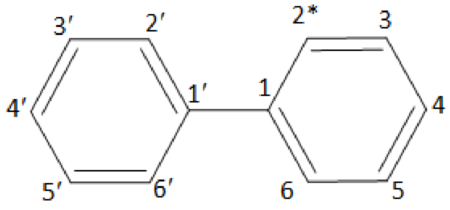
FLUORESCENCE QUENCHING OF VARIOUS ORGANIC AMINO FLUOROPHORES BY INORGANIC ANIONS

Abstract

Fluorescence quenching of Aromatic amino fluorophores [Such as 2-aminodiphenyl(**2ADP**), 4-aminodiphenyl (4ADP), 2-amino7-bromofluorine (**2ABF**), 2-aminodiphenylsulphone (**2ADPS**), 3,3′-diaminodiphenylsulphone (**3DADPS**), and 4,4′-diaminodiphenylsulphone (**4DADPS**),)] by inorganic anions [The inorganic anions used for quenching were the sodium salts of chloride (Cl^-), Br^-, SO_4^{2-} SO_3^{2-}, $S_2O_3^{2-}$, CO_3^{2-}, NO^{3-}, & HPO_4^{2-}] have been studied in 95% (v/v) water-ethanol mixture medium. 2ADP, 4ADP, 2ADPS, and 3DADPS of the fluorescence quenching were observed with only one or two anions and so the quenching of these compounds is not discussed. The quenching was dynamic in **2ABF and** (**4DADPS**). The plots of log k_q values with singlet transition energy (E_s) of the fluorophore and with E_{CTTS} of the quencher are linear indicating the presence of an electron transfer quenching mechanism. ΔG_{TH} values for charge transfer quenching have been determined for 4DADPS.

Keywords: Fluorescence Quenching, aminodiphenylsulphone, Inorganic Anions, Electron Transfer Mechanism



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I. INDRODUCTION

Fluroimetry is a very sensitive, accurate technique for sensing metal ions and anions. Recent research is mainly focused on the development of highly fluorescent probes for use as sensors. Naphthalene diols (NDs) are an important class of organic compounds having a high absorption coefficient with good emission characteristics [1-3]. Naphthalenediols are found to be potent chemo sensors for selective sensing of Cu and Ni cations respectively [4]. A number of investigations concerning the fluorescence quenching by inorganic anions have been reported [5-10]. Fluorescence of aromatic hydrocarbons and nitrogen heterocycles in acetonitrile or aqueous alcohol is quenched by a wide range of inorganic anions and the observed quenching rate constant tends to correlate moderately well with the standard oxidation potential of the anions [5] and charge transfer to solvent transition energy [6]. In general, fluorescence quenching of aromatic hydrocarbons, aza-aromatics, and dyes by inorganic anions occurs through the formation of a non-emissive exciplex [4, 5, and 9].

Electron transfer from anion to the excited aromatic molecules has been proposed for quenching [7, 11, and 12]. In the inorganic anion quenching of aromatic fluorophores, Shizuka *et al.* [7-12] and Shalini Nigham *et al* [13] have proposed an empirical method for the calculation of free energy which explains the free energy and activation energy barrier process better. It was found that heavy atom effect is responsible for the fluorescence quenching by I^- and Br^- . Moriya *et al* [14] have studied the quenching of natural compounds like coumarins by halide ions and have concluded that quenching is through a static quenching mechanism. Fluorescence quenching of benzimidazole[15] and aromatic amines[16] by inorganic anions has been investigated. In the fluorescence quenching of substituted naphthalene by inorganic anions, Behera *et al.*[17] reported that the quenching is dynamic with the involvement of electron transfer from anion to the fluorophores. They have also correlated the efficiency of quenching with free energy (DG) and activation energy (Ea) for the electron transfer quenching process.

II. EXPERIMENTAL

Various aromatic amino fluorophores (Such as 2-aminodiphenyl (**2ADP**), 4-aminodiphenyl (**4AD**P), 2-amino7-bromofluorine (**2ABF**), 2-aminodiphenylsulphone (**2ADPS**), 3,3′-diaminodiphenylsulphone (**3DADPS**), and 4,4′-diaminodiphenylsulphone (**4DADPS**),)) from Sisco Chemical Company – India were used after purification. Quenching experiments were performed using freshly prepared 10^{-4}M fluorophore solution in 95% water - ethanol mixture as per the procedure reported earlier [2]. Instrumental detail and the cyclic voltammetric measurements made are given elaborately in our earlier paper [2].

III. RESULTS AND DISCUSSION

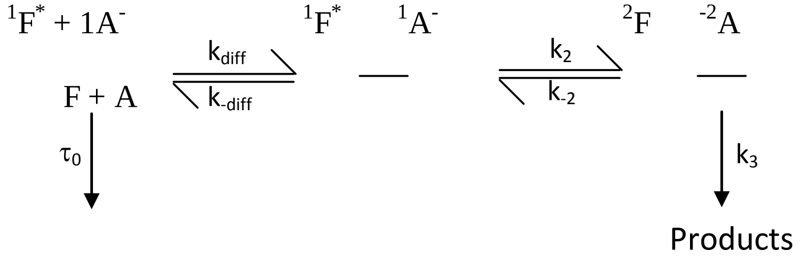
1. **Absorption and Fluorescence Spectra:** Analysis of the absorption and fluorescence spectra of the Various aromatic amino fluorophores (Such as 2-aminodiphenyl (2ADP), 4-aminodiphenyl (4ADP), 2-amino7-bromofluorine (**2ABF**), 2-aminodiphenylsulphone (**2ADPS**), 3,3′-diaminodiphenylsulphone (**3DADPS**), and 4,4′-diaminodiphenylsulphone (**4DADPS**),)) in presence and absence of anions as quenchers revealed the following (i) The shape and maxima of the spectra did not change with quenchers. (ii) No new emission band appeared at the longer wavelength of the fluorescence (iii) The excitation

and emission spectra resemble closely with and without inorganic anions. These results indicate that there is only one emissive species and there is no emissive exciplex or ground state complex formed between the fluorophores and inorganic anions. The counter ion Na+ was chosen for all anions as it has no effect on quenching [2, 9].

2. **Quenching Curves:** The Stern-Volmer (SV) plots of [(I0 / I)-1] Vs [Q] for the fluorescence quenching of two fluorophoress (2ABF & 4DADPS) by anions are linear (Figs.1-4). The Linearity of Stern-Volmer quenching curves indicates that only one quenching mechanism is operative. For all the fluorophores the singlet state lifetime (t_0) was determined using single photon counting method. These curves are linear. The Stern-Volmer quenching constant (K_D)values, obtained from the SV plot and kq values, determined using the lifetime (t_0) of fluorophores are given in Table 1 and 2 respectively. Iodide ion is the best quencher and the order of quenching by anions is < $S2O3^{2-}$ < $SO3^{2-}$ < $NO3^-$ < $HPO4^{2-}$ < $CO3^{2-}$

   No fluorescence quenching was observed with Cl-ion for all fluorophores. NO_3^- is the best quencher of 4DADPS and 2ABF. In case of 2ABF, the CO_3^{2-} is the non quencher but the CO_3^{2-} is the most efficient quencher of 4DADPS. The poor or non quenchers are bromide, sulphate and phosphate ions of both fluorophores the order of quenching by anions is more or less similar for all the fluorophores. The k_q values of 4DADPSand 2ABF with all anions are comparable with the k_{diff} values. (ie. 10.61 X 10^9 $M^{-1}S^{-1}$). The high k_q values and linearity of quenching curves indicate bimolecular and dynamic nature of quenching [2, 7, 9, and 10]. Since there was no change in the absorption spectra with quenchers, static quenching is ruled out.

3. **Electron Transfer Quenching:** Earlier reports reveal that in general quenching of aromatic hydrocarbon [7,10,12], substituted naphthalenes [2,3,16] and aromatic amines [15] by inorganic anions takes place via a transfer of electrons. The electron transfer scheme is depicted below [12].



   Where $^1F^*$ - $^1A^-$ is the collisional complex, ^2F - ^{-2}A is a radical pair or charge transfer complex, k_3 is the decay rate of ^2F - ^{-2}A. k_{diff} and k_{-diff} are diffusion and back diffusion controlled rate constants, k_2 and k_{-2} are the bimolecular "activation energy controlled" rate constants of electron transfer. Application of steady state approximation in Scheme I, gives

$$k_q = \frac{k_{diff}}{1 + (k_{diff} / k_2).\ [1 + (k_{-2} / k_3)]}$$

$$Kq = \frac{k_{diff}}{1 + (k2).\,[1 + (k\text{-}2)]}\ 1 + k2\ k\text{-}2 - k\text{-}2$$

Scheme I has two rate-determining steps on the bimolecular quenching-Translational diffusion (k_{diff}) and Electron transfer process (k_2). Now assuming electron transfer to be exothermic $k_{-2} << k_{diff}$ and the value of k3, equation (3) can be simplified as,

$kq = (k_2 – ‘k_{diff}) / (k_2 + k\text{-diff})$............. (4)

$k_q k_2 + k_q\, k_{diff} = k_2 - k’_{-diff}$

The free energy change DGTH in the electron transfer process can be estimated from Treinin and Hayon equation [18]

ΔG_{TH} = ECTTS – E1/2 – ES – 4.7 .... (3)

Where ECTTS is the charge-transfer to solvent transition energy of the inorganic quenchers, E1/2 is the redox potential and ES is the singlet transition state energy (eV) for the fluorophores.

Since ECTTS varies with IP, this energy can be used instead of IP [6]. This ECTTS will vary with the ion used and also depends on the solvent shell-ion distance. We could not use the Rehm-Weller [19] equation to calculate free energy because of the non availability of oxidation potential energy E (X - / X) for all the inorganic anions.

Similarly we confined our calculation of ΔG_{TH} to two fluorophores ((2ABF and 4DADPS)) and five inorganic anions (Br^-, I^-, $SO_4^{2-,}$ S $2O_3^{2-}$ and SO_3^{2-}) due to the non availability of the data. The singlet transition energy (E_S) and reduction potential of fluorophores (E1/2), E_{CTTS} energy of inorganic anions along with DG_{TH} of two fluorophores are presented in Table 1. From the table it can be seen that k_q in general, decreases with increase in E_{CTTS} energy of inorganic anions and increases with the increase of E_S of the fluorophores. Since E_{CTTS} values are larger for SO_4^{2-} and Br^- they are either poor quenchers or non-quenchers. The plots of log kq against E_S of the two fluorophores and log k_q against E_{CTTS} of the quenchers for aromatic amino fluorophores (2ABF and 4DADPS) are fairly linear are shown Figs 3.1.3. The trends in the plots are as expected and the linearity in the plots indicates the mechanism involving the electron transfer from anion to the fluorophores.

Since the $E_{1/2}$ values could be determined cyclic volumetrically only for 2ABF and 4DADPS, the ΔG_{TH} values were calculated for these fluorophores. The ΔG_{TH} values for SO_4^{2-} and Br- are either positive or least negative and so their quenching abilities are very less. Plots between ΔG_{TH} and log kq for two fluorophores (2ABF and 4DADPS) are given in Fig 3. Since the slopes are different, they are drawn separately. The plot of 2ABF and 4DADPS is fairly linear. The slopes and intercepts of both lines can be calculated and can be written as:

$\log k_q = - 0.28\ \Delta G_{TH} + 9.04$ (4)

The electron transfer quenching of these fluorophores 2ABF and 4DADPS by anions is evidenced by linearity. When the electron transfer becomes the rate-determining step, $k_{diff} > k_2$ and equation (2) becomes,

$K_q = (k_2 \,.\, k_{diff}) / (k_{diff})$ .... (5)

k_2 can be expressed by the Arrhenius equation as,
$k_2 = A_{exp}{}^{(-Ea / RT\ )}$ .... (6)

where A is the collisional frequency at unit molar concentration of reactants within the encounter complex and Ea is the potential barrier in the electron transfer process. Eqn. (5) on substitution becomes

$K_q = [\ (k_{diff} \,.\, A) /(k_{diff})\ ] \,.\, {}_{exp}{}^{(-Ea / RT)}$ .... (7)

Assuming kdiff ≈ k-diff, eqn. (7) becomes,

$K_q = A_{exp}{}^{(-Ea / RT)}$......................... (8)

Taking the frequency factor A to be 10^{10} as suggested by shizuka et al. [12], Eqn. (8) can be written as

$K_q = 10^{10} \exp^{(-Ea / RT)}$.................... (9)

Taking the frequency factor A to be 1010 as suggested by Shizuka et al. [12], Eqn. (8) can be written as

$Kq= 1010 \exp^{(-Ea / RT)}$.................... (9)

From Eqn. (4) at room temperature, an expression similar to the Polanyi rule formation [20] can be derived,

$Ea_{TH}=[0.28DG_{TH}+0.96]\ RT$............. (10)

This corresponds to the understanding that $\Delta\ Ea_{TH}$ is proportional to Δ (DG). ΔG_{TH} for the fluorophores calculated using the above equation is given in Table 2.

From Eqn. (10) the value of Ea_{TH}(activation energy when G_{TH} is zero) comes to 0.09 RT , which is comparable to those derived for similar systems [2, 12]. Equation (10) also suggests that a ΔG_{TH} value indicates the quenching process will be almost completely barrier less and purely diffusion-controlled. The increase of excited state polarity of 2ABF and 4DADPS may increase the formation of non-emissive exciplex. This is the reason why the correlation coefficient for 2ABF and 4DADPS is less.

IV. CONCLUSION

1. The results of the fluorescence quenching of all the fluorophores by nine inorganic anions are discussed.
2. No fluorescence quenching is observed for Cl^- with all the fluorophores. All the anions except Cl^-, Br^- , SO4^{2-} and HPO_4^{2-}quench the fluorescence of 2ABF and 4DADPS
3. The quenching was dynamic in all systems.
4. Linearity of plots of k_q values with (E_S) of the fluorophores and with E_{CTTS} of the quencher evidences Electron transfer qquenching mechanism involving electron transfer from the anion to the fluorophores.
5. Using the equation for the electron transfer mechanism the ΔG_{TH} values have been determined for 2ABF and 4DADPS by the method suggested by Shizuka[12].
6. The plot of log k_q against ΔG_{TH} is fairly linear. The linear relationships obtained for 2ABF and 4DADPS confirm the electron transfer mechanism in the anion quenching process.

V. ACKNOWLEDGEMENTS

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Table 1: K_{SV} (K_D M^{-1}) of ABF, and 4DADPS Fluorescence Quenching by Inorganic Anion in 95 % Water – Ethanol Mixture Medium

Fluorophore	Cl^-	Br^-	I^-	SO_4^{2-}	SO_3^{2-}	NO_3^-	$S_2O_3^{2-}$	CO_3^{2-}	HPO_4^{2-}
2ABF	nq	nq	20.85	Nq	21.34	15.78	14.10	nq	Nq
4DADPS	nq	nq	7.585	Nq	6.606	15.1482	5.624	8.514	Nq

Table 2: K_q and τ_0 (Ns) Of ABF and 4DADPS of Fluorescence Quenching by Inorganic Anions in 95 % Water – Ethanol Mixture Medium

Fluorophore	Life time (ns)	k_q (10^9 $M^{-1}S^{-1}$)								
		Cl^-	Br^-	I^-	SO_4^{2-}	SO_3^{2-}	NO_3^-	$S_2O_3^{2-}$	CO_3^{2-}	HPO_4^{2-}
2ABF	2.394	nq	nq	9.120	nq	8.9130	6.5914	5.8901	Nq	nq
4DADPS	2.754	nq	nq	2.291	nq	2.399	5.5004	2.042	3.0914	nq

Table 3: k_q, Es, $E_{1/2}$ and E_{CTTS} of ABF and 4 DADPS of Fluorophores – Inorganic Anions and ΔG_{TH} Values in 95% Water- Ethanol Mixture Medium.

Fluorophore	Es (ev)	$E_{1/2}$ (ev)	E_{CTTS}	5.46	7.06	5.43	5.74	6.24
				I^-	SO_4^{2-}	SO_3^{2-}	$S_2O_3^{2-}$	Br-
2ABF	3.77	---	k_q ΔG_{TH}	8.709	nq ---	8.913 ---	5.89 ---	nq ---
4DADPS	3.576	---	k_q ΔG_{TH}	2.291 ---	nq ---	2.399 ---	2.042 ---	nq ----

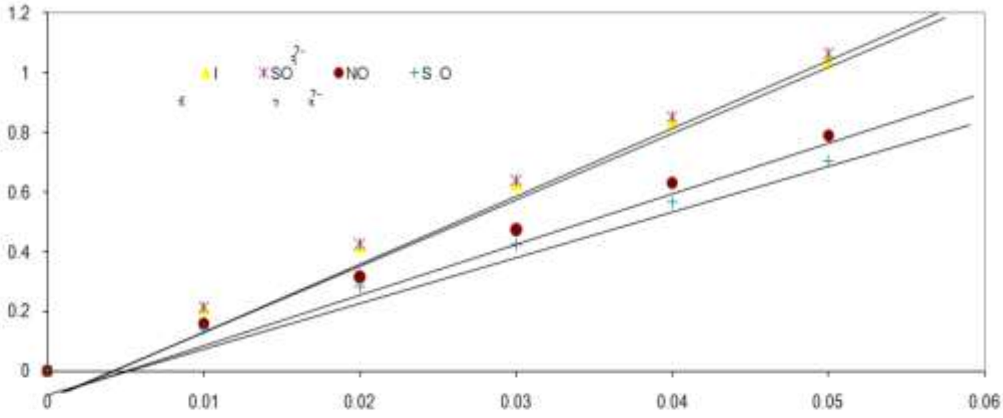

Figure 3.1.1: Stern-Volmer Plot of ABF Fluorescence Quenching by Inorganic Anions.

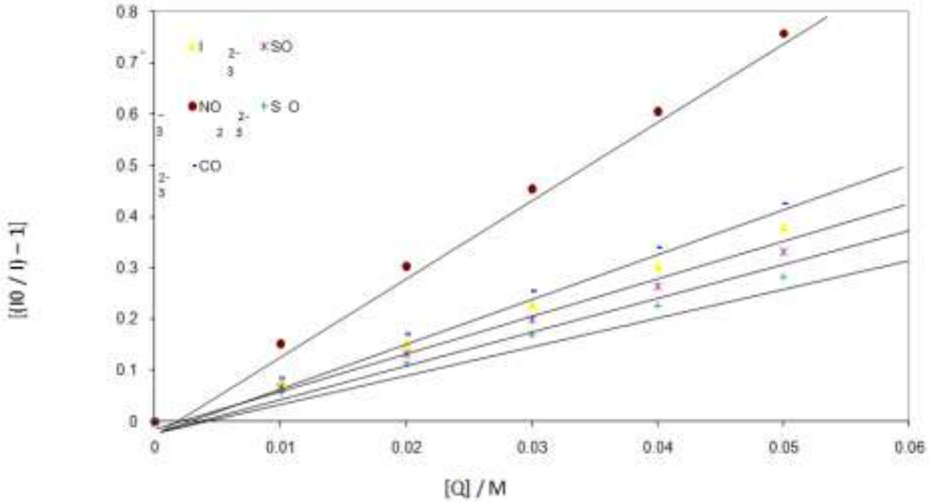

Figure 3.1.2: Stern-Volmer plot of 4DADPS Fluorescence Quenching by Inorganic Anions.

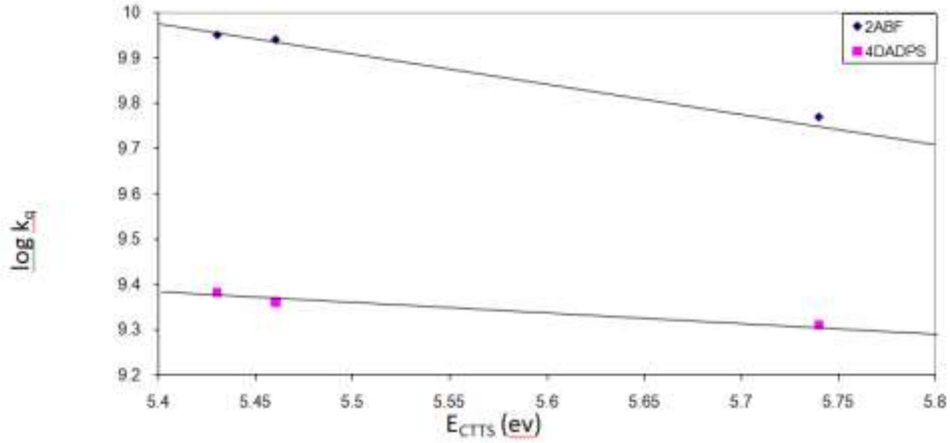

Figure 3.1.3: Plot of E_{CTTS} (ev) Vs log k_q for ABF and 4DADPS Fluorescence Quenching by Inorganic Anions.

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