Gamma Irradiation Effects on Energy Transfer Parameters for Acrvlaven – Rhodamine19 Binary Laser Dye Mixtures

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Abstract. Energy transfer was observed in a binary system of lasing dyes which consisted of Acrvlaven as donor while Rhodamine19 is acceptor. The mixture was influenced under action of Gamma irradiation, which has been investigated after 72 hour of exposure (the dose rate 250 Gy/h). The process of energy transfer from donor molecules to acceptor ones in the final liquid samples has been studded spectrally. Some of spectroscopic behaviors of energy transfer were observed as a function of concentration for acceptor molecules. In the present research, the main condition of energy transfer that belongs to Stern-Volmer relation was attained. The dominant mechanism of the energy transfer of dye mixture was inspected as Fluorescence Resonance Energy Transfer. The results show that the fluorescence spectra of acceptor dye were enhanced after irradiation.

Keywords: Gamma irradiation, Energy transfer, Laser dye, Acrvlaven – Rhodamine19

1. Introduction

The transfer of electronic energy can explain many reactions in photochemistry, radiation physics and biology that depend on consideration of the energy transfer processes which used in many zones of scientific research [1]. The electronic energy that transferred from one molecule to another generally occurs in one of two ways; radiative energy transfer mechanism and non-radiative energy transfer mechanism, which include the resonance energy transfer mechanism and the collisional energy transfer mechanism [2]. The mechanism of resonance energy causes an enhancement in the acceptor fluorescence whereas the donor fluorescence was quenched [3]. Fluorescence Resonance Energy Transfer (FRET) is a process that distance dependent radiation less transfer of energy from an excited donor molecule to a suitable acceptor one [4]. FRET happened due to long-range of dipole-dipole interaction. Actually, its distance depends on interaction between different excited electronic states of dye molecules. Excitation energy is transferred from donor molecule (D) to another acceptor molecule (A) with a distinguishable emission in the former molecular system [5]. Moreover, there is an overlap in the spectral lines of fluorescence of D and absorption of A, which is the main indication of the FRET process. Likewise, both of spectra should be within the minimal spatial range of the donor to transfer its exited energy to the acceptor [6]. As well known, gamma radiation is the most energetic ray, with an awfully in height frequency, and extremely penetrating electromagnetic radiation that can alternates the molecular structure of the irradiated molecular or mixture [7]. In the present research, the energy transfer of the mixture solution dyes Acrvlaven (Ac) as donor and Rhodamine19 (R19) as acceptor have been studied after and before gamma irradiation effects. Moreover, the variation effects of acceptor and donor molecules concentration on the energy transfer and its mechanism have been investigated. Besides, some of energy transfer parameters were investigated before and after gamma irradiation.

2. The Experimental Aspects

Two different dyes have been used in the present work, there chemical formula and properties were itemized in table (1)
Laser dye solution was prepared by dissolving the required amount of the dyes in ethyl alcohol, individually for each used dye. The weight of dye (w) was measured using the well-known formula
\[ w = \frac{M_w \times V \times C}{1000} \]
where, \( M_w \) is the molecular weight of the dye (g/mol), \( V \) is the volume of the solvent (ml), and \( C \) is the molar concentration (mol/L).

The main concentration that has been prepared is 10^-2 (mol/L) as a solvent dye stock solution. Then diluted to 10^-3 - 10^-5 (mol/L) concentrations, respectively. For diluting process, the following equation was used:
\[ C_1 \times V_1 = C_2 \times V_2 \]
where \( C_1 \) is the main concentration that has been prepared [M], \( V_1 \) is the volume before dilution(l), \( C_2 \) is the required concentration [M], and \( V_2 \) is the total volume after dilution. It’s worth mentioning that, the prepared dye solution samples of both Ac and R19 were mixed within 1:1 ratio in many different concentrations of D and A. Where, a fixed volume of the mixture solution has been divided into two equi-volume samples. The volume splitting process has been applied for the all prepared concentrations. The first samples have been directly spectral investigated. Also, the second part was irradiated with gamma ray for 72 hour.

The irradiation was performed in the air at room temperature using Co - 60 gamma irradiation cell with average energy 1.25 MeV. The dose rate in the time of the irradiation was 250 Gy/h. Therefore, the accumulation gamma dose is 18 kGy.

UV-visible absorption spectra have been carried out using Metertech SP-8001 UV/visible spectrophotometer (Halogen and deuterium lamps), which operates in wavelength range of 190 - 1100 nm.

While, the fluorescence spectra were recorded using F96 spectrofluormeter, Shanghai Leaguing Tech. Co. Ltd. within emission wavelengths range 180 - 900 nm, that used Xenon CW lamp as the excitation source.

3. Results and Discussion

The fluorescence spectral line of Ac dye and the absorption one of R19 dye have been recorded at a selected concentration of 10^-4 M and displayed in Figure (1).

In the above figure, the peak of fluorescence was registered at wavelength of 498 nm, while the peak of absorption of R19 at 528 nm.

The spectral overlapping between the fluorescence band and the absorption band was found within the wavelength range 495–535 nm, which is suitable for achieving the energy transfer process, where Ac acts as donor molecules to R19, which is the acceptor molecule.

As displayed in figures (2) and (3), the fluorescence spectra were recorded in dual cases with and without gamma irradiated of dye mixture, for two fixed donor concentrations 10^-4 and 10^-5 M of Ac, and with different concentrations of R19. These figures strongly illustrated that there is an enhancement in the acceptor fluorescence spectra and the fluorescence intensity of R19 was growth with increasing of its concentration at fixed donor concentration. This behavior may be referred to the decreasing of intermolecular distance between the molecules of both donors and acceptors, as mentioned in reference [8]. As the concentration of acceptor dye increases, it has been noted that a slight red shift in the emission wavelength peak of donor when compared with acceptor.

For Ac dye, the energy transferred caused a noticeable red shift in the donor fluorescence spectral curves. This behavior suggested that the excitation energy was transferred from donor to acceptor molecules with energetic emission from the former molecular system.

Moreover, this result indicates that there are two ways of excitation for the acceptor molecules (R19) in mixture. The first one is the enhancement, which was observed in the acceptor fluorescence spectra, because of the source direct pumping. Secondly, via the re-absorption of the energy that emitted from donor molecules.

In addition, same behaviors were noted in the spectral lines, under action of gamma ray irradiation.
The illustration of the fluorescence spectra of R19 with 10-5 M represents the significant result in the present research, because of the finest acceptor concentration that mixes with fixed donor concentrations 10-4 and 10-5 M in two cases; with and without gamma irradiation. The reason for this is due to the transforming of dye solutions from a transparent to a cloudy medium, i.e., increasing the density causing increasing in concentration [9].

However, one can observed noticeable increment in the fluorescence intensity of R19 dye in concentration 10-5 M, when compared with its other concentrations and it can be seen a high quenching was occurred in the fluorescence spectra of R19 in case of high concentrations. Furthermore, it has been noted that the donor molecules at a definite concentration may increase the inter distance between the acceptor molecules, which led to drop the acceptor molecules interactions. Accordingly, the fluorescence emission of R19 has been enhanced.

Meanwhile, FWHM of the emission band of R19 is decreased in the case of gamma irradiation compared with the normal case, as listed in table (2).

Some spectroscopic parameters that referred to energy transfer process have been calculated as that displayed in table (2). ID/IDA parameter is the ratio of fluorescence intensities of donor and mixture, respectively. KET is the rate constant of energy transfer, [A]1/2 is the half quenching concentration, and Ro is the critical distance of transferred molecules. In a nutshell, the understanding of these parameters can provide an indication about the mechanism of energy transfer of bi-molecules in mixture dye solution. The energy transfer rate constant (KET) was deduced using Stern-Volmer relation as given in equation (3), which mentioned in reference [10]:

\[ \frac{I_D}{I_{DA}} = 1 + K_{ET} \tau_D [A] \]  

(3)

Here, \( \tau_D \) is the fluorescence lifetime of donor in the absence of acceptor.

The fluorescence intensities ratio increase linearly with the acceptor concentration and thus Stern-Volmer relation of energy transfer has been realized. The value of KET has been noticed in the range of 1011 to 1010 (l/mols), which can be calculated from the slope of the straight line. So that, the prevailing mechanism of energy transfers process in bimolecular dye mixture is the non-radiation resonance energy transfer [11].

It is noteworthy that the critical transfer distance named Forster radius (Ro) is the essential quantity in Forster’s theory of resonance energy transfer. The values of Ro depends on the half quenching concentration of the acceptor [A]1/2, which is the required concentration that makes a reduction by one half in fluorescence of the donor, as given in equation (4):

\[ K_{ET} = \frac{1}{\tau_D \langle [A] \rangle_{(1/2)}} \]  

(4)

Thereafter, Ro can be experimentally determined form the Stern-Volmer plots using the formula (5)

\[ R_o = \frac{7.35}{\langle [A] \rangle^{1/2}} \]  

(5)

After gamma irradiation process, the optimum measured values of Ro were found to be 106 and 111.5 Å for fixed donor concentrations of 10-4 and 10-5, respectively. From this range of Ro values, one can be judged that the dominant mechanism of energy transfer in binary system molecules of dye mixture is non-radiative resonance energy transfer.

The efficiency of energy transfer (T) can be calculated using the following formula:

\[ T = 1 - \frac{I_{DA}}{I_D} \]  

(6)

Table (3) shows the increments in the calculated values of energy transfer efficiency with decreasing the acceptor concentration. The degradation of the acceptor molecules density leads to enhance the efficiency at a fixed donor concentration. However, the same behavior of the efficiency was observed after gamma irradiation.

4. Conclusions

The results of this work strongly suggested that the non-radiative resonance energy transfer process is a dominant mechanism of energy transfer for bi-molecules matrix of the dye solution mixture.

Further, the gamma irradiation of the dye solution mixture enhanced the intensity of the spectrum lines, and bandwidth was narrowed at FWHM. Therefore, the irradiation process was directly improved the energy transfer in dye mixture. This was noted from the efficiency of the energy transfer,
which has monitored to be higher than that recorded in the normal case. Where, 57% is the highest ratio that recorded after irradiation at equimolar concentration 10^{-5} for both donor and acceptor.

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Table (1): The chemical properties of the used materials

| Material      | Chemical formula     | Molecular weight | Company           |
|---------------|----------------------|------------------|-------------------|
| Acrvlaven     | C_{27}H_{25}CIN_{6}  | 429.271 g/mol    | Lambda Physic     |
| Rhodamine 19 | C_{26}H_{27}N_{2}O_{7}Cl | 514.96g/mol     | Lambda Physic     |
| Ethyl alcohol | C_{2}H_{5}OH         | 46.07 g/mol      | Fisher Scientific (UK) |

Table (2): Some of energy transfer parameters of R19 and Ac dye mixture.

| Solvent | Sample | Acceptor con. (mole) | Accepter | After irradiation | Normal case |
|---------|--------|----------------------|----------|-------------------|-------------|
|         |        |                      | FW (nm)  | I_{DA}/I_{A}      | R_{o} (Å)   |
|         |        |                      | K_{ET} 10^{10} l/mol s | [A] / [A'] (M) | R_{o} (Å)   |
| Eth.    | 10^{-4} | 10^{-3}  | 86.14 | 1.12 | 143.77 | 0.001 | 94.7 | 68.03 | 1.11 | 38.51 | 0.001 | 89.52 |
|         | 10^{-4} | 10^{-3}  | 73.34 | 1.62 | 97.54 | 0.004 | 106 | 60.45 | 1.14 | 4.45 | 0.006 | 97.38 |
|         | 10^{-5} | 10^{-3}  | 86.01 | 1.93 | 72.49 | 0.006 | 74.4 | 60.35 | 1.34 | 5.11 | 0.009 | 68.02 |

|         | 10^{-5} | 10^{-3}  | 88.62 | 1.40 | 224.87 | 0.002 | 97.13 | 67.54 | 1.09 | 55.34 | 0.001 | 103.06 |
|         | 10^{-4} | 10^{-3}  | 93.58 | 1.72 | 109.31 | 0.005 | 111.5 | 67.25 | 1.44 | 4.92 | 0.005 | 114.55 |
|         | 10^{-5} | 10^{-3}  | 94.43 | 2.32 | 8.92 | 0.007 | 85.36 | 67.93 | 1.87 | 5.32 | 0.008 | 98.82 |

Table (3): The calculated efficiency befor and after gamma irradiation for all studied concentrations of dye mixture.
| Concentration (mol) | Efficiency $T$ (%) | Donor | Acceptor |
|---------------------|---------------------|-------|----------|
|                     |                     | Normal case | After irradiation |
| $10^{-4}$           |                     | $10^{-3}$ | 10%      | 11%  |
|                     |                     | $10^{-4}$ | 12%      | 38%  |
|                     |                     | $10^{-5}$ | 25%      | 48%  |
| $10^{-5}$           |                     | $10^{-3}$ | 8%       | 29%  |
|                     |                     | $10^{-4}$ | 31%      | 42%  |
|                     |                     | $10^{-5}$ | 47%      | 57%  |

Figure (1): The overlap between fluorescence spectra of Ac dye and absorption spectra of R19 at $10^{-4}$ M concentrations.

Figure (2): The fluorescence spectra of dye mixture for $10^{-4}$ M donor concentration and for acceptor concentrations; $10^{-3}$ M the red curve, $10^{-4}$ M the black curve, and $10^{-5}$ M the blue curve.
Figure (3): As in figure (2), but for $10^{-5}$M donor concentration.