Energy Transfer Studies in Binary Dye Solution Mixture of Coumarin 440 + Coumarin 540 and its Lifetime Calculations

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A B S T R A C T

The sensitized fluorescence emission from the bimixture [Coumarin 440 (donor) + Coumarin 540 (acceptor)] has been measured as a function of dye concentration using a fluorescence spectrophotometer. The concentration of Coumarin 440 (donor) is kept constant at $5 \times 10^{-3}$M while the concentration of Coumarin 540 (acceptor) is varied. The spectroscopic parameters for this bimixture have been calculated from the concentration dependence of peak fluorescence intensity curves. Also the data obtained from the Horiba Jobin Yvon Time Resolved Fluorescence Spectrophotometer was analyzed for the determination of lifetimes at various emission peaks. A comparative study between theoretically calculated lifetimes and experimentally obtained lifetimes shows a good agreement. The results indicate that the energy transfer process between unlike molecules can be studied by lifetime measurements (which could also be determined from the fluorescence emission spectral studies).

Introduction

Many attempts have been made in studies aimed to improve dye lasers efficiency and to extend their spectral range of operation. Energy transfer dye lasers (ETDL) have generated considerable interest as they are useful in obtaining enhanced laser output, wide tuning range, reduced concentration and pump threshold requirements and ultra-short pulse width in contrast to their single dye counterpart [1-7]. Energy Transfer Dye Lasers using numerous donor-acceptor dye pairs have been reported by various investigators during the last five decades. Fluorescence energy transfer is the transfer of the excited state energy from a donor (D) to acceptor (A) [8-19]. This transfer occurs without the appearance of photon and is primarily a result of dipole–dipole interaction between the donor and the acceptor. The rate of energy transfer depends upon the extent of overlap of the emission spectrum of the donor with the absorption spectrum of the acceptor, the relative orientation of the donor and acceptor transition dipoles and the distance between these molecules. The non-radiative energy transfer occurs as a result of dipole–dipole coupling between the donor and the acceptor and does not involve the emission and reabsorption of photons. In contrast to these trivial factors non-radiative energy transfer depends upon the molecular details of donor-acceptor pairs. Non-radiative energy transfer is effective over distance ranging of 50Å. The intervening of solvent or other macromolecules has little effect on the efficiency of the energy transfer, which depends primarily on the D-A distance [18]. Dye lasers have some limitations as the dye solution used as an active medium absorbs energy from the excitation source in a very limited range and so the emission band also has these limitations. If a dye laser has to be used as an ideal source its spectral region needs to be extended. In order to extend the spectral region of operation mixtures of different dye solutions/dye molecules embedded in solid matrices are being used. The use of such energy transfer in dye lasers is also helpful in minimizing the photo-quenching effects and thereby, increasing the laser efficiency. In the present studies the energy transfer mechanism has been investigated in the ethanol solution mixture, i.e. Coumarin 440 and Coumarin 540 from their absorption and emission spectra. The dependence of lifetimes of the dye molecules on their...
concentrations in ethanol solution has been studied and the results are found to be in good agreement as reported in the literature.

**Experimental:**

Coumarin 440, Coumarin 540 dyes were procured from Sigma Chemicals (USA). They were used as received without further purification. Samples of various concentrations were prepared in Ethanol (spectroscopic grade, procured from Merck India Ltd.).

The concentrations of the dyes were varied in the range of $10^{-3}$ M to $10^{-6}$ M. For preparation of $10^{-3}$ M solution of Coumarin 440, 8.7595 mg was added to 50 ml of Ethanol. And the solutions of concentrations $5 \times 10^{-4}$ M, $10^{-4}$ M, $5 \times 10^{-5}$ M, $10^{-5}$ M and $10^{-6}$ M were prepared using $10^{-3}$ M stock solution. Similarly, the other dye solutions were prepared.

For the energy transfer mechanism in the binary dye mixture solution, Coumarin 440 plus Coumarin 540, the donor (Coumarin 440) concentration was fixed at $5 \times 10^{-5}$ M as it was found to be most efficient at this concentration.

The absorption spectra were recorded using Shimadzu (260) UV–Visible spectrophotometer. Cary Eclipse Spectrophoto-fluorometer (Varian make), was used to record the fluorescence emission spectra of the dye solutions and their mixtures under investigation.

The lifetimes for the various concentrations of the individual and binary dye mixture solutions were recorded using Horiba JobinYvon Time Resolved Fluorescence Spectrophotometer

**Results & discussions:**

**Excitation (absorption) and Emission spectra Overlaps:**

The selection of dyes for this binary combination in the study was done such that the emission spectrum of the first dye (donor) overlaps the absorption spectra the other ones (acceptors). The extent of overlap decides the efficiency of energy transfer.

The overlapping of the excitation (absorption) and emission spectra of bimixture under investigation are as shown in the figure 1.

The graph shown in Figure 1 shows the excitation and emission spectra of binary dye mixture i.e. Coumarin 440 plus Coumarin 540. The excitation plot of Coumarin 440 is taken at emission wavelength 428nm and emission plot is taken at excitation of 378nm. Similarly, the excitation plot of Coumarin 540 is taken at emission wavelength 501nm and emission plot is taken at excitation of 463nm.

**The Excitation and Fluorescence Emission Spectra of Individual dyes and of binary dye mixture**

The excitation and fluorescence emission spectra are recorded using Cary Eclipse Spectro-photo-fluorometer (Varian make) of individual dyes are represented in Figure 2 & 3 shown below.

**Coumarin440**

Fluorescence emission spectra of the Coumarin 440 dye solution in ethanol excited by 378 nm for different concentrations are shown in the figure 2. The excitation spectra of the Coumarin 440 dye solution (keeping emission at 428 nm) has also been shown in the Figure 2.

**Coumarin540**

Fluorescence emission spectra of the Coumarin 540 dye solution in ethanol excited by 463 nm for different concentrations are shown in the Figure 3. The excitation spectra of the Coumarin 540 dye solution (keeping emission at 501 nm) has also been shown in the Figure 3.
It can be clearly seen from the graph plots that for the concentration 5×10⁻⁵ M Coumarin 440 have a maximum emission and for the Coumarin 540 the maximum emission is at 10⁻⁵ M solution.

**Coumarin 440 and Coumarin 540 binary dye mixture solution:**

The excitation and fluorescence emission spectra Coumarin 440 (5×10⁻⁵ M) in the presence of varied concentrations of Coumarin 540 in ethanol solution is shown in the Figure 4.

![Fluorescence emission spectra of binary dye mixture of Coumarin 440 and Coumarin 540. The concentration of Coumarin 440 (donor) is fixed at 5x10⁻⁵ M while concentration of Coumarin 540 (acceptor) is varied.](image)

Figure 4: Fluorescence emission spectra of binary dye mixture of Coumarin 440 and Coumarin 540. The concentration of Coumarin 440 (donor) is fixed at 5x10⁻⁵ M while concentration of Coumarin 540 (acceptor) is varied.

The excitation (absorption) wavelength was kept at 378 nm so that it does not get practically absorbed by Coumarin 540 dye and the energy emitted by Coumarin 440 only is absorbed (accepted) by the acceptor dyes to get their characteristic emissions. The successive quenching of the Coumarin 440 emission is accompanied by enhancement in the intensity of the characteristic emissions of the acceptors (Coumarin 540). It could therefore, be clearly seen in these spectra that there is an energy transfer from the donor (Coumarin 440) to the acceptor (Coumarin 540). The observed blue shifts in the donor emission spectra with increasing acceptor concentrations, in cases, are due to radiative energy transfer and the red shift in the acceptor emission spectrum could be radiative migration amongst the acceptor molecules[43-47].

**Gaussian Fits and Error Plots:**

Comparison of experimental and theoretically fitted spectra by the Gaussian spectral convolution – deconvolution method at different number of Gaussian peaks. The other dye mixture solutions were also fitted using the same method at different number of Gaussian peaks. The other fluorescence emission spectra of other dyes mixture solutions are shown as:

![Gaussian Fits and Error Plots.](image)

![Experimental and Theoretical fitted spectra by the Gaussian spectral convolution-deconvolution method for a typical fluorescence emission spectrum of Coumarin 440+Coumarin 540 and its corresponding error plot.](image)

After plotting the data obtained from spectrofluorometer in origin revealed that for different dye mixture solutions there were more than one peak unlike the single dye solution. To calculate the lifetime and to study the energy transfer these plots were deeply studied. Due to the presence of different dyes in mixtures the emission plots were unlike the individual plots i.e. due to the overlapping of each dye’s emission spectra these peaks were obtained and hence they were affected by each other’s presence and it resulted in increased broad band spectra, which is quite useful in various lasing applications like in optical sensing. Thus in order to study individual dye’s effect for calculating the parameters needed for lifetime these plots was deconvoluted. Deconvolution helps in distinguishing all the different plots leading to multi peak plot and analyzing them separately on the basis of number of differentiating the curves for each and every dye present in the solution. For the calculations each and every single peak deconvoluted plot was examined and all the various parameters like area under the curve, half bandwidth were calculated and used for calculating the lifetime. The overlapping effect represented by the overlapping integral was analyzed and its effect was taken under consideration. This overlapping was seen after deconvolution. The area under the curve was calculated after selecting the deconvoluted plot. This curve was set as active and integrated with respect to emission wavelength & half

\[
I = I_0 + \frac{A}{w^2} \exp \left( -\frac{2(\lambda - \lambda_c)}{w^2} \right)
\]

where \(I_0\) is the initial value of the intensity (baseline offset), \(I\) is the intensity at wavelength \(\lambda\), \(A\) is the total area under the curve from the baseline, \(\lambda_c\) is the peak position (centre of the peak/‘mean’), \(w\) is sigma (the ‘variance’), approximately 0.849, \(w/2\) is the ‘standard deviation’. The deconvoluted peaks were then convoluted and overlapped on the experimental spectrum to see the quality of the fitting. The overlapping of the experimental and theoretically simulated peaks and the resulting residue plot shows a good quality fitting. All the other emission spectra of other dye mixture solutions were also fitted using the same method at different number of Gaussian peaks. The other fluorescence emission spectra of other dyes mixture solutions are shown as:

\[
I = I_0 + \frac{A}{w^2} \exp \left( -\frac{2(\lambda - \lambda_c)}{w^2} \right)
\]
bandwidth was also noted down for the calculations. The different parameters were noted for the calculations of the natural lifetime and the fluorescence quantum yield. So by using these values a theoretical study of the lifetime was done.

**Stern Volmer Plots**

The non-radiative energy transfer rate constant has also been calculated from the Stern-Volmer plot by the following equations:

\[
\frac{1}{\tau_d} = k_T[A] + \frac{1}{\tau_{0d}}
\]

and in terms of the relative emission intensities of the donor in the absence and presence of the acceptor it could be written as

\[
\frac{I_d}{I_{0d}} = 1 + k_T[A]\tau_{0d}
\]

where \(I_{0d}\) is the initial intensity of the donor in the absence of the acceptor which gets reduced to \(I_d\) in the presence of the acceptor, \(\tau_{0d}\) and \(\tau_d\) are the donor lifetimes in the absence and in the presence of acceptor having concentration \([A]\), respectively.

![Figure 6](image)

**Figure 6:** Stern–Volmer plot of \(I_{0d}/I_d\) versus concentration of acceptor for binary dye mixture of Coumarin 440 and Coumarin 540

Stern–Volmer curves, plotted with varying concentrations of the acceptor, for binary dye mixture is shown in fig. 6. It could be easily seen that Stern–Volmer, \(I_{0d}/I_d\) versus concentration plots are linear in nature. The plot is drawn by varying the concentration of Coumarin 540 (i.e. acceptor) and keeping concentration of Coumarin 440 (i.e. donor) constant. The value of the energy transfer rate constant \(K_T\) (\(K_D\rightarrow A\)) hence calculated by the stern volmer plot was found to be 3.2925 M⁻¹.

**Lifetime Results (Experimental)**

The data obtained from the Horiba JobinYvon Time Resolved Fluorescence Spectrophotometer was analyzed for the determination of lifetimes for the various concentrations and emission peaks of the individual and binary dye mixture solutions.

The values of experimental lifetimes obtained for individual dyes at various concentrations are tabulated in Table 1 below.

Table 1: Experimental Lifetimes obtained for individual dyes at various concentrations

<table>
<thead>
<tr>
<th>Dye</th>
<th>Concentration</th>
<th>Experimental Lifetime(ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Coumarin 440</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10⁻³</td>
<td>4.17</td>
<td></td>
</tr>
<tr>
<td>5×10⁻⁴</td>
<td>3.96</td>
<td></td>
</tr>
<tr>
<td>10⁻⁴</td>
<td>3.91</td>
<td></td>
</tr>
<tr>
<td>5×10⁻⁵</td>
<td>3.13</td>
<td></td>
</tr>
<tr>
<td>10⁻⁵</td>
<td>3.19</td>
<td></td>
</tr>
<tr>
<td>10⁻⁶</td>
<td>3.28</td>
<td></td>
</tr>
<tr>
<td>5×10⁻⁶</td>
<td>3.69</td>
<td></td>
</tr>
<tr>
<td>10⁻⁷</td>
<td>2.89</td>
<td></td>
</tr>
<tr>
<td>5×10⁻⁸</td>
<td>2.73</td>
<td></td>
</tr>
<tr>
<td>10⁻⁸</td>
<td>2.60</td>
<td></td>
</tr>
<tr>
<td>10⁻⁹</td>
<td>2.57</td>
<td></td>
</tr>
<tr>
<td><strong>Coumarin 540</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10⁻³</td>
<td>3.2925</td>
<td></td>
</tr>
<tr>
<td>5×10⁻⁴</td>
<td>3.28</td>
<td></td>
</tr>
<tr>
<td>10⁻⁴</td>
<td>3.69</td>
<td></td>
</tr>
<tr>
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<td></td>
</tr>
<tr>
<td>10⁻⁶</td>
<td>2.60</td>
<td></td>
</tr>
<tr>
<td>10⁻⁷</td>
<td>2.57</td>
<td></td>
</tr>
</tbody>
</table>

![Figure 7](image)

**Figure 7:** Experimental Lifetime Decay and Fitted plots for Coumarin 440 for various concentrations
The decay and fitted curves are plotted between Counts and Time (ns) where the Y-axis, i.e. Counts are taken in the logarithm scale. These curves are plotted for various concentrations of Coumarin 440, Coumarin 540.

From the lifetime decay and fitted plots, the value of lifetime for a particular dye or dye mixture (binary) is calculated at $\tau = 1/e$, i.e. where the decay plot has been decayed to the 63% (approximately).

These experimentally evaluated values of lifetimes are found to be in good agreement as reported in the literature.

Figure 8: Experimental Lifetime Decay and Fitted plots for Coumarin 540 for various concentrations

The samples, under study for lifetime decay and fitted plots, of binary dye mixture, the concentrations of the donor and acceptor are kept such that in fluorescence emission broad-band spectra, equal-intensity peaks are obtained. 

**Lifetime Results (Theoretical):**

The lifetimes for the various concentrations and emission peaks of the individual and binary dye mixture solutions were calculated theoretically using the formulae discussed in the theory section.

The values of theoretical lifetimes obtained for the individual dyes at various concentrations are tabulated in Table 2.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Concentration</th>
<th>Theoretical Lifetime(ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coumarin 440</td>
<td>$5 \times 10^{-5}$</td>
<td>2.98</td>
</tr>
<tr>
<td>Coumarin 540</td>
<td>$10^{-5}$</td>
<td>2.41</td>
</tr>
</tbody>
</table>

The values of theoretical lifetimes obtained for the binary dye mixture at various wavelengths are tabulated in Table 3.

<table>
<thead>
<tr>
<th>Binary Dye Mixture</th>
<th>Wavelength (nm)</th>
<th>Theoretical Lifetime(ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coumarin 440 + Coumarin 540</td>
<td>503</td>
<td>4.48</td>
</tr>
<tr>
<td></td>
<td>572</td>
<td>5.78</td>
</tr>
</tbody>
</table>

**Comparative Study of Experimental and Theoretical Lifetimes**

Comparison between the theoretical and experimental lifetimes is done for individual, binary and ternary dye mixture solutions. The lifetimes of the individual, binary and ternary dye mixture solutions in ethanol have been studied and the results are found to be in good agreement as reported in the literature. The lifetime decay and fitted curves are plotted at various wavelengths of the binary dye mixture at the equal broadband condition.

The values of theoretical and experimental lifetimes obtained for the individual dyes at various concentrations are tabulated in Table 4.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Concentration</th>
<th>Lifetime(ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coumarin 440</td>
<td>$5 \times 10^{-5}$</td>
<td>2.98</td>
</tr>
<tr>
<td>Coumarin 540</td>
<td>$10^{-5}$</td>
<td>2.41</td>
</tr>
</tbody>
</table>

The values of theoretical and experimental lifetimes obtained for the binary dye mixture at various concentrations are tabulated in Table 5.

<table>
<thead>
<tr>
<th>Binary Dye Mixture</th>
<th>Lifetime(ns) at wavelength(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Theoretical</td>
</tr>
<tr>
<td>Coumarin 440 + Coumarin 540</td>
<td>4.48 at 503 nm</td>
</tr>
<tr>
<td></td>
<td>5.78 at 572 nm</td>
</tr>
</tbody>
</table>

**Conclusion**

The results indicate that the energy transfer processes between unlike molecules can be studied by lifetime measurements (which could also be determined from the fluorescence emission spectral studies). The energy transfer rate constants are calculated by using Stern-Volmer plots and concentration dependence of radiative and non-radiative transfer efficiencies have also been determined. The values of the energy transfer rate constant $K_T$ (KD→A) are found to be 3.2925 M$^{-1}$ for the binary dye mixture LeCoumarin 440 + Coumarin 540. The experimental results indicate that dominant mechanism responsible for the efficient excitation transfer in these mixtures is of non-radiative nature and is due tois due to long-range dipole-dipole interaction. The theoretical and experimental comparison of lifetimes is also done and theoretical results successfully agreed with the experimental results.
References: