

On the Fluorescence Quenching of Substituted Coumarins

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In the present work the effect of different concentration of halide quenchers (Cl^- , Br^- , I^-) on 4-methyl-5-ethoxy-7-methoxy coumarin (1) and 4-methyl-5,7-diethoxy coumarin (2) in aqueous solutions have been carried out at 20^o temperature. It was observed that the fluorescence intensity of these coumarin derivatives decrease with increase in the concentration of the quenchers except Cl^- quencher. Further, it was observed that the quenching due to halide ions proceeds via both a diffusional and static quenching process. The rate constants for diffusional as well as static component of quenching process have been calculated using modified Stern–Volmer relation. From the observed data it was found that I^- ion has very high quenching ability than Br^- ion and Cl^- ion behaves almost like a non-quencher. It was interpreted in terms of the sphere of action model by showing that the value of radius of sphere of action of the halide ion quencher is greater than the sum of the radii of the respective coumarin and quencher. Consequently, the order of the quenching ability of the halide quencher was found to be as $\text{I}^- > \text{Br}^- > \text{Cl}^-$ and interestingly this is in the same order as of the ionizing energy of these halide ions. The present quenching process has been attributed to the electron transfer resulting between the colliding species.

Keywords: Halide quenchers, Coumarin derivatives, Stern–Volmer relation.

1. INTRODUCTION

Coumarin (Figure 1) is almost non fluorescent however properly substituted coumarin derivatives yield intense fluorescence emission. Coumarin derivatives are widely used as research tools in polymer sciences [1,2]. Many of these coumarins have been used as dye lasers [3] owing to their remarkable characteristics in terms of tenability and conversion efficiency. These compounds also show a large Stokes shift and consequent small overlap between the absorption and emission spectra. Coumarin compounds are widely investigated due to their importance as non linear optical chromophores and as excellent probe to studying solvation dynamics in the homogeneous solutions as well as organized media along with variety of numerous applications [4-9].

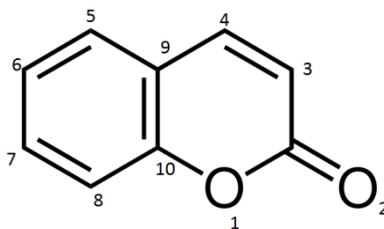


Fig. 1: 4-methyl-5-ethoxy-7-methoxy coumarin (1); 4-methyl-5,7-diethoxy coumarin (2)

In a series of our earlier work the defect of solvents, substituents and temperature on the various photophysical properties of coumarin compounds have been reported [5-7]. In all these studies it was found that the nature of solvents and substituents brings about a change in the values of fluorescence wavelength maxima, quantum yield, lifetime, polarization and excited state dipole moment of the coumarins.

It was found that the fluorescence quenching of substituted coumarins in aqueous solutions is not well understood. Therefore to understand various quenching process, a systematic study of fluorescence quenching of 4-methyl-5-ethoxy-7-methoxy coumarin (1) and 4-methyl-5,7-diethoxy coumarin (2) (as shown in Figure 1), by halide ions was carried out in the present work. Numbers of quenching parameters have been calculated to understand the nature of the possible quenching mechanism. Such studies of efficient quenching by the I^- quencher on the substituted coumarins can be useful for the detection of trace amounts of iodine at the concentration level $10^{-7}M$ or even below. Besides this several other useful applications can be expected from the present studies to name a few monitoring of iodine in all cases where iodine is generated or produced, and the fibre optic sensing of iodine, etc. and also for other analytical purposes. In order to undertake the present studies the experimental work is carried as per the detail given in our earlier paper [4].

2. RESULTS AND DISCUSSION

In case of fluorescence quenching of 4-methyl-5-ethoxy-7-methoxy coumarin (1) and 4-methyl-5,7-diethoxy coumarin (2) by halide ions various spectral parameters have been calculated following the mathematical relations as discussed in our earlier paper [4] and Calculated values of collisional constant (K_{sv}) and quenching rate constant (K_q) at $20^\circ C$ along with the values of activation energy (E_q) and static quenching constant (V) of coumarins are listed in Table 1.

Table 1: Quenching parameters of Coumarins for halide ions.

Coumarin	Quencher	K_{sv} ($\text{mol}^{-1} \text{dm}^3$)	K_q ($\times 10^{-9} \text{mol dm}^3 \text{s}^{-1}$)	E_q (kJ mol^{-1})	V ($\text{mol}^{-1} \text{dm}^3$)
1	Br^-	16.40	10.71	0.20	0.44
	I^-	17.20	10.21	0.18	1.80
2	Br^-	16.82	6.27	7.92	0.79
	I^-	11.05	4.12	9.25	2.14

It was observed that the fluorescence intensity of both the coumarin derivatives (1 and 2) decrease with increase in the concentration of Br^- and I^- ions but remains almost constant in case of Cl^- ions. It is established that quenching due to halide ions proceeds via both diffusional and static quenching processes. The rate constant for diffusional as well as static component of quenching process have been calculated using modified Stern- Volmer relation and listed in Table 1.

It is further observed that I^- ion has very high quenching ability than Br^- ion and Cl^- ion which are almost behaves as a non quencher. It is explained in terms of the sphere of action model by showing that the value of radius of sphere of action of the halide quencher is greater than the sum of the radii of the respective coumarin and quencher. The radii of sphere of action of coumarin (1 and 2) for Br^- and I^- quenchers were calculated using the following equation [10] and given by:

$$\frac{V}{N} = \frac{4}{3} \pi r^3$$

Where N is Avogadro' s number per mili mole, r the radius of sphere of action called kinetic distance and V is the static quenching constant and represents an active volume element surrounding the fluorophore in its excited state.

Calculated values of radii of sphere of action (r) of coumarin 4-methyl-5-ethoxy-7-methoxy coumarin (1) and 4-methyl-5,7-diethoxy coumarin (2) in case of quencher Br^- and I^- along with the values of radii of (R_1) of Coumarin (1) and (2) and the quencher radii (R_2) of Br^- and I^- and sum of radii of coumarin with halide are listed in Table 2.

Table 2: Calculated values of radii of sphere of action (r) of coumarin and halide quenchers.

Coumarin	Quencher	r (Å)	(R_1) (Å)	(R_2) (Å)	R (Å)
1	Br^-	5.61	3.51	1.96	5.47
	I^-	6.20		2.16	5.67
2	Br^-	6.61	3.62	1.96	5.58
	I^-	9.22		2.16	5.78

On comparing the data of various radii given in Table 2 it is evident that for coumarin (1) for Br^- quencher: $r = 5.61 \text{ \AA}$ (radius of sphere of action for Br^- quencher) $> R = 5.47 \text{ \AA}$ (sum of the radii of the coumarin (1) and the quencher Br^-)

and for I^- quencher: $r = 6.20 \text{ \AA}$ (radius of sphere of action for I^- quencher) $> R = 5.67 \text{ \AA}$ (sum of the radii of the coumarin (1) and the quencher I^-)

For coumarin (2) for Br^- quencher: $r = 6.61 \text{ \AA}$ (radius of sphere of action for Br^- quencher) $> R = 5.58 \text{ \AA}$ (sum of the radii of the coumarin (1) and the quencher Br^-)

and for I^- quencher: $r = 9.22 \text{ \AA}$ (radius of sphere of action for I^- quencher) $> R = 5.78 \text{ \AA}$ (sum of the radii of the coumarin (1) and the quencher I^-)

Thus in the present case it has been established that quenching will only take place when the value of radii of sphere of action for different quenchers is greater than the sum of radii of fluorophore and quencher. This shows that the static quenching can occur if the quencher is very near to or in close contact with the fluorescent molecule when it is excited. Also, the respective values of r of both coumarins studied in the present case for quencher Br^- is smaller than the corresponding value of I^- . This can be attributed to weak or less quenching ability of Br^- than I^- quencher.

It is also established that the quenching efficiency of the halide ions and their respective ionization energies follow the same trend [11]. Therefore, it seems that the present quenching process is related with the electron transfer from the halide quenchers to the fluorescent molecules in their excited state.

Further, pattern of the quenching ability of the halide quenchers is found to be as $\text{I}^- > \text{Br}^- > \text{Cl}^-$ and interestingly this is in the same order as of their ionization energy. Finally, the present quenching process has been attributed to the electron transfer resulting between colliding species i.e. coumarin derivative and halide quenchers.

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