**Anion Induced Fluorescence Quenching of Various Aromatic amino fluorophores**

**N. Radha\*, M. Swaminathan\*\***

\* PG and Research Department of Chemistry, Alagappa Government Arts College, Karaikudi, Tamil Nadu, India.

\*\* Nanomaterials Laboratory, Department of chemistry, Kalasalingam Univeristy, Krishnankoil, Tamil Nadu, India.



1

1′

6

3

4

5

2\*@22

2′

4′

3′

5′

6′

**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–, SO42– SO32–, S2O32–, CO32–, NO3–, & HPO42–] have been studied in 95% (v/v) water –ethanol mixture medium. 2ADP, 4ADP, 2ADPS and 3DADPS of the fluorescence quenching was observed with only one or two anions and so the quenching of these compounds is not discussed. The quenching was found to be dynamic in all systems. The plots of log kq values with singlet transition energy (Es) of the fluorophore and with ECTTS of the quencher are linear indicating the presence of electron transfer quenching mechanism. ΔGTH values for charge transfer quenching have been determined for aminodiphenylsulphone.

**Keywords:** Fluorescence Quenching, minodiphenylsulphone, Anionic Quenching, Electron Transfer Mechanism

**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 important class of organic compounds having 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 tend to correlate moderately well with standard oxidation potential of the anions [5] and charge transfer to solvent transition energy [6]. In general, it has been suggested that fluorescence quenching of aromatic hydrocarbons, aza-aromatics and dyes by inorganic anions proceed via formation of a non emissive exciplex with pronounced charge transfer character [4, 5, and 9].

A quenching mechanism involving electron transfer from anion to the excited aromatic molecules has been proposed by Förster[11] and is supported by several authors[7-12]. In a detailed study of inorganic anion quenching of aromatic fluorophores Shizuka *et al.* [7-12] and Shalini Nigham *et al* [13] have proposed an empirical method for calculation of free energy which explains the free energy and activation energy barrier process better. Moreover, it has been found that in solution very efficient intersystem crossing from S1 to triplet state is observed for an aromatic molecule in the presence of I‑ and Br‑ (heavy atom effect). They have concluded that the species that is responsible for the fluorescence quenching and the enhancement of the intersystem crossing may be either a coalitional complex A\*- -X– or radical pair. 2 A--2 X. 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 (4ADP), 2-amino7-bromofluorine (**2ABF**), 2-aminodiphenylsulphone (**2ADPS**), 3,3′-diaminodiphenylsulphone (**3DADPS**), and 4,4′-diaminodiphenylsulphone (**4DADPS**),)) were obtained from Sisco Chemical Company – India and further purified by recrystallisation with suitable solvents. The concentration of fluorophore was 10-4M in 95% water - ethanol mixture. The solvent mixture was chosen to ensure that both Fluorophore and metal ions are completely soluble. The inorganic anions used for quenching were the sodium salts of chloride (Cl-), bromide (Br-), iodide (I-), sulphate (SO42-), sulphite (SO32-), thiosulphate (S2O32-), carbonate (CO­32-), nitrate (NO3-) and phosphate (HPO42-). The inorganic salts used during the experiments were purchased from E.Merck, Qualigens and S.D.Fine Chemicals and they were recrystallised from triply distilled water for 2-3 times before use. Triply distilled water was used for the preparation of experimental solutions. The quencher concentrations were varied using the respective stock solutions, so as to achieve a desirable final concentration. The pH of the solution was maintained at 6 to prevent the hydrolysis of metal ions. Freshly prepared solutions were used for all experiments.

Absorption and fluorescence spectra were obtained using a Hitachi U-2001 Doluble beam spectrometer and JASCO FP – 550 spectrofluorimeter respectively. The excitation wavelengths chosen were the absorption maxima of the respective fluorophores. Measurements of lifetime of the fluorophores were made on a time correlated single photon counting picosecond spectrofluorimeter Tsunami, spectra physics USA with the excitation source Ti-sappire laser. The average output power tsunami measured using the photometer is 680mW with a pump power of 4.5W. The pulse width of the laser is >2ps. The observed fluorescence decays were monoexponential for the fluorophore in the absence as well as in the presence of quenchers. Fluorescence lifetimes were obtained by deconvouluting the excitation and instrument response function from the measured fluorescence decay. The data analysis was carried out by the software provided by IBH (DAS-6) which is based on reconvolution technique using iterative non-linear least square methods. The reconvolution is preceded by the series of iterations until a reduced chi-square is obtained. In our measurements, only those values with c2 less than 1.3 were accepted.

Cyclic voltammetric measurements were made with potentiostat wenking LB 75M model and voltage scan generator model VSG-72 model X –Y recorder. The three electrode configurations are planer Beckmann model platinum inlay or glassy carbon as working electrode, a platinum flag sealed in a soft glass as auxiliary electrode and saturated calomel electrode as a reference electrode, and are uncorrected for junction potentials. Tetrabutylammonium perchlorate (TBAP) was used as the supporting electrolyte. A sealed all glass cell was used and measurements were made under atmosphere of dinitrogen and acetonitrile as solvent at 298K. The reference electrode was separated from the experimental solutions by a fitted bridge, which was filled with supporting electrolyte and the same solvent. Half –wave potentials were measured as the average of anodic peak potentials.

**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 inorganic anions as quenchers revealed the following characteristics. (i) The shape and maxima of the spectra did not change on addition of quenchers. (ii) No new emission band was observed at the longer wavelength of the fluorescence spectra. (iii) The excitation spectra in presence of any inorganic anion closely resembled the excitation and absorption spectra in the absence of 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 inorganic anions because it has no effect on quenching [2, 9].

**b. Quenching Curves**

The Stern-Volmer (SV) plots of [(I0 / I)-1] Vs [Q] for the fluorescence quenching of two fluorophore (2ABF & 4DADPS) by anions are linear( Figs.1-4).Linearity of Stern-Volmer quenching curves indicates that only one quenching mechanism is operative. For all the fluorophores the singlet state lifetime (t0) was determined using single photon counting method. These curves are linear. The Stern-Volmer quenching constant (KD )values, obtained from SV plot and kq values, determined using the lifetime (t0) of fluorophores are given in Table 1 and 2 respectively. Iodide ion is the best quencher and The order of quenching by anions is

1. < S2O32- < SO32-< NO3- < HPO42- < CO32-

No fluorescence quenching was observed with Cl-ion for all fluorophore. NO3- is the best quencher of 4DADPS and 2ABF. In case of 2ABF, the CO32- is the non quencher but the CO32- is the most efficient quencher of 4DADPS. The poor or non quenchers are bromide, sulphate and phosphate ions of both fluorophore. The order of quenching by anions is more or less similar for all the fluorophore. The kq values of 4DADPSand 2ABF with all anions are comparable with the kdiff values. (ie. 10.61 X 109 M -1S-1). The high kq values and linearity of quenching curves indicate that the quenching is bimolecular and purely dynamic in nature [2, 7, 9, and 10]. Since there was no change in the absorption spectra with quenchers, static quenching is ruled out.

1. **Electron Transfer Quenching**

In earlier works, it has been reported that in general the 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 can be shown as [12]

k-diff

kdiff

k2

k-2

k3

τ0

Products

1F\* + 1A- 1F\* 1A- 2F -2A

F + A

Where 1F\* - 1A- is the collisional complex, 2F - ‑2A is a radical pair or charge transfer complex, k3 is the decay rate of 2F - -2A. kdiff and k-diff are diffusion and back diffusion controlled rate constants, k2 and k-2 are the bimolecular “activation energy controlled” rate constants of electron transfer. Applying steady state approximation to the various intermediates in Scheme I, we can write,

kq = kdiff

1 + (kdiff / k2) . [1 + (k-2 / k3 )]

kdiff

Kq = , 1 + k2 k-2 - k-2

1 + ( k2) . [1 + (k-2)]

From scheme I it can be seen that there are two rate-determining steps on the bimolecular quenching. First one is the translational diffusion (kdiff) and second one is the electron transfer profess (k2). Now assuming electron transfer to be exothermic k-2 << kdiff and the value of k3, equation (3) can be simplified as,

kq = (k2 – ‘kdiff) / (k2 + k-diff)............. (4)

kqk2 + kq kdiff = k2 - k’-diff

The free energy change DGTH in the electron transfer process can be calculated from treinin and hayon equation [18]

DGTH = 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 for the fluorophores.

All the units are in electron volts (ev). 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 DGTH to two fluorophores ((2ABF and 4DADPS)) and five inorganic anions (Br-, I-, SO42-, S 2O32- and SO32-) due to the non availability of the data. The singlet transition energy (ES) and reduction potential of fluorophores (E1/2), ECTTS energy of inorganic anions along with DGTH of two fluorophores are presented in Table 1. From the table it can be seen that kq in general, decreases with increase in ECTTS energy of inorganic anions and increases with the increase of ES of the fluorophores. Since ECTTS values are larger for SO42- and Br- they are either poor quenchers or non-quenchers. The plots of log kq against ES of the two fluorophore and log kq against ECTTS 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 fluorophore.

Since the E1/2 values could be determined Cyclic voltametrically only for 2ABF and 4DADPS, the DGTH values were calculated for these fluorophores. The DGTH values for SO42- and Br- are either positive or least negative and so their quenching abilities are very less. Plots between DGTH and log kq for two fluorophore (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 an equation of type.

log kq = - 0.28 DGTH + 9.04 (4)

The linearity strongly suggests the electron transfer nature of the quenching of these fluorophore 2ABF and 4DADPS by inorganic anions. Considering the electron transfer to be the rate-determining step in the quenching, we have kdiff >k2 and equation (2) can be written as,

Kq = (k2 . kdiff) / ( kdiff) .................. (5)

And the values of k2 can be expressed by the Arrhenius equation as,

k2  = 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. Substituting eqn. (5) we can write

Kq = [ (kdiff . A) /( kdiff) ] . exp (-Ea / RT) .................. (7)

Once more assuming kdiff ≈ k-diff, eqn. (7) becomes,

Kq = A exp (-Ea / RT)......................... (8)

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,

EaTH = [0.28 DGTH + 0.96] RT.............. (10)

This corresponds to the understanding that D EaTH is proportional to D (DG). DGTH for the fluorophores calculated using the above equation, are given in Table 2. From eqn. (10) the value of Ea TH (activation energy when GTH is zero) comes to 0.09 RT which is comparable to those derived for similar systems [2, 12]. Equation (10) also suggests that a DGTH value indicate 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:**

* The results of the fluorescence quenching of all the fluorophores by nine inorganic anions are discussed.
* No fluorescence quenching is observed for Cl- with all the fluorophores. All the anions except Cl-, Br- , SO42- and HPO42-quench the fluorescence of 2ABF and 4DADPS
* The quenching was found to be dynamic in all systems. The plots of log kq values with singlet transition energy (ES) of the fluorophore and with ECTTS of the quencher are linear.
* This indicated the presence of quenching mechanism involving electron transfer from anion to the fluorophore.
* Using the equation for electron transfer mechanism the ΔGTH values have been determined for 2ABF and 4DADPS by the method suggested by Shizuka[12].
* The plot of log kq against ΔGTH is fairly linear. The linear relationships obtained for 2ABF and 4DADPS confirm the electron transfer mechanism in the anion quenching process.

**V Acknowledgements:**

The authors are thankful to the National Centre for Ultra Fast Processes (NDUFP), Univerisity of Madras, and Chennai for the facilities provided to take lifetime measurements and also to the Central Electro Chemical Research Institute (CECRI), Karaikudi for taking cyclic voltametric measurements.

**VI References :**

1. Rajendiran, N., Radha, N., & Swaminathan, M. (2001). *Indian Journal of Chemistry A,* 40, 331-339.
2. Radha, N. & Swaminathan, M. *(2016). Journal of Scientific and Technical Research Volume 8 Issue 1 June , pp.1-8*
3. Radha, N. & Swaminathan, M. *(2018).* Indian Journal of Chemistry, Vol. 57A, July 2018, pp. 915-919.
4. Kavitha, R., Stalin, T., & Luminesce, J. (2015). *Journal of* ***Luminescence,*** 158, 313-321.
5. Bortolus, P., Bartocci, G., & Mazzucato, U. (1975) *Journal Physical Chemistry,* 79, 21-25.
6. Brooks, C. A. G., & Davis, K. M. C. (1972) *Journal of the Chemical Society, Perkin Transactions,* 2, 1649-1652.
7. Shizuka, H., Saito, T., & Morita, T. (1978) *Chemical Physics Letter, 56*, 519-522.
8. Abdullah, K. A., & Kemp, T. J. (1985). Journal of Photochemistry, 28(1), 691-69.
9. Anusuya, J., & Swaminathan, M. (1990). *Journal of the Indian Chemical Society,* 67(12), 993- 994.

10. Mac, M., Wach, A., & Nijbar, J. (1991) *Chemical Physics Letters,* 176, 167.

11. Th. Förster, “Fluorescenz Organischer Vebindingen” Vandenhoeck and Ruprecht : Gottingen,

(1951),Chap – 10.

12. Shizuka, H., Nakamura, M., & Morita, T. (1980) *Journal of Physical Chemistry*, 84, 989.

13. Nigham, S., Srinivastva, S., & Dogra, S. K. (1994). *Indian Journal of Chemistry,* 33A, 206 –

211.

14. Moriya, T. (1984). *Bulletin of the Chemical Society of Japan,* 59(4), 961-968.

15. Moriya, T. (1986). *Bulletin of the Chemical Society of Japan,* 57, 1723-1730.

16. Sarpal, R. S., & Dogra, S. K. (1994). *Indian Journal of Chemistry,* 33A, 111-114.

17. Behera, P. K., Mukerjee, T., & Mishra, A. K. (1995). *Indian Journal of Chemistry*, 34A, 419-

422.

18. Treinin, A., & Hayon, E. (1976). *Journal of the American Chemical Society,* 98(13), 3884-3891.

19. Rehm, D., & Weller, A. (1970). *Israel Journal of Chemistry,* 8, 259.

20. Horluchi, J., & Polanyi, M. (1935). *Acta physicochimica URSS,* 2, 505.

**Table 1: KSV (KD M-1) of ABF,**and **4DADPS fluorescence quenching by inorganic anion in 95 % water – ethanol mixture medium.**

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Fluorophore | **Cl-** | **Br-** | **I-** | **SO42-** | **SO32-** | **NO3-** | **S2O32-** | **CO32-** | **HPO42-** |
| **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: kq and τ0 (ns)of ABF and 4DADPS of fluorescence quenching by inorganic anions in 95 % water – ethanol mixture medium**

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Fluorophore | **Lifetime (ns)** | **kq (109 M-1S-1)** | | | | | | | | |
| **Cl-** | **Br-** | **I-** | **SO42-** | **SO32-** | **NO3-** | **S2O32-** | **CO32-** | **HPO42-** |
| 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 : kq, Es, E1/2 and ECTTS of** ABF and 4DADPS of fluorophore – inorganic anions and

ΔGTH  values in 95% water- Ethanol mixture medium.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Fluorophore | **Es (ev)** | **E1/2**  **(ev)** | **ECTTS** | **5.46** | **7.06** | **5.43** | **5.74** | **6.24** |
|  | **I-** | **SO42-** | **SO32-** | **S2O32-** | **Br-** |
| 2ABF | 3.77 | --- | kq  ΔGTH | 8.709 | nq  --- | 8.913  --- | 5.89  --- | nq  --- |
| 4DADPS | 3.576 | --- | kq  ΔGTH | 2.291  --- | nq  --- | 2.399  --- | 2.042  --- | nq  ---- |

**Fig 3.1.1 : Stern-Volmer plot of ABF fluorescence quenching by   
 inorganic anions.**

2-

2-

-

-

3

3

2

3

[Q] /M



[( I0 / I ) – 1]

**Fig 3.1.2 : Stern-Volmer plot of 4DADPS fluorescence quenching by   
 inorganic anions.**

[( I0 / I ) – 1]

[Q] /M



3

3

3

3

2

-

-

2-

2-

2-

**Fig 3.1.3 Plot of ECTTS (ev) Vs log kq for ABF and 4DADPS fluorescence quenching**

ECTTS (ev)



**by inorganic anions.**

log kq