Anion Induced Fluorescence Quenching of Various Naphthalenediols

N. Radha[1], and M. Swaminathan[2*]

[1]PG and Research, Department of Chemistry, Alagappa Government Arts College, Karaikudi, Tamil Nadu, India

[2]Nanomaterials Laboratory, International Research Centre, Kalasalingam Univeristy, Krihnankoil, Tamil Nadu, India

*Corresponding Author: chemsam50@gmail.com

Abstract: Fluorescence quenching of four naphthalenediols [1,5-; 1,7-; 2,7-; and 2,3- Naphthalenediols (NDs)] by inorganic anions [Cl−, Br−, SO_4^{2-} SO_3^{2-}, $S_2O_3^{2-}$, CO_3^{2-}, NO_3^-, and 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 naphthalenediols.

Keywords: Fluorescence quenching, Naphthalenediols, Anionic quenching, Electron transfer mechanism.

I. Introduction

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]. Naphthalenediols are found to be potent chemosensors for selective sensing of Cu and Ni cations respectively [2]. A number of investigations concerning the fluorescence quenching by inorganic anions have been reported [3-8]. 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 [3] and charge transfer to solvent transition energy [4]. 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 [2,3,7].

A quenching mechanism involving electron transfer from anion to the excited aromatic molecules has been proposed by Förster [9] and is supported by several authors [5-8]. In a detailed study of inorganic anion quenching of aromatic fluorophores Shizuka *et al* [5,10] and Shalini Nigham *et al* [11] 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 S_1 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 collisional complex A^*- -X^- or radical pair ^2A--^2X.

Moriya *et al* [12] 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 [11] and aromatic amines [13] by inorganic anions has been investigated. In the fluorescence quenching of substituted naphthalenes by inorganic anions, Behera *et al* [14] 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 (ΔG) and activation energy (E_a) for the electron transfer quenching process.

II. Experimental

Four Naphthalenediols (1,5-; 1,7-; 2,7- and 2,3- NDs) were obtained from Sisco Chemical Company – India and further purified by recrystallisation with suitable solvents. The concentration of fluorophore was 10^{-4}M in 95% water - ethanol mixture. The solvent mixture was chosen to ensure that both NDs and metal ions are completely soluble.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 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 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

A. Absorption and Fluorescence Spectra

Analysis of the absorption and fluorescence spectra of the four naphthalenediols (1,5-; 1,7-; 2,7- and 2,3- NDs) 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 [7].

B. Quenching Curves

The Stern-Volmer (SV) plots of $[(I_0 / I)-1]$ Vs [Q] for the fluorescence quenching of all naphthalenediols 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 (t_0) was determined using 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 (t_0) of fluorophores are given in Table 1 and 2 respectively. The order of quenching by anions is

$$I^- < S_2O_3^{2-} < SO_3^{2-} < NO_3^- < HPO_4^{2-} < CO_3^{2-}$$

No fluorescence quenching was observed with Cl^- ion for all the four naphthalenediols (NDs). The CO_3^{2-} is the most efficient quencher. The poor quenchers are bromide and sulphate ions. The order of quenching by anions is more or less similar for all the four naphthalenediols. The k_q values of all the NDs 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 that the quenching is bimolecular and purely dynamic in nature [5,7,8]. Since there was no change in the absorption spectra with quenchers, static quenching is ruled out.

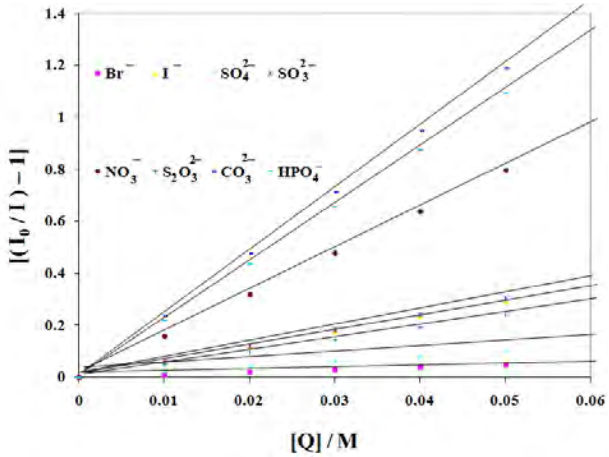


Fig. 1. Stern-Volmer plot of 1,5-ND fluorescence quenching by inorganic anions

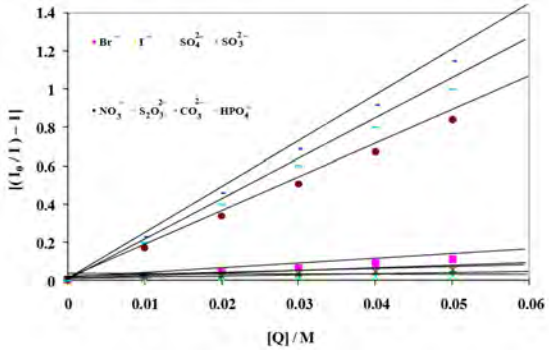


Fig. 2. Stern-Volmer plot of 1,7-ND fluorescence quenching by inorganic anions

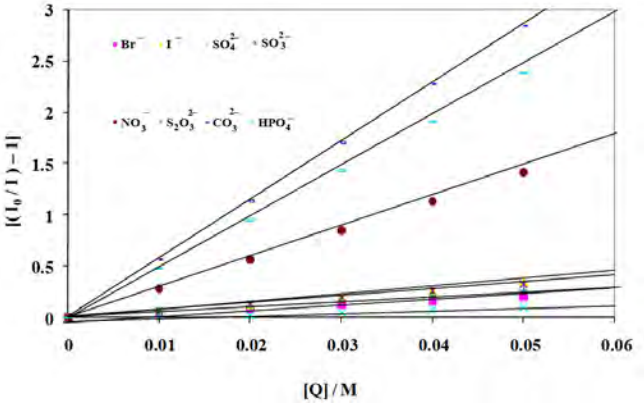


Fig. 3. Stern-Volmer plot of 2,7-ND fluorescence quenching by inorganic anions

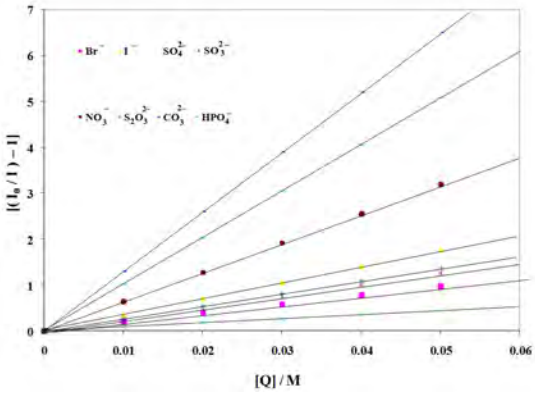


Fig. 4. Stern-Volmer plot of 2,3-ND fluorescence quenching by inorganic anions

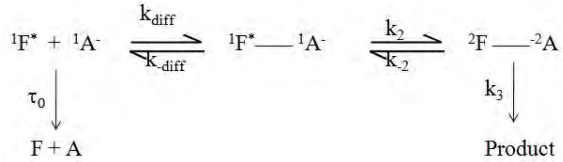
TABLE I: K_D (K_{SV}) (M^{-1}) OF FOUR NAPHTHALENEDIOLS FLUORESCENCE QUENCHING BY INORGANIC ANIONS IN 95 % WATER – ETHANOL MIXTURE

Fluorophore	*Cl^-*	*Br^-*	*I^-*	*SO_4^{2-}*	*SO_3^{2-}*	*NO_3^-*	*$S_2O_3^{2-}$*	*CO_3^{2-}*	*HPO_4^{2-}*
1,5-ND	nq	0.9345	5.796	2.055	6.070	15.923	4.818	23.77	21.918
1,7-ND	nq	2.154	0.977	0.427	1.049	16.834	0.833	22.913	19.987
2,7-ND	nq	4.086	6.88	2.278	6.482	28.30	5.151	56.789	47.752
2,3-ND	nq	19.499	35.481	9.119	25.208	63.776	27.546	130.181	101.584

nq- no appreciable quenching

C. Electron Transfer Quenching

In earlier works, it has been reported that in general the quenching of aromatic hydrocarbon [5, 8, 10], substituted naphthalenes [14] and aromatic amines [13] by inorganic anions takes place via a transfer of electrons. The electron transfer scheme can be shown as



Scheme 1

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. Applying steady state approximation to the various intermediates in Scheme I, we can write,

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

From scheme I it can be seen that there are two rate-determining steps on the bimolecular quenching. First one is the translational diffusion (k_{diff}) and second one is the electron transfer process (k_2). Now assuming electron transfer to be exothermic $k_{-2} << k_{diff}$ and the value of k_3 to be greater than k_2, equation (1) can be simplified as,

$$k_q = (k_2 \cdot k_{diff}) / (k_{2} + k_{-diff}) \qquad (2)$$

The free energy change ΔG_{TH} in the electron transfer process can be calculated from Treinin and Hayon equation [15]

$$\Delta G_{TH} = E_{CTTS} - E_{1/2} - E_S - 4.7 \qquad ...(3)$$

where E_{CTTS} is the charge-transfer to solvent transition energy of the inorganic quenchers, $E_{1/2}$ is the redox potential and E_S is the singlet transition state energy for the fluorophores. All the units are in electron volts (ev). Since E_{CTTS} varies with IP, this energy can be used instead of IP [4]. This E_{CTTS} will vary with the ion used and also depends on the solvent shell-ion distance. We could not use the Rehm-Weller [16] 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 (2, 7-ND and 2, 3-ND) 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 ($E_{1/2}$), E_{CTTS} energy of inorganic anions along with ΔG_{TH} of four 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 k_q against E_S of the four naphthalenediols and log k_q against E_{CTTS} of the

quenchers for naphthalenediols are shown (Fig. 5 and 6). 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.

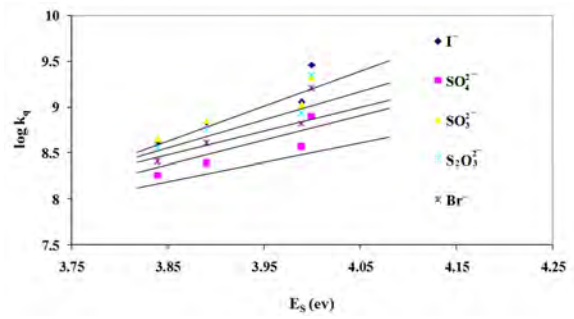


Fig. 5. Plot of E_S Vs log k_q for various naphthalenediols fluorescence quenching by inorganic anions

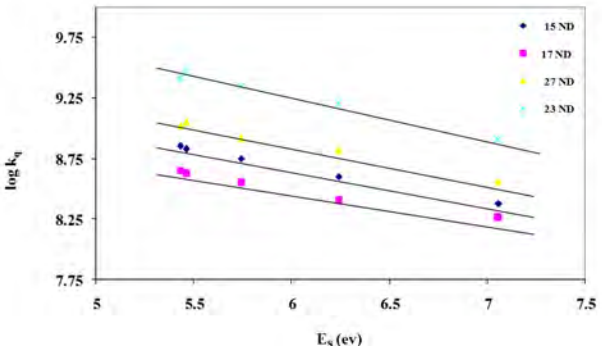


Fig. 6. Plot of E_{CTTS} Vs log k_q for various naphthalenediols fluorescence quenching by inorganic anions

Since the $E_{1/2}$ values could be determined Cyclic voltametrically only for 2, 7-ND and 2, 3-ND, 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. A plot between ΔG_{TH} and log k_q for naphthalenediols are given in Fig. 7. Since the slopes are different, they are drawn separately. The plot of naphthalenediols is fairly linear. The slopes and intercepts of both lines can be calculated and can be written as an equation of type.

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

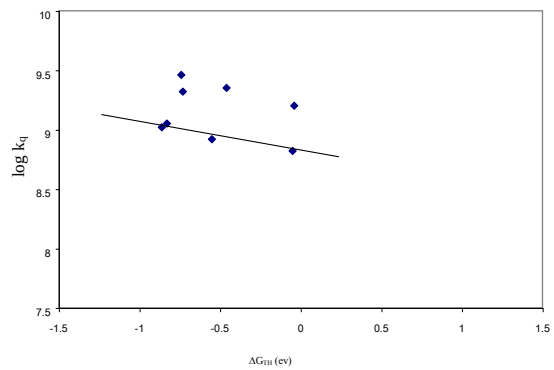


Fig. 7. Plot of ΔG_{TH} Vs log k_q for 2,7-ND and 2,3-ND fluorescence quenching by inorganic anions

The linearity strongly suggests the electron transfer nature of the quenching of these naphthalenediols 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,

$$k_q = (k_2 \cdot k_{diff}) / (k_{-diff}) \quad (5)$$

And the values of k_2 can be expressed by the Arrhenius equation as,

$$k_2 = A_{exp}\ (-E_a / RT) \quad (6)$$

where A is the collisional frequency at unit molar concentration of reactants within the encounter complex and $E_{aTH}(\Delta G^{\#}_{TH})$ is the potential barrier in the electron transfer process. Substituting eqn. (5) we can write

$$k_q = [(k_{diff} . A) /(k_{diff})] . _{exp}\ (-\Delta G^{\#}_{TH} / RT) \quad (7)$$

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

$$k_q = A_{exp}\ (-\Delta G^{\#}_{TH} / RT) \quad (8)$$

Taking the frequency factor A to be 10^{10} as suggested by shizuka et al [10],

Eqn. (8) can be written as

$$k_q = 10^{10}{}_{exp}\ (-\Delta G^{\#}_{TH} / RT) \quad (9)$$

From eqn. (4) at room temperature, an expression similar to the polanyi rule formation [17] can be derived,

$$\Delta G^{\#}_{TH} = 0.28\ \Delta G_{TH} + 0.096 \quad (10)$$

This corresponds to the understanding that ΔE_{aTH} is proportional to $\Delta(\Delta G)$. $\Delta G^{\#}_{TH}$ for the fluorophores can be calculated using the above equation. A plot of $\Delta G^{\#}_{TH}$ and log kq gives a straight line (Fig. 7). From eqn. (10) the value of $\Delta G^{\#}_{TH}$ (Free energy of activation when ΔG_{TH} is zero) comes to 0.096 which is comparable to those derived for similar systems [10]. Equation (10) also suggests that a $\Delta G^{\#}_{TH}$ value indicate the quenching process will be almost completely barrier less and purely diffusion controlled.

Among the naphthalenediols the 1, 7-ND is reported to be more polar when compared to other NDs in the excited state. This behaviour is explained by its point group symmetry [1] which is different from other naphthalenediols. Hence the k_q values for 1,7-ND are higher than for other NDs. The increase of excited state polarity of 1,7-ND may increase the formation of non-emissive exciplex. This is the reason why the correlation coefficient for 1,7-ND 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^- quench the fluorescence of Naphthalenediols.
- The fluorescence quenching is found to be dynamic in all cases.

TABLE II: k_q AND τ_0 (ns) OF FOUR NAPHTHALENEDIOLS FLUORESCENCE QUENCHING BY INORGANIC ANION 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^-	$S_2O_3^{2-}$	CO_3^{2-}	HPO_4^{2-}
1,5-ND	8.5737	nq	0.1090	0.676	0.2398	0.708	1.8571	0.562	2.7731	2.5563
1,7-ND	2.348	nq	0.9174	0.416	0.182	0.447	7.1695	0.355	9.7585	8.5123
2,7-ND	6.1907	nq	0.660	1.112	0.3678	1.047	4.572	0.832	9.172	7.713
2,3-ND	12.3027	nq	1.585	2.884	0.7413	2.049	5.1838	2.239	10.5812	8.2568

nq-no appreciable quenching

- 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.
- Using the equation for electron transfer mechanism the ΔG_{TH} values have been determined for naphthalenediols.

V. ACKNOWLEDGEMENTS

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