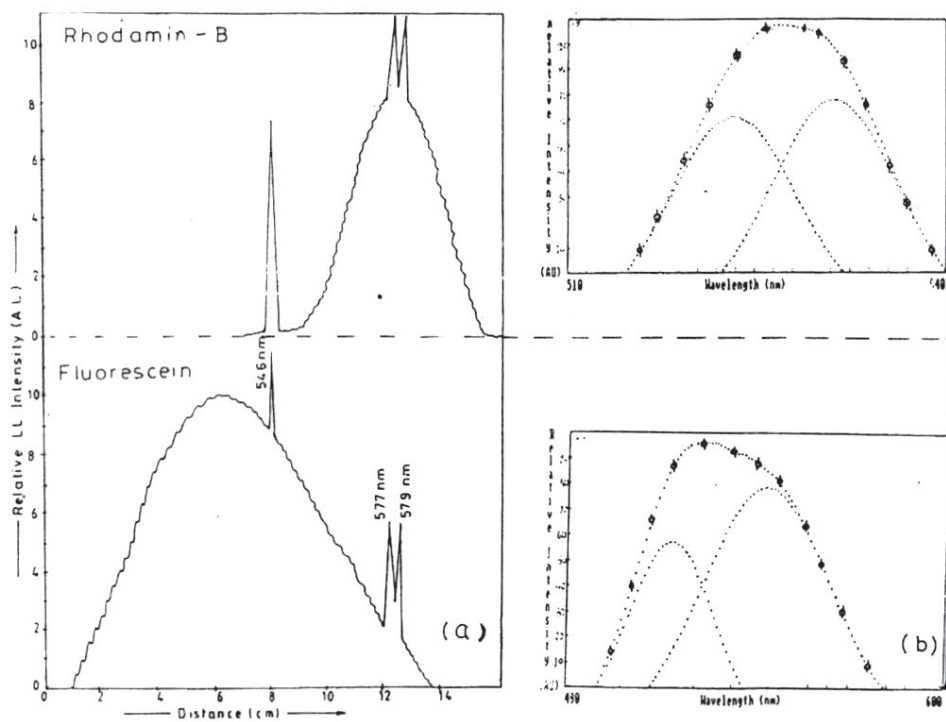


Fig. 4: The (a) Microphotometric and (b) resolved LL emission spectra for fluorescein rhodamin - B in aqueous

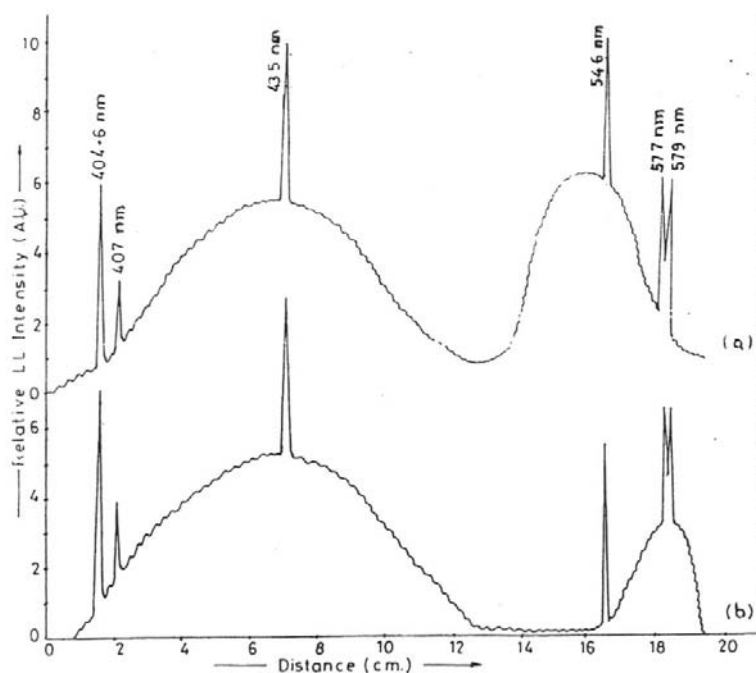


Fig. 5: The (a) Microphotometric analysis of LL emission spectra of luminol in presence in (a) rhodamine - B and (b) fluorescein in aqueous ethyl amine using NaCl

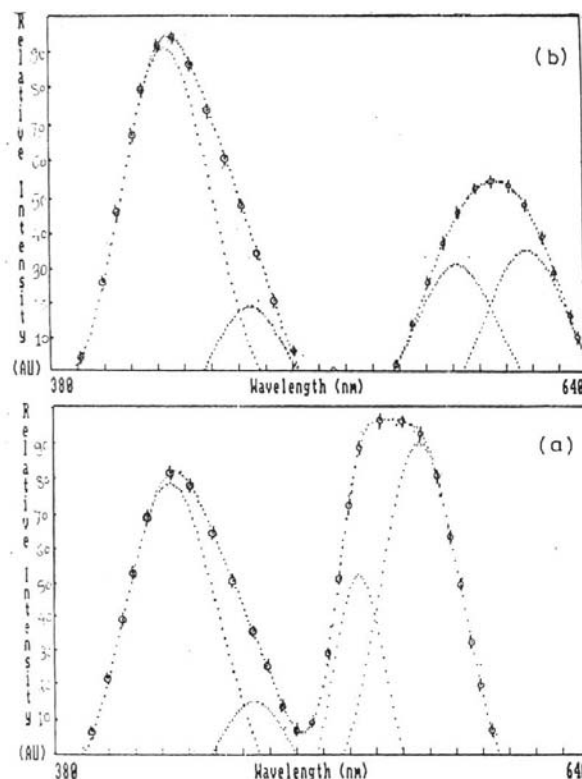


Fig. 6: The resolved LL emission spectra of (a) luminol fluorescein and (b) luminol -R-B mixture in aqueous ethyl amine using NaCl* salt

The LL intensities of luminol and fluorescein are measured at 430 nm and 530 nm respectively by varying the concentration of fluorescein in luminol in fluorescein mixture. The LL intensity of luminol & R-B are measured at 430 nm & 570 nm respectively by varying the concentration of R-B in luminol R-B mixture. The plot of relative intensities of luminol and dye versus dye concentration is shown in (figure 2). The LL intensity of luminol are maximum at a concentrations of 9×10^5 M fluorescein and 8×10^5 M R-B respectively.

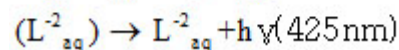
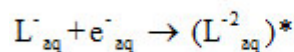
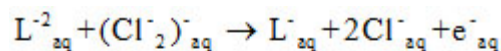
DISCUSSION:

LL Mechanism of single activator

LL Mechanism of luminol

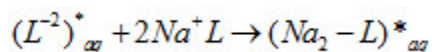
Atari^{6, 21} has proposed the mechanism of LL of luminol is similar to that of chemiluminescence (CL) of luminol¹. He suggested that species responsible for both LL and CL is identical as the CL and LL band of luminol is

identical. Kalkar et al.,^{18, 21} proposed the mechanism exactly different way. The species which is formed during LL and CL is different. Luminol itself activate due to reaction of colour centers. Which is based on the different conclusions. The electrons and hole centres released from irradiated NaCl react with L^{2-} (dinegative ions of luminol) in the following way at the solid liquid interlace.



The excited dinegative ions are responsible for emission band of 425 nm. The Na^{+} ions simultaneously released during the disintegration of NaCl crystal associated with the excited dianion of

luminol producing associated excited species of luminol.



The 460 nm emission band is mainly due to the association producing neutral excited species.

LL Mechanism of Xanthene Dyes

In the present investigation fluorescein should two LL band at 512 nm and 540 nm respectively. In the case of Rhodamin-B two bands appears at 564 nm and 594 nm respectively in aqueous ethyl amine. This clearly indicate that two excited species are formed during LL process in both the dyes shown in (figure 3)

Table 1: Analysis of LL/FL emission spectra of various activators in aqueous ethyl amine

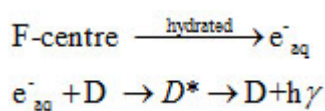
Activator	Mode of Emission	Emission	Emission Range (nm)	Band Maxima (nm)	Half band width (nm)	Relative peak Intensity (A.U.)
Fluorescein	LL	Observed	490-582	525	40	95
		i)	490-540	512	18	57
		ii)	507-582	540	26	78
	FL	Observed	495-560	520	25	96
		i)	495-540	515	15	88
		ii)	525-560	540	20	25
Rhodamin-B	LL	Observed	530-640	49	49	98
		i)	530-605	28	28	60
		ii)	565-640	28	28	66
	FL	Observed	565-635	590	28	96
		i)	565-615	587	17	90
		ii)	600-635	615	20	20

Table 2: Analysis of LL emission spectra of luminol dye mixtures in aqueous ethyl amine

Mixed Activator	LL Emission	Emission Range (nm)	Band Maxima (nm)	Half Band width (nm)	Relative peak Intensity (A.U.)
Luminol + Fluorescein	Observed	390-480	440	35	82
	Resolved band of	480-600	535	30	96
	a) Luminol i)	390-465	433	30	78
	ii)	445-480	470	24	15
	b) Fluorescein iii)	487-523	518	16.5	52
	c) iv)	498-600	546	26	90
Luminol + Rhodamin-B	Observed	390-482	435	35	95
	Resolved band of	560-642	580	38	56
	a) Luminol i)	390-465	433	30	92
	ii)	442-482	470	24	18
	b) Fluorescein iii)	560-612	564	28	31
	iv)	590-642	596	28	37

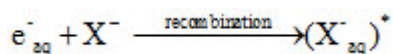
Westermarck³ and Ahnstrom¹⁰ reported that light emission is considerably increase on addition of fluorescent substances to the solvent. Atari Ettinger²¹ observed LL enhancement of fluorecein solution for NaCl salt exposed to higher doses. The enhancement factors reported by Kalkar^{19, 20} for LL of fluorescein in alkaline medium and Rhodamine-B in neutral medium are 580 nm and 870 nm respectively.

Mechanism proposed by Atari for the enhancement of fluorecene dyes as follows,

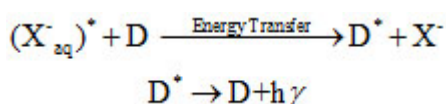


Where D represent dye molecule.

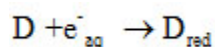
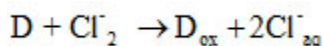
Another mechanism proposed on the basis of energy transfer from excited halogen (X^-)^{*} ions. The LL mechanism of irradiated alkali halide in the pure water is given by the following equation.



The excited halogen ions transfer its energy to the dye molecule in the second step.



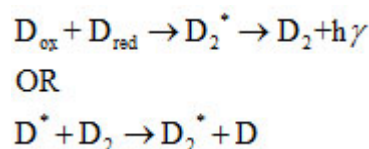
Comparing the fluorescence emission spectrum and LL spectrum of dyes Kalkar^{19, 20} proposed the following mechanism based on reactions of colour centers with dye molecule.



Dye exhibit a pronounced tendency to aggregate into dimmers or higher polymeric forms. The effect of concentration upon dye fluorescence

is important in which fluorescene of the monomer and the dimmer are observed. The fluorescene spectra fluorescein and rhodamine-B (fig. 4) shows that intence FL band at 515 nm and weak band at 540nm in aqueous ethyl amine for fluorescein and for rhodamin-B shows intense emission at 587nm and less intense emission at 615nm. The shorter wavelength emission band is due to excited dimmers. (Table 1).

It is observed that the LL bands are matching well with fluorescence bands of respective dyes. The longer wavelength band is due to the excited dimmer formed directly by recombination of oxidese and reduced species or by energy transfer from excited monomer.



In conclusion the LL of luminol, fluorescein and rhodamin-B induced by irradiated NaCl is due to internal excitation of the activator as a result of its reactions with colour centers. On the other hand fluorescence of luminol and xanthene dyes is known to occurs as a result of external excitation by photons. In both LL and FL process, emission characteristic of the activator is observed.

LL mechanism of mixed activator

A characteristic LL emission of luminol occurs at 430nm when γ -irradiated NaCl is dissolved in aqueous alkaline luminol solution. On the other hand a three and seven fold increase in LL intensity of luminol is observed at 9×10^{-5} M fluorescein and 8×10^{-5} M rhodamin-B in luminol dye mixture as compared to the LL intensity of same concentration of luminol alone. Qualitatively, the LL spectral distribution of the mixed activators agree well with the enhancement in the LL intensity if luminol obtained by using a interference filters and photomultiplier-picoummeter assembly. The resolved LL emission spectra of luminol-dye mixture shows four banded emission, two corresponds to luminol and two corresponds to dye (Fig. 5, 6 & table 2).

The luminol and dye can react independently with the colour centres during dissolution process. Therefore, the mechanism of LL of luminol in mixture must be similar to that of pure luminol.

The LI mechanism of both luminol and dye in mixture indicate that the concentration of activators remains unaltered after LL is over.

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