

Anion Induced Fluorescence Quenching of Various Aromatic Amino Fluorophores

N. Radha¹ and M. Swaminathan²

PG and Research Department of Chemistry, Alagappa Government Arts College, Karaikudi, Tamil Nadu, India¹
Nanomaterials Laboratory, Department of chemistry, Kalasalingam University, Krishnankoil, Tamil Nadu, India²

Abstract: Fluorescence quenching of 2-amino-7-bromofluorine (2ABF) and 4,4'-diaminodiphenyl sulphone (4DADPS),] by inorganic anions 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..The quenching was found to be dynamic in all systems. 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 electron-transfer quenching mechanism. ΔG_{TH} values for charge transfer quenching have been determined for aminodiphenylsulphone.

Keywords: Fluorescence Quenching, 2-amino-7-bromofluorine ,4,4-diaminodiphenylsulphone, Anionic Quenching, Electron Transfer Mechanism

I. INTRODUCTION

Fluorometry 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]. Several 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 a 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 the 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 Nigam 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. 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 $A^* \cdots X^-$ or radical pair. $2 A \cdots 2 X$. 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 quenching efficiency with free energy (ΔG) and activation energy (E_a) for the electron transfer quenching process. After introducing the concept of charge transfer (CT) complex formation by Mulliken and the discovery of crystalline picrate (association of picric acid and aromatic hydrocarbons) by Fritzsches, shown in this field. CT complexes have been explored and exploited for different applications for several decades. photo-catalytic activities and designing chemosensors. the CT complexes are exploited their for colorimetric real-time detection of hazardous materials like nitro explosives, anions, and toxic heavy metal ions in an aqueous medium. [17a]. the synthetic compounds are classified by various techniques such as FTIR, NMR,

Single-crystal X-ray diffraction, and UV–visible spectroscopy. These techniques indicate that the cation and anion are joined together by weak hydrogen bonding. "It shows a molecular framework is a result of inter $N^+ \cdots H \cdots O^-$ bonding between donor and acceptor moieties [17b].

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 recrystallization with suitable solvents. The concentration of fluorophores was 10⁻⁴M in a 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⁻), sulfate (SO₄²⁻), sulfite (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 were recrystallized from triply distilled water 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, using freshly prepared solutions for all experiments.

Absorption and fluorescence spectra were obtained using a Hitachi U-2001 Double beam spectrometer and JASCO FP – 550 spectrofluorimeter respectively. The excitation wavelengths chosen were the absorption maxima of the respective fluorophores. Measurements of the lifetime of the fluorophores were made on a time-correlated single-photon counting picosecond spectrofluorimeter Tsunami, spectra physics USA with the excitation source Ti-sapphire 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 deconvoluting 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 convolution technique using iterative non-linear least square methods. The convolution is preceded by a series of iterations until a reduced chi-square is obtained. In our measurements, only those values with χ^2 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 the 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 the 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

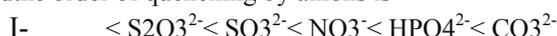
3.1 Absorption and Fluorescence Spectra

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 the 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 are 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].

3.1.1 Quenching Curves

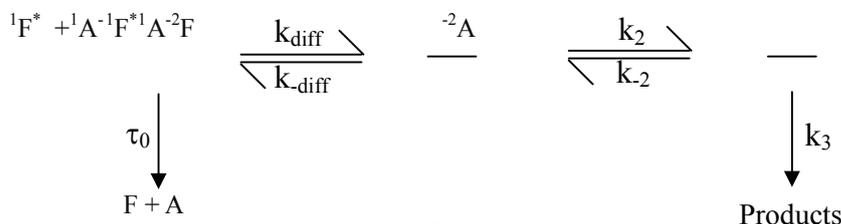
The Stern-Volmer(SV) plots of [(I₀ / I)-1] Vs[Q] for the fluorescence quenching of two fluorophores (2ABF & 4DADPS) by anions are linear(Figs.1-4). The linearity of Stern-Volmer quenching curves indicates that only one quenching mechanism is operative. For all the fluorophores the singlet-state lifetime (t₀) was determined using the single-photon counting method. These curves are linear. The Stern-Volmer quenching constant (K_D) values, obtained from SV plot and k_q 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



No fluorescence quenching was observed with Cl⁻ ion for all fluorophores. NO₃⁻ is the best quencher of 4DADPS and 2ABF. In the 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, sulfate, 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 4DADPS and 2ABF with all anions are comparable with the k_{diff} values. (ie. 10.61 X 10⁹ M⁻¹ S⁻¹). The high k_q 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.

3.2 Electron Transfer Quenching

In earlier works, it has been reported that in general the quenching of aromatic hydrocarbon [7, 10, 12], substituted naphthalene's[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]



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. k_{diff} and k_{-diff} are diffusions 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,

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

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

From **Scheme I** it can be seen that there are two rate-determining steps on the bimolecular quenching. The first one is the translational diffusion (k_{diff}) and the second one is the electron transfer process (k₂). Now assuming electron transfer to be exothermic k₋₂ << k_{diff} and the value of k₃, equation (3) can be simplified as,

$$k_q = (k_2 - k_{diff}) / (k_2 + k_{diff}) \dots\dots\dots (4)$$

$$k_q k_2 + k_q k_{diff} = k_2 - k_{diff}$$

The free energy change DG_{TH} in the electron transfer process can be calculated from treinin and hayonequation [18]
 DG_{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 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 DG_{TH} 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 (E_s) and reduction potential of fluorophores (E1/2), E_{CTTS} energy of inorganic anions along DG_{TH} of two fluorophores are presented in Table 1. From the table, it can be seen that k_q in general, decreases with an 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 k_q against ES of the two fluorophore and log k_q against E_{CTTS} of the quenchers for aromatic amino fluorophores (2ABF and 4DADPS) are fairly linear are shown in 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 E1/2 values could be determined Cyclic voltammetrically only for 2ABF and 4DADPS, the DG_{TH} values were calculated for these fluorophores. The DG_{TH} values for SO₄²⁻ and Br⁻ are either positive or least negative and so their quenching abilities are very less. Plots between DG_{TH} and log k_q 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 an equation of type.

$$\log k_q = -0.28 DG_{TH} + 9.04 \quad (4)$$

The linearity strongly suggests the electron transfer nature of the quenching of this fluorophore 2ABF and 4DADPS by inorganic anions. Considering the electron transfer to be the rate-determining step in the quenching, we have $k_{diff} > k_2$ and equation (2) can be written as,

$$K_q = (k_2 \cdot k_{diff}) / (k_{diff}) \quad \dots\dots\dots (5)$$

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

$$k_2 = A \exp\left(\frac{-E_a}{RT}\right) \quad \dots\dots\dots (6)$$

where A is the collisional frequency at a unit molar concentration of reactants within the encounter complex and E_a is the potential barrier in the electron transfer process. Substituting Eqn. (5) we can write

$$K_q = \left[\frac{(k_{diff} \cdot A)}{(k_{diff})} \right] \cdot \exp\left(\frac{-E_a}{RT}\right) \quad \dots\dots\dots (7)$$

Once more assuming $k_{diff} \approx k_{diff}$, eqn. (7) becomes,

$$K_q = A \exp\left(\frac{-E_a}{RT}\right) \quad \dots\dots\dots (8)$$

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

$$K_q = 1010 \exp\left(\frac{-E_a}{RT}\right) \quad \dots\dots\dots (9)$$

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

$$E_{aTH} = [0.28 DG_{TH} + 0.96] RT \quad \dots\dots\dots (10)$$

This corresponds to the understanding that D E_{aTH} is proportional to D (DG). DG_{TH} for the fluorophores calculated using the above equation is given in Table 2. From Eqn. (10) the value of E_{aTH} (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 DG_{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

- 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 $\log k_q$ values with singlet transition energy (E_S) of the fluorophores and with E_{CTTS} of the quencher are linear.
- This indicated the presence of a quenching mechanism involving electron transfer from anion to the fluorophores.
- Using the equation for electron transfer mechanism the ΔG_{TH} values have been determined for 2ABF and 4DADPS by the method suggested by Shizuka et al. [12].
- 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.

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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 ₂ O 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	Lifetime (ns)	k_q ($10^9 M^{-1}S^{-1}$)								
		Cl ⁻	Br ⁻	I ⁻	SO ₄ ²⁻	SO ₃ ²⁻	NO ₃ ⁻	S ₂ O 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 , E_s , $E_{1/2}$ and E_{CTTS} of ABF and 4DADPS of fluorophore – inorganic anions and ΔG_{TH} values in 95% water- Ethanol mixture medium.

Fluorophore	E_s (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 ₂ O ₃ ²⁻	Br ⁻
2ABF	3.77	---	k_q ΔG_{TH}	8.709	nq	8.913	5.89	nq
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Figure 3.1.1: Stern-Volmer plot of ABF fluorescence quenching by inorganic anions.

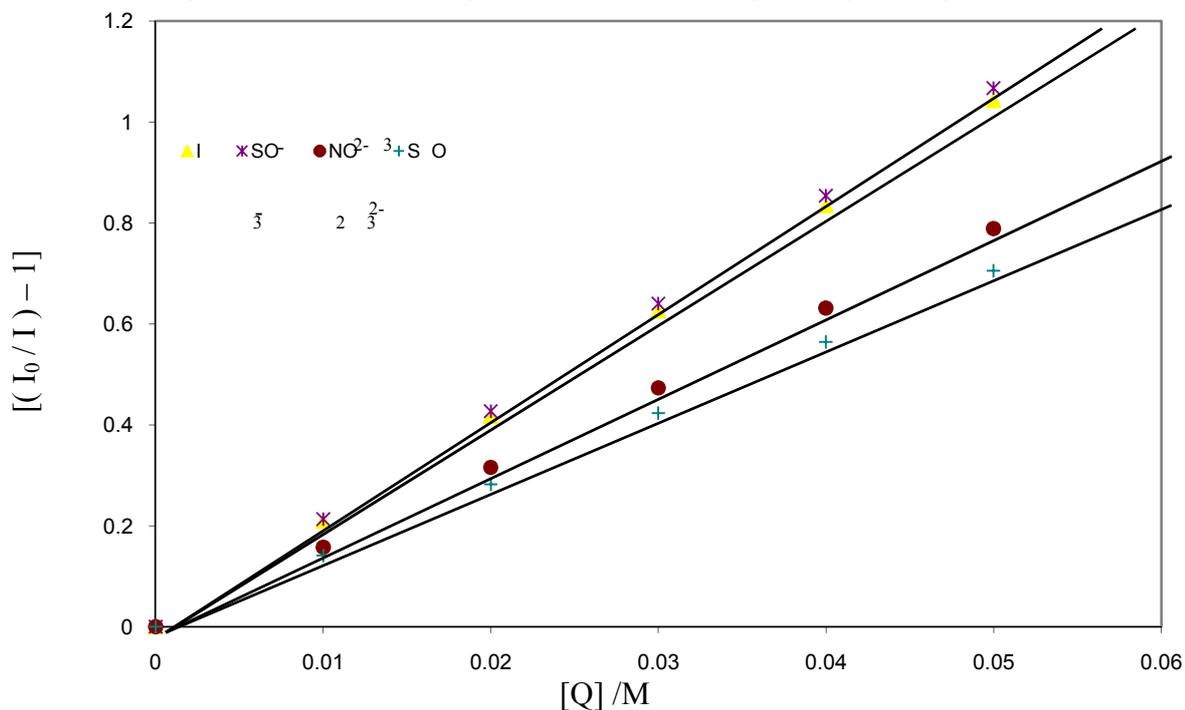


Fig 3.1.2: Stern-Volmer plot of 4DADPS fluorescence quenching by inorganic anions.

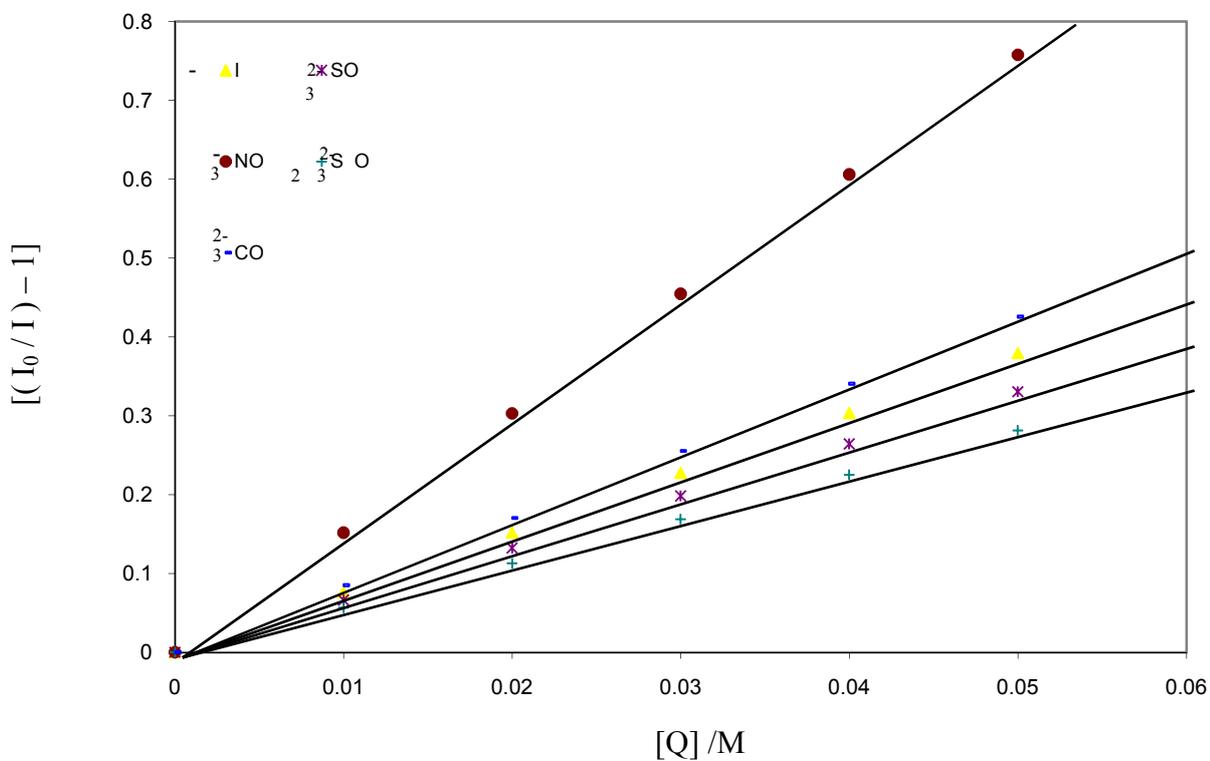


Fig 3.1.3 Plot of E_{CTTS} (ev) Vs $\log k_q$ for ABF and 4DADPS fluorescence quenching by inorganic anions.

