

Study of Electron Transfer between Amines and Biologically Active 4 - Aryloxymethylcoumarin

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Abstract

Electron transfer from aliphatic and aromatic amines to biologically active 4-aryloxymethyl coumarin1-(4-iodophenoxymethyl)-benzo[*f*]coumarin (IIPMBC) has been investigated in acetonitrile solvent. The variation of quenching rate parameter with reduction potential of amines indicates the electron transfer from amines to investigated coumarin molecule. Experimentally determined values of quenching rate parameter k_q are well correlated with the standard free energy changes (ΔG^0) within the framework of Marcus electron transfer theory. In the investigated systems, solvent reorganization energy appears to play a major role in governing electron transfer dynamics.

Keywords: Coumarin, Amines, Quenching, Electron transfer, Marcus plot.

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1. Introduction

Coumarin based organic molecules are a class of dyes which exhibit strong fluorescence in the ultraviolet and visible region of electromagnetic spectrum. The fluorescent characteristics of these classes of compounds have found widespread applications in natural sciences and medicine [1-4]. Also, coumarins occupy an important position in view of their wide ranging biological, fluorescent labeling and protease inhibiting properties [5-7]. 4-aryloxymethyl coumarins are reported to be exhibiting antimicrobial activity, long range coupling and centrosymmetric nature [8, 9]. It has been shown that 4-aryloxymethyl coumarin 1-(4-iodo phenoxy methyl)-benzo[*f*]coumarin (1IPMBC) exhibits better anticancer and anti-mycobacterial activities [10]. In our previous investigation [11, 12], we have investigated the effect of solvents and silver nanoparticles on photo physical properties of 1IPMBC. The estimated relative quantum yield of 1IPMBC in a series of solvents is in the range of 0.0269 to 0.0596. The Stokes' shift of 4533cm^{-1} is observed for 1IPMBC in non-polar solvent toluene, whereas Stokes' shift of 4812cm^{-1} is observed in polar aprotic solvent acetonitrile. This indicates that this dye is sensitive to nature of solvent. The absorption and fluorescence spectra of 1IPMBC have been modified in the presence of silver nanoparticles. Excellent biological activity of this coumarin and investigated photo physical properties indicate that it fulfills the conditions required for a good fluorophore.

In literature coumarin fluorophores were intensively investigated for their wide range of applications as laser dyes, ionophores, fluorescence markers and probe molecules for examination of electron transfer processes and ultrafast solvation effects [13-15]. Electron transfer (ET) process from a donor to an acceptor is one of the most fundamental reactions in chemistry and biology [16-21]. Photoinduced ET reaction in which either an acceptor or a donor is excited by light to initiate the electron transfer reaction, is the best suitable experimental scheme and has been used quite extensively to investigate various factors that control the ET mechanisms and dynamics in various ET systems [16-20]. The electron transfer reaction between a number of excited coumarins and different amine donors under diffusive and non-diffusive conditions has

been previously studied [13-15, 22-31]. The compound 1IPMBC exhibiting good fluorescent characteristics could be used as a probe molecule to examine electron transfer process. In the present investigation, to shine more light on electron transfer reaction with this compound as electron acceptor and a series of amines as donors, the possible deactivation paths and particularly in its implication in electron transfer reaction is investigated by steady state absorption and fluorescence spectroscopy.

2. Materials and methods

Coumarin dye 1IPMBC was synthesized by our group [10]. The molecular structure of 1IPMBC is given in Figure 1. Acetonitrile solvent used in the present study was of spectroscopic grade and procured from S.D. Fine Chemicals Ltd., India. Analytical grade aliphatic amines namely triethyl amine (TEAM) and tributyl amine (TBAM), and aromatic amines namely aniline (AN), N-methyl aniline (MAN), N-ethyl aniline (EAN), dimethyl aniline (DMAN) and diethyl aniline (DEAN) were also obtained from S.D. Fine Chemicals Ltd., India. These amines were used after purification by vacuum distillation.

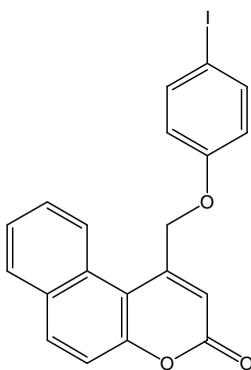


Fig 1. Molecular structure of 1IPMBC

The absorption and fluorescence spectra were recorded using UV-VIS spectrophotometer (Model: Shimadzu UV-1800) and fluorescence spectrophotometer (Model: Hitachi F-2700) respectively at room temperature. The excitation and emission slit

widths of fluorescence spectrophotometer were maintained at 10nm. Also the scan speed of 1500 nm/min and photomultiplier tube voltage of 400V were maintained in fluorescence spectrophotometer. The dye concentration was kept low ($5 \times 10^{-5} \text{M}$) in order to reduce the effect of self-absorption and aggregation formation. The fluorescence lifetime of the dye in acetonitrile was measured using a pico second time correlated single photon counting spectrometer (TCSPC-Model: chronosBH, Make: ISSInc., USA) with light emitting diode as excitation source. The fluorescence decay curves were analyzed using a reconvolution program, which is an iterative nonlinear least squares fit method. The goodness of fit was evaluated by χ^2 criterion and visual inspection of the residuals of the fitted function to the data. In the present case the decay profile is bi-exponential.

The reduction potential of the dye in acetonitrile was measured by cyclic voltammetry experiment on the AUTOLAB electrochemical device using a cell equipped with three electrodes, the working electrode (Pt disc), the counter electrode (Pt disc) and the reference electrode (Saturated Calomel Electrode (SCE)). The cyclic voltammograms were recorded at a scan rate of 100 mVs^{-1} .

3. Results and discussion

3.1 Acceptor and donor properties

The relative fluorescence quantum yield of 1IPMBC reported in our previous work in acetonitrile is 0.0364 [11]. The lifetime in acetonitrile is found to be 0.607ns. The typical fluorescence decay profile of 1IPMBC is shown in Figure 2. Figure 2 also includes the instrument response function (IRF). The excitation energy (E_{00}) of the dye was calculated by taking the crossing point of excitation and emission spectra, and is found to be 3.280eV.

The reduction potential, $E(\text{A}/\text{A}^-)$ of 1IPMBC obtained by cyclic voltammetry is 0.0321 V. The oxidation potential, $E(\text{D}/\text{D}^+)$ of amines is taken from literature [28] and is given in Table 1. The estimated radii (r_{D}) of donors (amines) using additive method of Edward [32] are also given in Table 1. The estimated radius (r_{A}) of acceptor (1IPMBC) is 4.085 Å.

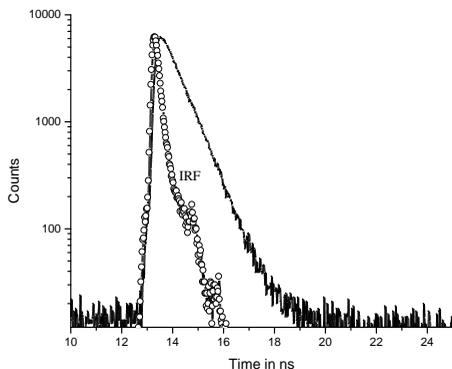


Fig 2. Fluorescence decay profile of 1IPMBC in acetonitrile

Table 1. The values of oxidation potential ($E(D/D^+)$), molecular radii of amines (r_D), SV constant (K_{SV}), quenching rate parameter (k_q) and free energy change (ΔG^0)

| Donor | $E(D/D^+)$ (eV) | r_D (Å) | K_{SV} (M^{-1}) | k_q ($\times 10^9 M^{-1} s^{-1}$) | ΔG^0 (eV) |
|-------|-----------------|-----------|-----------------------|---------------------------------------|-------------------|
| TEAM | 1.05 | 3.112 | 7.86 | 12.95 | -2.423 |
| TBAM | 1.01 | 3.790 | 3.71 | 6.11 | -2.457 |
| AN | 0.93 | 3.098 | 16.00 | 26.36 | -2.543 |
| MAN | 0.81 | 2.973 | 14.56 | 23.99 | -2.664 |
| EAN | 0.80 | 3.118 | 13.66 | 22.51 | -2.673 |
| DMAN | 0.76 | 3.367 | 8.70 | 14.33 | -2.715 |
| DEAN | 0.72 | 3.589 | 6.88 | 11.33 | -2.749 |

3.2 Steady state absorption and fluorescence studies

The optical absorption spectra of 1IPMBC in acetonitrile were recorded in the absence and presence of amines. The concentration of amines has been varied from 0.00M to 0.10 M. From absorption measurements, it is observed that absorption spectra of the dye do

not undergo any noticeable change in the presence of both aliphatic and aromatic amines. The absorption spectra of IPMBC in the absence and presence of an aliphatic amine TEAM and an aromatic amine AN are shown in Figure 3. From Figure 3, it is observed that as the concentration of amines increases, there is an increase in the optical density at the absorption maximum of the dye. But, there is no change in shape and position of absorption band even with the highest concentration of amines. Similar results were observed for other amines also. From these results it is clear that there is no ground state complex formation between coumarin and amines.

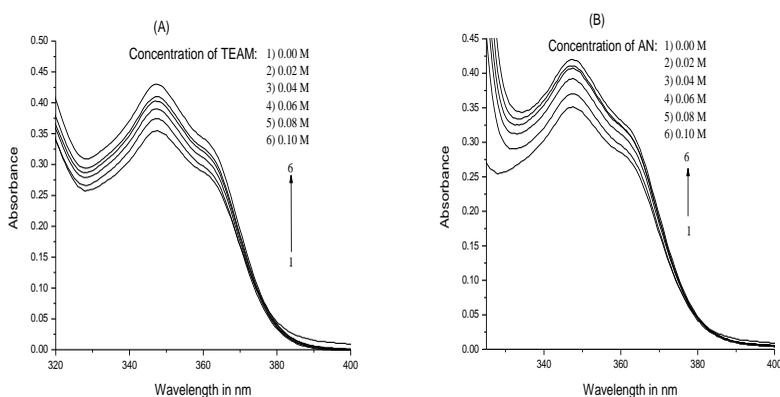


Fig 3. Absorption spectra of 1IPMBC in the presence of (A) TEAM (B) AN

Steady state fluorescence quenching measurements were carried out in acetonitrile for the above mentioned concentration of aliphatic and aromatic amines. In these measurements, the dye was excited at its respective absorption maxima. The typical fluorescence emission spectra of 1IPMBC in acetonitrile at various concentrations of quenchers TEAM and AN are shown in Figure 4. From Figure 4, it is clear that the fluorescence of 1IPMBC is quenched by the addition of TEAM and AN. Similar results were obtained in the fluorescence spectra the dye with other aliphatic and aromatic amines. Fluorescence quenching has been analysed by employing Stern-Volmer (SV) relationship as shown in equation (1) [33].

$$\frac{I_0}{I} = 1 + K_{SV} \times [Q] \quad (1)$$

Where I_0 and I are fluorescence intensities of dye in the absence and presence of amines respectively, K_{SV} is Stern-Volmerquenching constant and $[Q]$ is the quencher concentration. SV plots are drawn for 1IPMBC in all the amines according to equation (1). The typical plots in the presence of amines TEAM and AN for 1IPMBC are shown in Figure 5.

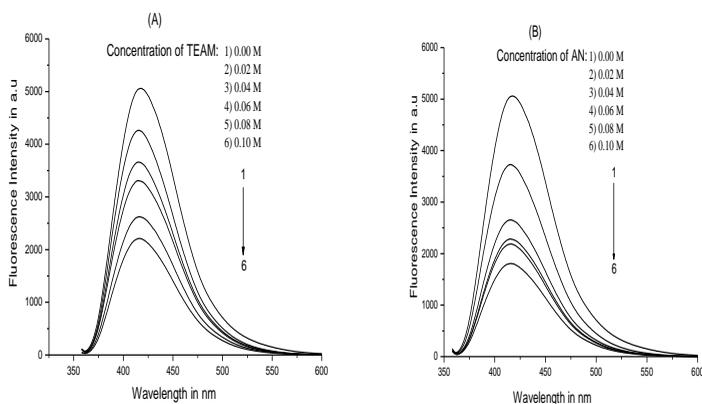


Fig 4. Fluorescence spectra of 1IPMBC in the presence of (A) TEAM (B) AN

From Figure 5, it is clear that SV plots of fluorescence quenching are linear. Similar results were observed in case of other amines. From these plots the values of K_{SV} were determined and are given in Table 1. The quenching rate parameter kq ($= K_{SV} / \tau_0$) was also calculated and is given in Table 1, where τ_0 is the fluorescence lifetime of the dye in the absence of amines. The large values of kq indicate efficient quenching by amines. From Table 1, it is observed that kq values gradually show a decreasing trend with decrease in $E(D/D^+)$ values of amines. This trend is true separately for aliphatic and aromatic amines. These observations indicate the involvement of a charge transfer or ET type of interaction in the present systems. The values of kq in case of aliphatic amines TEAM and TBAM are less compared to aromatic amines AN, MAN, EAN

and DMAN. This could be due to more steric effect arising by virtue of more functional groups in case of aliphatic amines TEAM and TBAM compared to aromatic amines AN, MAN, EAN and DMAN. Larger steric effect hinders the interaction of amines with fluorescent molecule. However, in case of DEAN quenching constant k_q is less compared to its value in TEAM. This could be due to more steric effect in DEAN compared to TEAM, which has more functional groups. From this discussion we conclude that quenching ability of amines depends on steric effect also. Therefore quenching ability of amines in the present case depends on nature of amines (aliphatic or aromatic) as well as on their steric effect. The ET mechanism is elaborated in the following section.

3.3 Electron transfer mechanism

It is well known that fluorescence quenching of coumarin dyes by amines is due to electron transfer [25, 29]. However, to rationalize the experimental data other possible mechanisms are considered too. Fluorescence quenching due to ground state complex formation is ruled out as the absorption maximum of the dye is unaltered in the presence of different concentration of amines. A careful examination of the emission spectra of coumarindye and absorption spectra of amines used in the present study shows that there is no overlap between them. For instance, E_{em} (1IPMBC) = 2.97 eV but E_{ab} has varied from 3.84 eV to 6.13 eV for the amines used. Hence the involvement of energy transfer in the deactivation process is also ruled out. Also, fluorescence band neither shows any new band towards the longer wavelength side nor undergoes any observable change in shape and position in the presence of amines. This indicates the absence of excimer and exciplex formation.

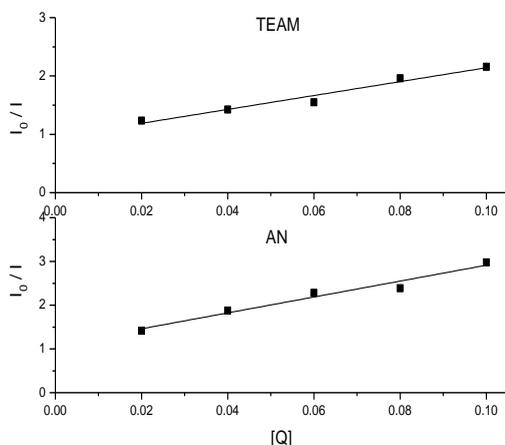


Fig 5. S-V plots of IIPMBC

In order to shine more light on electron transfer in the present systems, quenching rate parameter k_q is correlated with Marcus ET theory [16]. The possibility of ET from a ground state donor (amines) to an excited state acceptor (coumarin) is governed by the standard free energy change, ΔG^0 , of the ET reaction. The ΔG^0 for an ET reaction is given by the Rehm-Weller formula given by equation (2) [34]:

$$\Delta G^0 = E\left(\frac{D}{D^+}\right) - E\left(\frac{A}{A^-}\right) - E_{00} - \frac{e^2}{\epsilon \times (r_D + r_A)} \quad (2)$$

where $E(D/D^+)$, $E(A/A^-)$ and E_{00} have their usual meanings, e is the charge of electron and ϵ is the dielectric constant of solvent, r_D is radius of donor and r_A is radius of acceptor. The ΔG^0 values estimated for different coumarin-amine pairs are listed in Table 1.

Electron transfer under a diffusive condition, as in the present case can be represented by the following kinetic scheme [16-20, 29].



where the excited acceptor (A^*) and the ground state donor (D) first diffuse together to form an encounter complex $(A \cdots D)^*$. k_d and k_{-d} represent diffusion controlled rate constants for the formation and dissociation of the precursor complex, k_{ET} and k_{-ET} are the rate

constants for the forward and back electron transfer reactions and k_p is a general rate constant describing all the reactions leading to disappearance of the ion pair ($A^{\cdot-} \dots D^+$). If it is assumed that the back electron transfer reaction has low probability and that the equilibrium constant for the diffusion process $K = k_d/k_{-d}$ is close to unity, the following expression for quenching rate parameter k_q is obtained.

$$k_q = \frac{k_d}{1 + (k_d / K \times k_{ET})} \quad (3)$$

The rate constant for ET reaction k_{ET} can be expressed as

$$k_{ET} = \nu \exp\left(\frac{-\Delta G^*}{kT}\right) \quad (4)$$

where ν is the frequency factor and ΔG^* is the free energy of activation for the ET process. The value of ν ranges from 10^{12} s^{-1} to 10^{14} s^{-1} depending on the systems [35, 36]. The term ΔG^* is related to the standard free energy change ΔG^0 for the ET reaction by the following relation.

$$\Delta G^* = \frac{(\Delta G^0 + \lambda)^2}{4 \times \lambda} \quad (5)$$

Where λ is the total reorganization energy, and is the sum of solvent reorganization energy (λ_s) and intra molecular reorganization energy (λ_i)

$$\text{i.e. } \lambda = \lambda_s + \lambda_i \quad (6)$$

In coumarin-amine systems, it is reported that λ_i value is reasonably low and is in the range of 0.2eV to 0.3eV [31, 37-39]. In the present study maximum value of 0.3eV was used. The value of λ_s can be estimated by using following equation.

$$\lambda_s = e^2 \left\{ \frac{1}{2r_D} + \frac{1}{2r_A} - \frac{1}{2r_{DA}} \right\} \left\{ \frac{1}{n^2} - \frac{1}{\epsilon} \right\} \quad (7)$$

Where r_{DA} is the separation between the donor and acceptor in the encounter complex and is considered to be equal to the sum of

r_D and r_A values, n is the refractive index and ϵ is the dielectric constant of solvent. In the present case, the average values of r_D ($=3.38\text{\AA}$), the value of r_A ($=4.085\text{\AA}$) and r_{DA} ($=7.465\text{\AA}$) were used to estimate λ_s . This is because a small difference in radius of amines and coumarin do not make any observable changes in the calculated λ_s values. The calculated value of λ_s from equation (7) is 1.21 eV and hence λ obtained using equation (6) for the present systems is 1.51 eV.

Using equations (3), (4) and (5), the quenching rate parameters (k_q) were calculated for different ΔG^0 values. Different combinations of k_d , ν and λ values were tried to get a good correlation between the calculated and experimental k_q values. The best correlation thus obtained with $k_d = 1.57 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, $\nu = 10^{14} \text{ s}^{-1}$ and $\lambda = 1.87 \text{ eV}$ is shown in Figure 6 (Marcus plot), where symbols are the experimental points and the continuous curve is the calculated k_q values for different ΔG^0 . From Figure 6, it is observed that calculated k_q value initially rises sharply as ΔG^0 becomes more negative and then at highly negative ΔG^0 values it levels off at diffusion controlled limit. In Figure 6, open circle symbols represent data for 1IPMBC for various aliphatic and aromatic amines. Since the number of data points in the Marcus plot are not sufficient enough to explain the behaviour of coumarin used, a few literature values of other coumarins are also included in the plot. The literature values are represented by open squares [15, 25]. In the Marcus plot, the dye 1IPMBC corresponds to more negative ΔG^0 values than those for the other coumarins. But, they still appear on the plateau of Marcus plot. Figure 6 also indicates that the present systems under diffusive conditions behave the same way as observed for a good number of ET reactions under identical condition [15, 34-36]. It is interesting to note that the λ value of 1.87 eV, as obtained from the correlation in Figure 6, is slightly higher than λ_s value (1.21 eV) obtained using equation (7). This indicates that the contribution of solvent reorganization energy λ_s for ET is more compared to intra molecular reorganization energy λ_i . This is the expected result in diffusive conditions.

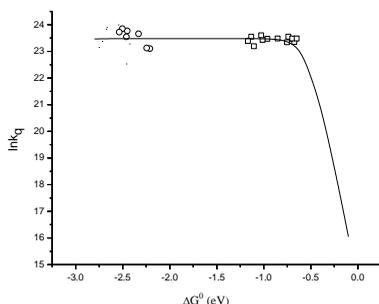


Fig 6. Plot of $\ln k_q$ versus ΔG^0 for different coumarin-amine systems in acetonitrile

Conclusion

Fluorescence of biologically active coumarin dye 1IPMBC is quenched by a series of aliphatic and aromatic amines in acetonitrile solvent. The quenching mechanism has been ascribed to electron transfer from the ground state amines to excited state of coumarin. The quenching rate parameter k_q as estimated from fluorescence measurements is well correlated with standard free energy change ΔG^0 within the scope of Marcus theory. The solvent reorganization appears to play the major role in governing the electron transfer dynamics under the investigated experimental conditions compared to intra molecular reorganization. The present investigation, in addition to our previous results on photo physical properties of 1IPMBC shows that this dye fulfills the conditions to be suitable as fluorescent probe for electron transfer study.

Acknowledgements

The authors wish to thank the Management, Director, Dean and Principal of B.N.M. Institute of Technology, Bangalore, India for their encouragement and support.

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