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Quenching of fluorescence of Rhodamine 610 in binary and ternary mixture solutions

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Abstract

The sensitized fluorescence emission from bimixtures, Coumarin 500 (donor) + Rhodamine 610 (acceptor) and Rhodamine 610 (donor) + Nile Blue 590 (acceptor) and also from the ternary mixture, Coumarin 500 (donor) + Rhodamine 610 (inter mediator) + Nile Blue 590 (acceptor), have been measured as a function of dye concentration and excitation wavelength using a fluorescence spectrophotometer. The spectroscopic parameters for the bimixtures have been estimated from the concentration dependence of the peak fluorescence intensity curves.

Keywords: Energy transfer; Fluorescence quenching; Aggregate formation; Laser grade dyes

1. Introduction

The present communication discusses the fluorescence energy transfer characteristics among unlike organic dye molecules in solution, which has attained considerable theoretical as well as experimental attention [1–5]. Earlier, a detailed study of these dyes has been made via gain spectra using a single excitation frequency of nitrogen laser [6–9]. It has now become a matter of curiosity to find out the most suitable excitation frequency and the characteristics of the resulting spectra particularly from the point of view of fluorescence energy transfer among dyes.

The fluorescence and absorption spectra of three dyes under investigation are shown in Fig. 1. It is clear that there is no overlapping between the Coumarin 500 dye emission spectrum and the Nile Blue dye absorption spectrum, thereby neglecting the possibility of energy transfer in C 500 + NB bimixture. When an intermediator dye molecule (Rh 610) is used, the NB dye can be made to lase. Further, before studying the energy transfer in ternary mixture solutions, a detailed study of the concentration dependence of the fluorescence spectra and hence that of the peak fluorescence intensity and peak wavelength in case of bimixture systems: C 500 + Rh 610 and Rh 610 + NB has been made. The non-radiative energy transfer rate constants have also been calculated from the Stern–Volmer plots given by the following equation:

$$I_{fo}/I_f = 1 + k\tau_{fo}[A]$$

where I_{fo} and I_f are the fluorescence intensities of donor in absence and presence of acceptor respectively, k is the non-radiative transfer rate constant and $[A]$ is the acceptor concentration. By knowing the value of τ_{fo}, the fluorescence lifetime of donor in absence of acceptor, k can be calculated from the slope of I_{fo}/I_f versus $[A]$ curve, which is a straight line. This, in turn, leads to the evaluation of the critical transfer radius (R_o) given by [10],

$$R_o = 7.35([A]_{1/2})^{-1/3}$$

where $[A]_{1/2}$ is the half quenching concentration. The results have been compared with the fluorescence measurements of these dyes in single solutions as well. It has been found that the fluorescence intensity of Rh 610 in bimixture solutions of C 500 + Rh 610 and Rh 610 + NB is quenched.

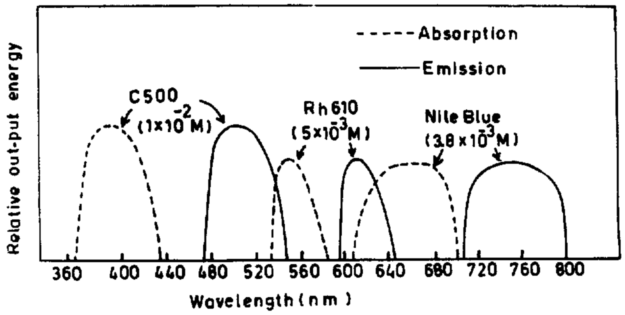

Fig. 1. Absorption and emission spectra of C 500, Rh 610 and Nile Blue.

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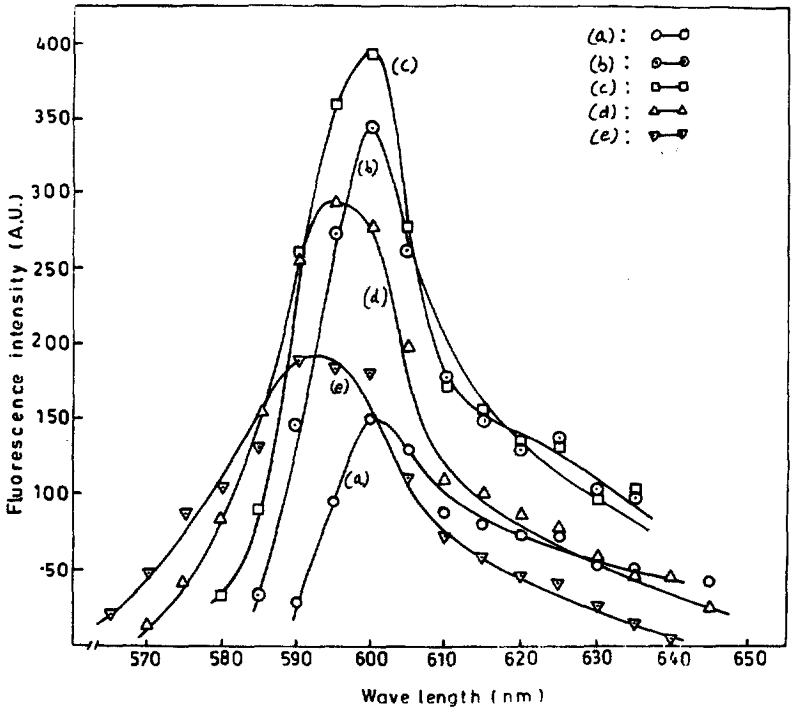

Fig. 2. Fluorescence spectra of Rh 610 at $\lambda_{ext.}=450$ nm, (a): 2×10^{-3} mol l^{-1}; (b): 1×10^{-3} mol l^{-1}; (c): 5×10^{-4} mol l^{-1}; (d): 2×10^{-4} mol l^{-1}; (e): 1×10^{-4} mol l^{-1}.

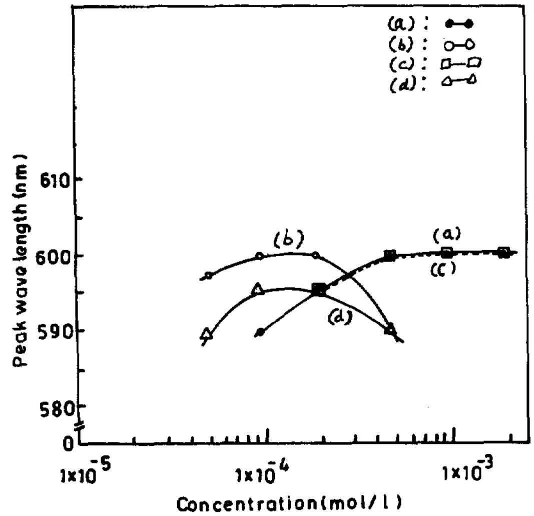

Fig. 3. Peak fluorescence wavelength versus concentration, (a): Rh 610; (b): Nile Blue; (c): C 500 (5×10^{-3} mol l^{-1}) + Rh 610 (1×10^{-4} to 2×10^{-3} mol l^{-1}); (d): Rh 610 (5×10^{-4} mol l^{-1}) + Nile Blue (1×10^{-9} to 5×10^{-4} mol l^{-1}).

The experimental set up for the measurement of fluorescence spectra at different concentration of the dyes is shown elsewhere [11]. The laser grade dyes studied in the present work were obtained from Exciton, Ohio, USA, and were used without further purification. The solutions were made in spectroscopically pure ethanol in the concentration range from 1×10^{-2} mol l^{-1} to 1×10^{-5} mol l^{-1} and observations were taken at room temperature. The dye solution taken in a quartz dye cell (of internal area of cross-section 8 mm × 8 mm) was excited with a Xenon lamp. The fluorescence spectra was recorded with a Hitachi fluorescence spectrometer. The observed fluorescence spectra is corrected for the non-linear response of the detector photomultiplier tube and the non-uniform emission of the excitation source. The recorded fluorescence maxima are accurate within ±2 nm. The excitation spectra was observed to find out the most suitable excitation wavelength ($\lambda_{ext.}$) corresponding to optimum fluorescence

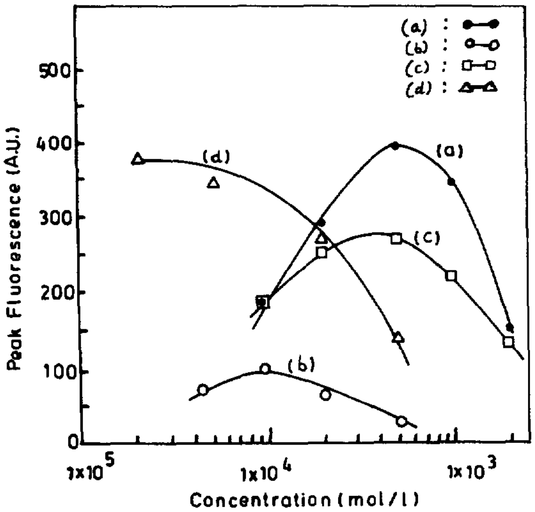

Fig. 4. Peak fluorescence/intensity versus concentration, (a): Rh 610; (b): Nile Blue; (c): C 500 (5×10^{-3} mol l^{-1}) + Rh 610 (1×10^{-4} to 2×10^{-3} mol l^{-1}); (d): Rh 610 (5×10^{-4} mol l^{-1}) + Nile Blue (1×10^{-4} to 5×10^{-4} mol l^{-1}).

output. The $\lambda_{ext.}$ was kept invariant during a particular set of observations.

2. Results and discussion

The fluorescence spectra of Rh 610 at various concentrations and at fixed excitation wavelength of 450 nm has been shown in Fig. 2. The behaviour of Rh 610 is studied in the bimixtures: C 500 + Rh 610 (I) and Rh 610 + NB (II) where it acts as acceptor and donor respectively. The bimixtures (I) and (II) are studied at fixed donor concentration of 5×10^{-3} mol l^{-1} and 5×10^{-4} mol l^{-1} and at fixed excitation wavelength of 455 nm and 450 nm, respectively. The donor concentration in the two cases is the one at which the peak fluorescence intensity is found to be maximum and the excitation wavelength for a bimixture is the same as the excitation wavelength for donor alone in that particular mixture. The acceptor concentration is always taken less than or equal to the donor concentration [12] and is varied from 2×10^{-3} mol l^{-1} to 1×10^{-4} mol l^{-1} for bimixture (I) and from 5×10^{-4} mol l^{-1} to 5×10^{-5} mol l^{-1} for bimixture (II).

2.1. Concentration dependence of peak fluorescence wavelength

The variations of peak wavelength of the fluorescence spectra of the two dye mixture solutions with acceptor concentration as well as of Rh 610 alone are shown in Fig. 3. The figure depicts that the peak wavelength variations are almost the same for the bimixture (I) as that for Rh 610 alone; whereas for the bimixture (II) the peak wavelength first shows a red shift and then it is blue shifted as compared to Rh 610 alone. In the former case, Rh 610 is acting as acceptor dye, so the contribution to the fluorescence spectra is mainly from Rh 610. However, when it is compared with the fluorescence spectra of C 500 dye solution alone [13], it is found that the peak wavelength for the bimixture (I) is red shifted.

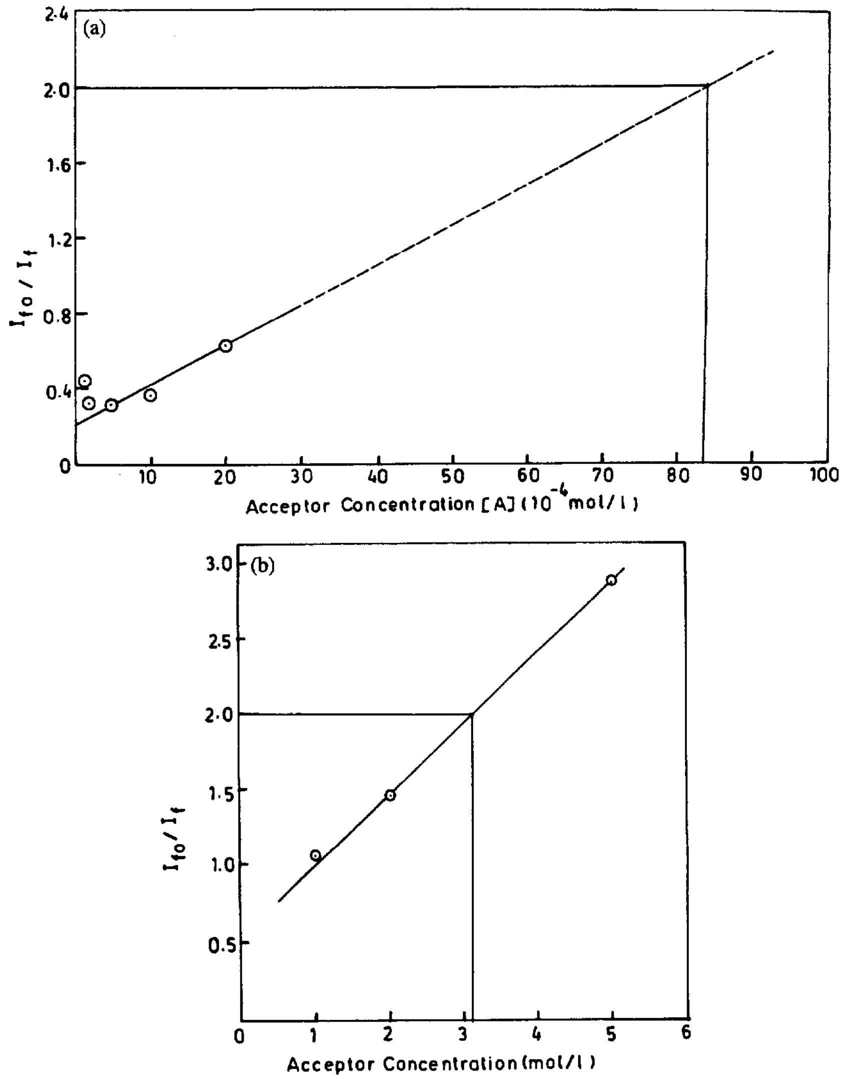

Fig. 5. a: I_{fo}/I_f versus acceptor concentration for C 500 and Rh 610 bimixture at fixed donor concentration of 5×10^{-3} mol l^{-1}. b: I_{fo}/I_f versus acceptor concentration for RH 610 and Nile Blue bimixture at fixed donor concentration of 5×10^{-4} mol l^{-1}.

On the other hand, for the bimixture (II), where Rh 610 is acting as donor (at $5\times10^{-4}\ \mathrm{mol\ l^{-1}}$ concentration), peak wavelength is first red shifted and then blue shifted with increasing acceptor concentration. This type of behaviour of peak wave length for bimixture (II) is attributed to be due to the reduction in aggregate formation in the acceptor molecule due to formation of new donor-acceptor aggregates with increasing acceptor concentration [13]. However, on further comparing the results of bimixture (II) with Nile blue alone, it is found that the contribution is mainly from Nile blue.

2.2. Concentration dependence of peak fluorescence intensity

The variation of peak fluorescence intensity of the fluorescence spectra of the binary mixture solution with acceptor concentrations as well as of Rh 610 dye alone are shown in Fig. 4. It is clear from the figure that the peak fluorescence intensity for Rh 610 alone is quenched on addition of either C 500 or Nile Blue at all the concentrations. In case of bimixture (I), it may be understood to be due to the strong overlapping of the triplet–triplet absorption band of the donor dye (C 500), which lies at the long wavelength side of its fluorescence band, with the fluorescence band of the acceptor dye (Rh 610). However, for the bimixture (II), the significant quenching of the donor fluorescence occurred due to the energy transfer from Rh 610 donor dye to Nile Blue acceptor dye. Here, it is remarkable to note that the peak fluorescence intensity of Nile Blue alone is increased many times when Rh 610 is added (Fig. 4b). These results are in good agreement with the theoretical model predicted by Ali et al. [1–5].

2.3. Spectroscopic parameters

In order to calculate the non-radiative energy transfer rate constant, $I_{\mathrm{fo}}/I_{\mathrm{f}}$ is plotted against acceptor concentration $[A]$ for both the bimixtures (Fig. 5). The variation $I_{\mathrm{fo}}/I_{\mathrm{f}}$ versus $[A]$ is linear in nature satisfying the Stern–Volmer kinetics. The calculated values of K and R_{o} for the bimixture (I) is $5.175\times10^{10}\ \mathrm{l\ mol^{-1}\ s^{-1}}$ and 36.157 Å respectively using $[A]_{1/2}=8.4\times10^{-3}\ \mathrm{mol\ l^{-1}}$ (Fig. 5a) and for bimixture (II) K and R_{o} are $5.376\times10^{11}\ \mathrm{l\ mol^{-1}\ s^{-1}}$ and 108.57 Å at $[A]_{1/2}=3.1\times10^{-4}\ \mathrm{mol\ l^{-1}}$ respectively. This shows that energy transfer is quite less in case of bimixture (I) in comparison to that in bimixture (II).

Thus, even though both donor and acceptor dyes individually may be efficient and have good energy transfer spectral overlaps, overlap of donor triplet–triplet absorption with acceptor emission can quench fluorescence and hence the laser emission.

Further, the ternary mixture C 500 + Rh 610 + NB appeared to be interesting ETDL candidate and two sets mentioned below are studied:

1. C 500 ($5\times10^{-3}\ \mathrm{mol\ l^{-1}}$) + Rh 610 ($5\times10^{-4}\ \mathrm{mol\ l^{-1}}$) + NB ($5\times10^{-4}$–$1\times10^{-4}\ \mathrm{mol\ l^{-1}}$) and
2. C 500 ($2\times10^{-3}\ \mathrm{mol\ l^{-1}}$) + Rh 610 ($1\times10^{-3}\ \mathrm{mol\ l^{-1}}$) + NB ($5\times10^{-4}$–$1\times10^{4}\ \mathrm{mol\ l^{-1}}$).

At all the concentrations of NB, the fluorescence reduced considerably as compared to single as well as mixed bimixture solutions. This clearly indicates that the fluorescence of Rh 610 is quenched twice in the ternary mixture solution.

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