



# Effect of quencher and temperature on fluorescence intensity of laser dyes: DETC and C504T



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## ABSTRACT

Fluorescence quenching of 7-Diethylamino-3-thenylcoumarin (DETC) and 2,3,6,7-tetrahydro-1,1,7,7-tetramethyl-11-oxo-1H,5H,11H-[1]benzopyrano[6,7,8-ij]quinolizine-10-carboxylic acid, ethyl ester (C504T) by aniline (AN), dimethylaniline (DMA) and diethylaniline (DEA) was investigated in toluene by steady state and transient methods. The quenching parameters like frequency of encounter ( $k_d$ ), probability of quenching per encounter ( $p$ ), quenching rate parameters ( $k_q$ ) and activation energy of quenching ( $E_a$ ) were determined experimentally. The  $k_q$  values determined by steady state and time-resolved methods for the both dyes were found to be same, indicating the dynamic nature of interaction. Magnitudes of  $p$  and  $E_a$  suggested that the quenching reaction is predominantly controlled by material diffusion. The quenching mechanism is rationalized in terms of electron transfer (ET) from donors (aromatic amines) to the acceptors (coumarin derivatives) confirmed by correlating  $k_q$  with free energy changes ( $\Delta G^\circ$ ). Further, an effect of temperature on fluorescence intensity was carried out in toluene and methanol solvents. Fluorescence intensity of both the dyes decreases with increase in temperature. Temperature quenching in case of C504T is due to intersystem crossing  $S_1 \rightarrow T_2$ , whereas for DETC, quenching is due to intersystem crossing  $S_1 \rightarrow T_2$  and ICT  $\rightarrow$  TICT transition.

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## 1. Introduction

Fluorescence quenching is a process of relaxation without emission of a photon. During the relaxation, there are wide variety of quenching mechanisms occur including complex formation, molecular rearrangements, intersystem crossing, singlet-to-triplet excitation and intermolecular charge transfer both at ground state and excited state [1,2]. Fluorescence quenching of organic molecules in solutions by different quenchers such as chloroalkanes, aromatic amines, halides etc., have been the subject of interest to understand the nature of bimolecular reactions taking place under the steady state and transient conditions [3–7].

Substituted coumarin derivatives with efficient fluorescing ability have numerous photonic applications in science and technology as charge transfer complexes, solar energy concentrators, colorants, laser dyes in the blue-green range [8–10]. Fluorescence quenching of coumarin derivatives by aromatic amines/haloalkanes, with non-overlapping spectra of donor emission and acceptor absorption has been studied

using Stern–Volmer (S–V) equation by many researchers [11–14]. It is inferred that the quenching is due to electron transfer (ET) between donor and acceptor. ET is one of the most fundamental quenching reactions. Though ET reaction between donors and acceptors with both of them in the ground state is not encouraging, photo excitation of either of them often makes the ET process to occur with reasonable rates [15–19]. The study on ET between coumarin derivatives and amines gives us the significant information that ET rates in homogeneous solvents is faster than in any viscous solvents. It is because of that, in homogeneous medium the donors and acceptors are free to move and they can effectively diffuse together [20–22]. The dynamics of photoinduced electron transfer depends on temperature as well as nature of the medium [23].

Also the effect of temperature on the fluorescence intensity of many organic compounds has been discussed in the literature for coumarin [24–30], indole [31], anthracene [32,33] and rhodamine [34]. The change in temperature drives about a change in the probabilities of the radiative and non-radiative transitions. It is not only important to know the temperature dependence of the organic compounds but also it is equally important to understand the mechanism underlying these processes. In this paper, we present the effect of quenchers (aniline,

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dimethylaniline and diethylaniline) in toluene solvent and temperature dependence of fluorescence emission intensity of DETC and C504T in toluene and methanol solvents.

## 2. Theory

### 2.1. Fluorescence quenching

The phenomenon of quenching of fluorescence intensity in the liquid systems is studied by the well known Stern-Volmer equation given by:

$$\frac{F_0}{F} = 1 + K_{SV} [Q] \quad (1)$$

Similarly, the reduction in the fluorescence lifetimes of the dye molecules in presence of quencher molecules is governed by S-V equation [35].

$$\frac{\tau_0}{\tau} = 1 + K'_{SV} [Q] \quad (2)$$

where  $F_0$  and  $\tau_0$  are the fluorescence intensity and lifetime of dye molecules without quencher,  $F$  and  $\tau$  are the fluorescence intensity and lifetime in presence of a quencher.  $K_{SV}$  is SV constant and  $K'_{SV} = k_q \tau_0$ , where  $k_q$  is bimolecular quenching constant.

Some of the experimental results show upward deviation from the linear S-V equation due to static quenching, ground state complex formation and other possible processes including the dynamic quenching [36–39]. Both in static and dynamic quenching, the dye molecules encountered by the quencher molecules. In the dynamic process a close collision occurs between the excited dye molecules and the quencher molecules when they occupy a continuous position in the solution, and then they separated away. During their separation due to diffusion, molecules undergo several repeated mutual collisions, of which, each series of collisions are called encounters. The probability of quenching per encounter ( $p$ ) is always less than unity. The expression for the frequency encounter ( $k_d$ ) is given by:

$$k_d = 4\pi N' DR \left( 1 + \frac{R}{(2D\tau_0)^{1/2}} \right) \quad (3)$$

where  $N'$  is Avogadro's number per mill mole. The constants  $D$ ,  $R$  represent the sum of the diffusion coefficients ( $D_Y + D_Q$ ), the sum of the molecular radii ( $R_Y + R_Q$ ) of the dye (Y) and the quencher (Q) molecules. The diffusion coefficients of the dyes ( $D_Y$ ) and quenchers ( $D_Q$ ) are estimated using Stokes-Einstein equation [40]. The quenching rate parameter  $k_q$  in terms of probability encounter  $p$  is

$$k_q = k_d p \quad (4)$$

The probability of quenching per encounter ( $p$ ) in terms of activation energy ( $E_a$ ) [37,41] for steady state is given by the Eq (5)

$$1/p = \left[ 1 + e^{(E_a - E_d)/RT} \right] \quad (5)$$

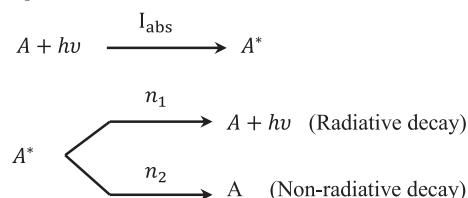
or

$$E_a = E_d + RT \ln \left[ \left( \frac{1}{p} \right) - 1 \right] \quad (6)$$

where  $E_d$  is the activation energy for diffusion, and generally its value is greater than the activation energy  $E_a$  for quenching reaction.

### 2.2. Effect of temperature on fluorescence intensity

The kinetic scheme for the fluorescence quenching in the absence of an external quencher can be written as:



By varying the temperature of the medium, one can obtain an insight into the thermally activated processes of deactivation from the excited state. When a thermally activated mechanism is possible, the fluorescence decay rate constant  $k_f$  can be written as

$$k_f = k^0 + k' \exp \left( - \frac{\Delta E}{RT} \right) \quad (7)$$

where  $k^0$  is the temperature independent rate constant and  $k'$  is the frequency factor for the thermally assisted process. The fluorescence decay rate constant at different temperature is estimated by finding the reciprocal of the lifetime which is calculated by the Eq (8)

$$\tau_0(T) = \tau_0(20) \frac{F(T)}{F_0(20)} \quad (8)$$

where  $\tau_0(20)$ ,  $\tau_0(T)$  and  $F_0(20)$ ,  $F(T)$  are lifetimes and the emission intensities at 20 °C and T °C respectively. The second term in Eq (7) is dominant and it involves the free energy of activation  $\Delta E$  due to entropy component of the liquid system [42]. A plot of  $\ln k_f$  versus  $1/T$  should give a straight line with the slope being  $(-\Delta E/R)$  and the intercept  $\ln k'$ . The magnitude of  $k'$  determines the degree or extent to which the values of fluorescence intensity and lifetime  $\tau$  vary with temperature.

## 3. Experimental details

The coumarin dyes namely DETC, C504T were procured from Exiton, USA and their molecular structure are given in Fig. 1. The spectroscopic

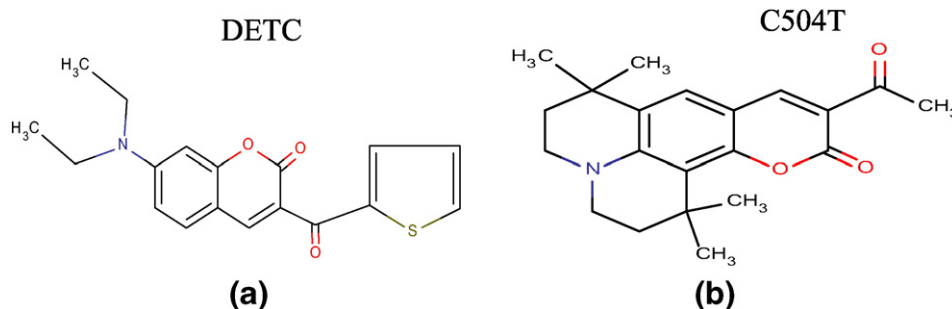


Fig. 1. The molecular structure of (a) DETC and (b) C504T.

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