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QUENCHING OF THE FLUORESENCES OF COUMARIN-1 BY AMINES

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ABSTRACT

The change of the emission properties of a Coumarin derivative, Coumarin-1, in the presence of two aliphatic amines was studied by means of steady-state fluorescence spectroscopy. The quenching process was characterized by Stern-Volmer (SV) plots which display the usual linear aspect. The analysis of the plots made in terms of the usual linear SV equation. The bimolecular quenching constants and the free energy change estimated by the Rehm-Weller releationship fit well the data for other Coumarin-amine systems.

KEYWORDS: Coumarin derivatives, Electron transfer, fluorescence quenching, aliphatic amines.

1. INTRODUCTION

Coumarin derivatives were intensively studied for their wide applications as laser dyes, ionophores, flouresence markers and probe, molecules for examination of electron transfer processes and ultrafast salvation effects.[1-8] The electron transfer reaction of some Coumarin derivatives with aromatic amines was studied in both diffusive (homogenous) and non diffusive conditions, in all cases the S_1 excited-state of coumrains being the acceptor.[9-12]

Coumarin dyes are good electron acceptors in their excited singlet (S1) state.[13-15] For the last couple of years, photoinduced electron transfer (PET) from amine donors to Coumarin dyes have been investigated quite extensively by different groups in the homogenous solutions.[9,12,13] In the present work the ET processe between the excited (S_1) coumarin dyes and the aliphatic amine donars in three different solvents water, DMF and DMSO have been investigated using study-state quenching measurement.

2. MATERIALS AND METHODS

Coumarin-1(C1), n-butyl amine(NBA), triethylamine(TEA), DMF and DMSO were purchase from Sigma Aldrich Company, Bangalore and were used without further purification. Steady state fluroscence measurement were made by CARRY ECLIPSE VARIAN FLUORESCENCE SPECTROPHOTOMETER.

3. RESULTS AND DISCUSSION

From steady state measurement, it is seen that the fluorescence of the Coumarin-1 dye in water, DMF and DMSO solutions is quenched by the added aliphatic amines. Typical fluorescence spectra of C1 in water, DMF and DMSO solutions in the absence and presence of different concentrations of NBA are shown in Fig.1-3. It is indicated from these figures that, though the fluorescence intensity of the dye is reduced substantially in the presence of the amine quenchers, the shape of the fluorescence spectra does not change even in the presence of the highest concentration of the amine used. Similar results were also obtained for the other cumarin-1 amine (TEA)systems in water, DMF and DMSO solutions. These results has indicate that there is no exciplex formation during the interactions of the exited Coumarin-1 dye with the amine quencher.[14-16]

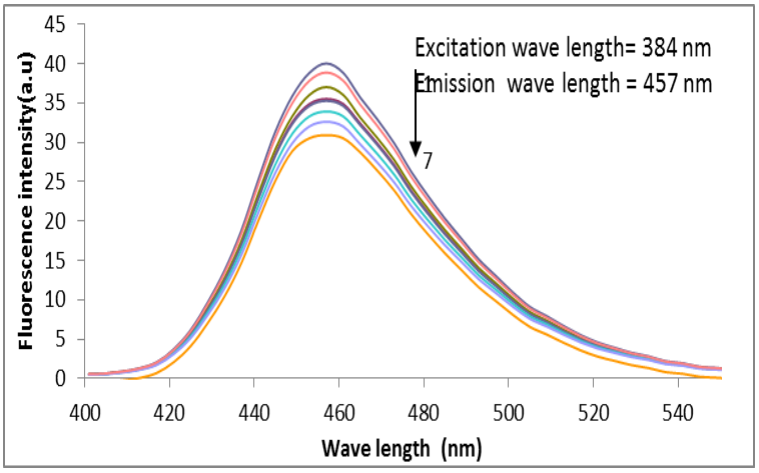

Fig.1: Fluorescence quenching spectra of Coumarin1 in different concentrations of NBA (mol dm^{-3}) in Water (1) 0, (2) 0.002, (3) 0.004, (4) 0.006, (5) 0.008, (6) 0.010, (7) 0.012

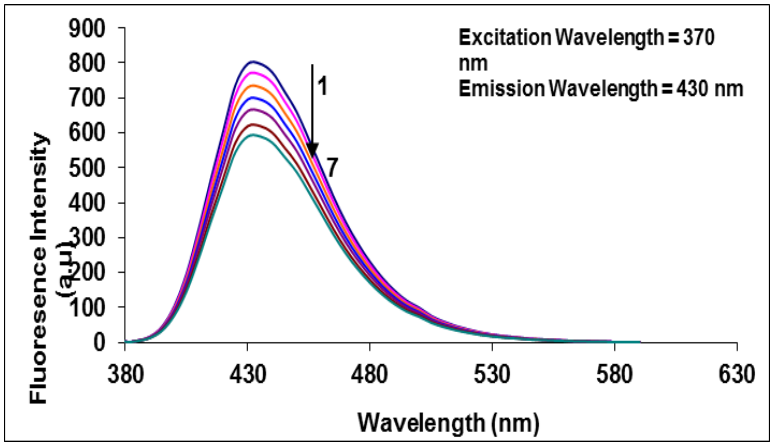

Fig.2.: Fluorescence quenching spectra of Coumarin1 in different concentrations of NBA (mol dm^{-3}) in DMF (1) 0, (2) 0.002, (3) 0.004, (4) 0.006, (5) 0.008, (6) 0.010, (7) 0.012

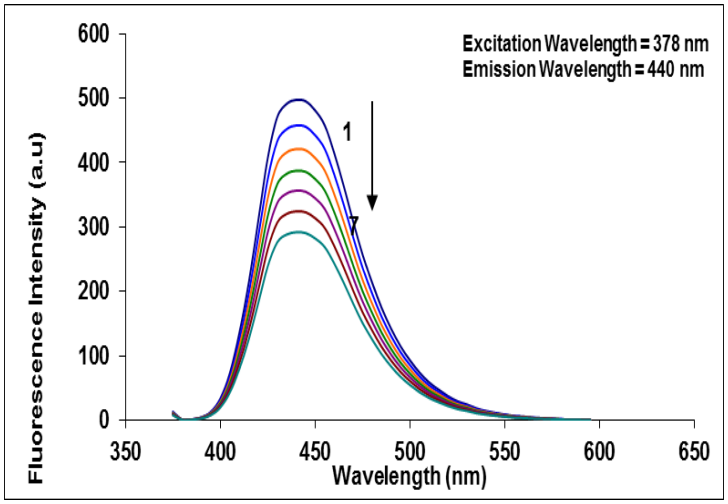

Fig.3: Fluorescence quenching spectra of Coumarin1 in different concentrations of NBA (mol dm^{-3}) in DMSO (1) 0, (2) 0.002, (3) 0.004, (4) 0.006, (5) 0.008, (6) 0.010, (7) 0.012

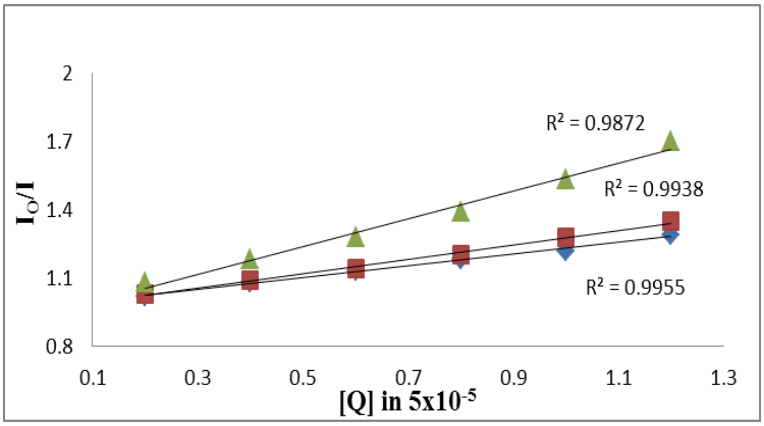

Fig.4. Stern-Volmer Plot of Coumarin1 with NBA in different solvents (1.Water, 2.DMF, 3.DMSO)

Table: 1. Stern – Volmer Constant (K_{SV}) and bimolecular quenching rate constant (K_q) of Coumarin1 with NBA in different solvents.

Solvents	K_{SV} x 10^3 ($Lmol^{-1}$)	K_q x 10^{12} ($Lmol^{-1}$ S^{-1})	R[a]	S.D[b]
Water	0.25	$6.77x10^{12}$	0.987	0.275
DMF	0.3	$8.13\ x10^{12}$	0.993	0.284
DMSO	0.55	$14.9\ x10^{12}$	0.995	0.378

[a] – R is the correlation coefficient.

[b] – S.D is the Standard Deviation.

To have an estimate of the quenching process in the present systems, SS fuoresence quenching results were correlated following the Stern-Volmer (SV) relations ship.[14-16]

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

Where I_0 and I are the fluorescence intensities for the Coumarin-1 dye in the absence and presence of the quenchers (Q-aliphatic amines, NBA & TEA) respectively, K_{SV} is the SV constant and [Q] is the concentration of the amine quenchers in the solution.

Typical $[I_0/I]$ Vs [Q] plots (SV plots) for Coumarin-NBA systems obtains from the SS fluorescence quenching measurements are shown in Fig.4. which show linear curves. Since a linearity in the (I_0/I) Vs [Q] plots is observed for the donar-acceptor pains studied in the present work, K_{SV} values for SS quenching were estimated from the slopes of the SV plots. The K_q values for SS quenching were then calculated from these K_{SV} values, knowing the τ_0 values of the Coumarin-1 dye in the absence of the quenchers. The estimated K_{SV} and K_q values were for different Coumarin-amine systems are listed in Table.1&2. Similar results were obtained for Cou-1 with TEA also. These results are shown in Fig-5-8 & Tables 3 & 4.

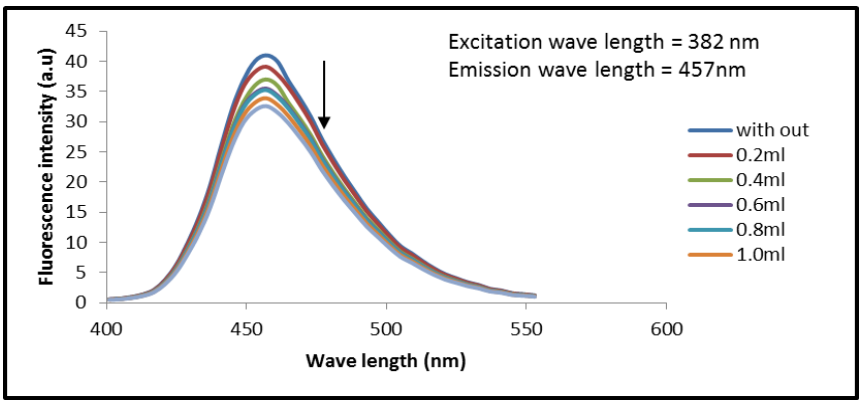

Fig.5: Fluorescence quenching spectra of Coumarin1 in different concentrations of TEA (mol dm^{-3}) in Water (1) 0, (2) 0.002, (3) 0.004, (4) 0.006, (5) 0.008, (6) 0.010, (7) 0.012

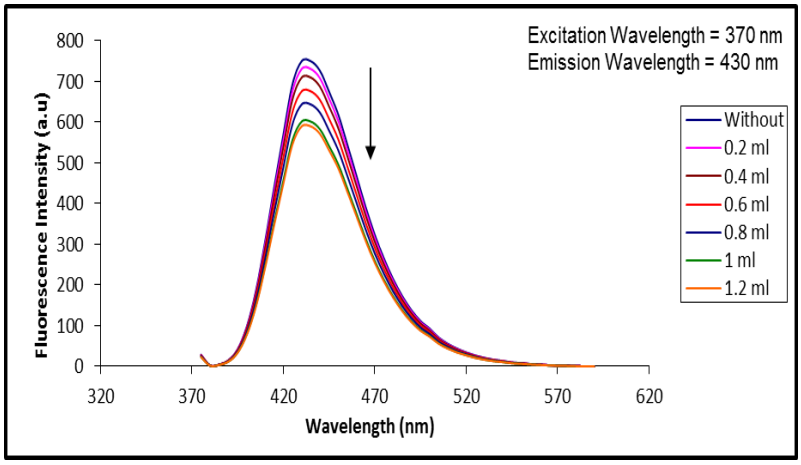

Fig.6: Fluorescence quenching spectra of Coumarin1 in different concentrations of TEA (mol dm-3) in DMF (1) 0, (2) 0.002, (3) 0.004, (4) 0.006, (5) 0.008, (6) 0.010, (7) 0.012

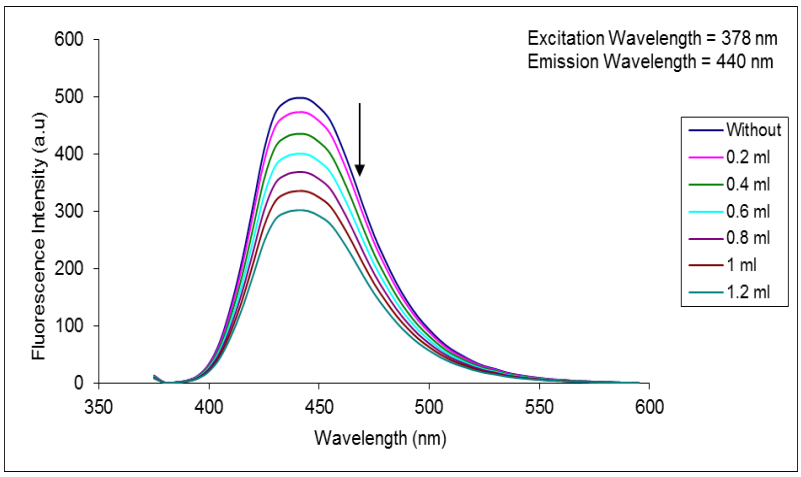

Fig.7: Fluorescence quenching spectra of Coumarin1 in different concentrations of TEA (mol dm^{-3}) in DMSO (1) 0, (2) 0.002, (3) 0.004, (4) 0.006, (5) 0.008, (6) 0.010, (7) 0.012

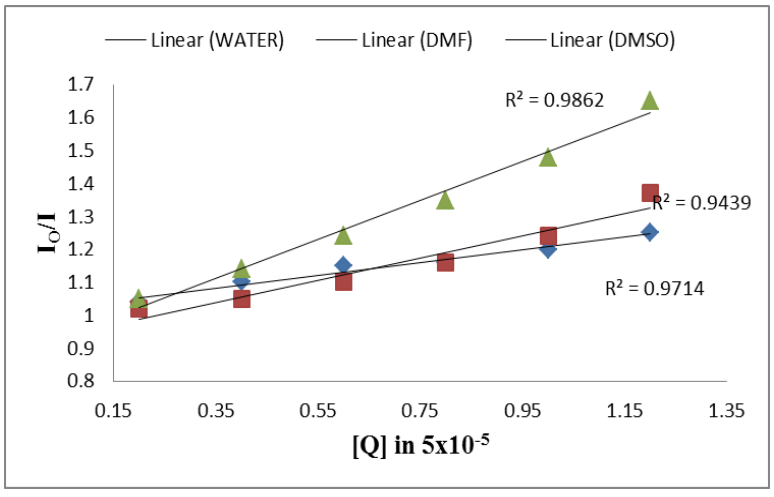

Fig.8. Stern-Volmer Plot of Coumarin1 with TEA in different solvents (1.Water, 2.DMF, 3.DMSO)

Table: 2. Stern – Volmer Constant (K_{SV}) and bimolecular quenching rate constant (K_q) of Coumarin1 with TEA in different solvents.

Solvents	$K_{SV} \times 10^3$ ($Lmol^{-1}$)	$K_q \times 10^{12}$ ($Lmol^{-1} S^{-1}$)	R^2	S.D[b]
Water	0.05	1.35	0.971	0.275
DMF	0.3	8.13	0.943	0.262
DMSO	0.55	14.9	0.986	0.355

[a] – R is the correlation coefficient.

[b] – S.D is the Standard Deviation.

4. CONCLUSIONS

Intermolecular ET from aliphatic amine to exited Coumarin-1 dye has been investigated in water, DMF & DMSO solutions by quenching measurements. NBA and TEA produce linear Stern-Volmer plots, pointing to a collisional process. It was found that the quenching process is diffusion limited.

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