

# Analysis of 2-Phenoxyaniline Fluorescence Quenching by Chloromethanes

Radha N., Swaminathan M.

**Abstract.** The fluorescence quenching of 2-phenoxyaniline (2PAN) by chloromethanes were studied in hexane, dioxane, acetonitrile and methanol. The quenching rate constants ( $k_q$ ) are large with  $CCl_4$  and  $CHCl_3$  and close to diffusion rate constant ( $k_{diff}$ ) and viscosity dependent, where with  $CH_2Cl_2$  they are less. No clear cut variation of solvent polarity or viscosity is observed for  $CH_2Cl_2$ . Intermediate donor-acceptor complex formation is suggested for  $CH_2Cl_2$  quenching.  $k_q$  varies with electron affinity of quenchers suggesting the formation of non-emissive exciplex in quenching.

**Keywords-** Fluorescence quenching; Chloromethanes; 2-phenoxyaniline; Non-emissive exciplex; Solvent effect.

## I. INTRODUCTION

Excited state energetics has been studied elaborately by fluorescence quenching. The accessibility of fluorophores to quenchers can be utilized to find the location of probes on macromolecules. This makes quenching mechanism important, not only in physical science but also in chemical, biological and medical sciences. Fluorescence quenching of organic fluorophores by various chemical species like aniline, carbon tetra chloride, metal ions etc. has been investigated [1-4]. Molecular interactions are taken for the analysis of quenching results with two different models (i) stern Volmer plots (ii) Smoluchowski-type quenching model [5-7]. Fluorescence quenching of aromatic hydrocarbons by haloalkanes was studied [7-14]. When the overlap of donor emission and acceptor absorption is negligible, quenching was justified in terms of a non-emissive exciplex [9] and its formation can only be inferred and not observed [15]. Contact complex intermediate formation with haloalkanes was postulated by Klein et al. [16] and the rate constant is given by eqn (1).

$$\ln k_q \propto -\frac{IP_D - EA_A - C - P - E_s}{k_b T} \text{ ---- (1)}$$

where  $IP_D$  - ionization potential of the donor,  $EA_A$  - electron affinity of the acceptor,  $C$  - coulomb energy,  $k_b$  - Boltzmann constant,  $P$  - polarization energy and  $E_s$  - energy of the first excited singlet state of the fluorophore. In this equation, the  $\ln k_q$  mainly depend on the  $IP_D$ ,  $EA_A$  and  $E_s$ .  $C$  and  $P$  are assumed to be constants. For one fluorescent donor and a series of different electron deficient quenchers,  $k_q$  can be correlated with  $EA$  values of quenchers.

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Quenching of aromatic amines [17], aminodiphenylamines [18] and 2-amino-7-bromofluorene [19] by halomethanes had been reported earlier. We report quenching of 2-phenoxyaniline fluorescence by halomethanes ( $CCl_4$ ,  $CHCl_3$  and  $CH_2Cl_2$ ) in hexane, dioxane, acetonitrile and methanol.

## II. EXPERIMENTAL

### A. Materials and methods

2-Phenoxyaniline from Aldrich Chemical Company and  $CCl_4$ ,  $CH_2Cl_2$ ,  $CHCl_3$  and solvents from Merck were used as such. Quenching experiments were carried out as reported [18]. Detail of instruments used for absorption, fluorescence spectra and life time measurements are described elsewhere [18].

## III. RESULTS AND DISCUSSION

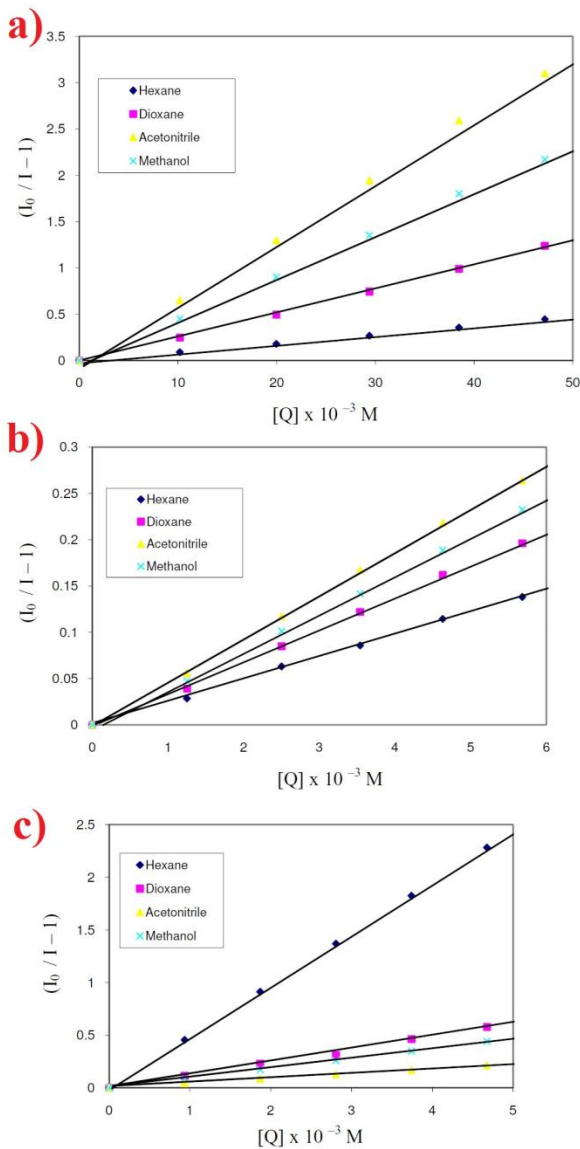
The absorption and fluorescence spectra of 2-phenoxyaniline were tested without and with three chloromethanes in hexane, dioxane, acetonitrile and methanol. We found the results:

- (i) No change in shape and band maxima of absorption and fluorescence spectra of the fluorophore with quencher.
- (ii) No red shifted emission band of fluorophore
- (iii) Excitation and absorption spectra are same. It is inferred from the above results that
- (i) The fluorophore-quencher interaction has no effect on absorption and fluorescence spectral properties, (ii) No emissive exciplex formed and there is no photochemical reaction. Stern-Volmer plots for 2PAN fluorescence quenching by  $CCl_4$ ,  $CHCl_3$  and  $CH_2Cl_2$  in four solvents, obtained using equation (2) are displayed in figure-1(a,b,c).

$$\frac{I_0}{I} = 1 + K_{SV} [Q] = 1 + k_q \tau_0 [Q] \text{ ---- (2)}$$

Perfect linearity in SV plots in all solvents indicates one quenching mechanism, which is bimolecular and dynamic. Table 1 lists  $k_q$  values dielectric constant and  $k_{diff}$  values of the solvents. In all solvents  $k_q$  values decrease from  $CCl_4$  to  $CH_2Cl_2$ .

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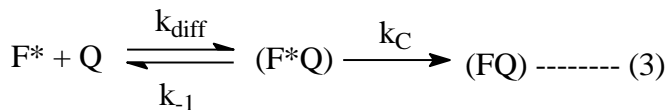


**Fig.1. Stern – Volmer plot of 2PAN fluorescence quenching by chloromethanes in different solvents (a) CCl<sub>4</sub>, (b) CHCl<sub>3</sub> and (c) CH<sub>2</sub>Cl<sub>2</sub>**

**Table 1. The k<sub>q</sub> values for 2PAN and 4PAN fluorescence quenching in different solvents with k<sub>diff</sub> and ε values of solvents**

Solvent	τ <sub>0</sub> (ns)		ε	k <sub>diff</sub> (10 <sup>10</sup> M <sup>-1</sup> s <sup>-1</sup> )	k <sub>q</sub> (M <sup>-1</sup> s <sup>-1</sup> )					
	2PAN	4PAN			2PAN			4PAN		
					CH <sub>2</sub> Cl <sub>2</sub> (10 <sup>9</sup> )	CHCl <sub>3</sub> (10 <sup>9</sup> )	CCl <sub>4</sub> (10 <sup>9</sup> )	CH <sub>2</sub> Cl <sub>2</sub> (10 <sup>9</sup> )	CHCl <sub>3</sub> (10 <sup>9</sup> )	CCl <sub>4</sub> (10 <sup>9</sup> )
Hexane	0.2975	3.955	1.89	34.2	1659.8	8.58	32.72	97.24	13.72	25.52
Dioxane	2.655	3.48	2.10	8.47	45.28	1.43	10.06	57.15	2.06	7.64
Acetonitrile	2.228	4.351	36.0	28.7	19.17	2.28	31.08	52.63	4.86	17.9
Methanol	2.836	4.037	32.6	18.30	32.65	1.56	16.83	28.14	2.46	12.47

For CCl<sub>4</sub> and CHCl<sub>3</sub> k<sub>q</sub> values are large and close to k<sub>diff</sub> values of solvents and less for CH<sub>2</sub>Cl<sub>2</sub>. A kinetic scheme is shown by eqn (3).

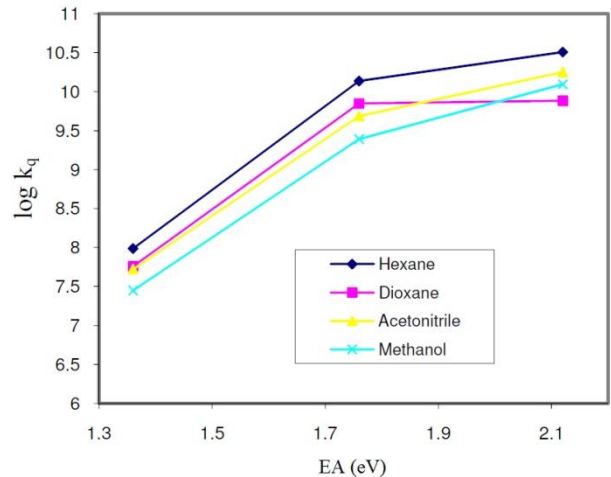


Under steady state conditions, equation 4 can be obtained.

$$k_q(\text{obs}) = \frac{k_c k_{diff}}{k_c + k_{-1}} \text{ ---- (4)}$$

There are three conditions:

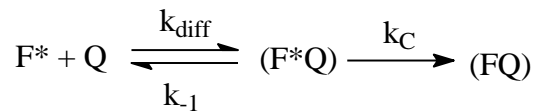
- (i) If  $k_c \gg k_{-1}$ , then  $k_q(\text{obs}) \approx k_{diff}$  and it depends on solvent viscosity
- (ii) If  $k_c \ll k_{-1}$ , then  $k_q(\text{obs}) \approx k_c(k_{diff}/k_{-1}) = k_c K$   
K- equilibrium constant of exciplex formation.  
Hence for weak quencher k<sub>q</sub>(obs) is independent of solvent viscosity. If the exciplex is polar, solvent polarity will stabilize the exciplex (reduces k<sub>-1</sub>) thereby increasing k<sub>q</sub>[20].
- (iii) If  $k_c = k_{-1}$ , then k<sub>q</sub>(obs) is less than k<sub>diff</sub> and solvent polarity or viscosity has no effect.



**Fig. 2. Plot of EA Vs log k<sub>q</sub> for 2PAN fluorescence quenching by chloromethanes in different solvents.**

Figure 2 displays a graph of log k<sub>q</sub> values of 2-PAN in each solvent against electron affinity (EA) of chloromethanes obtained from literature [21]. There is a rise of log k<sub>q</sub>, but not linear. The curves are leveling off to diffusion controlled rate constant. Same trend was observed for substituted naphthalenes [13] and aromatic amines[17,22]. Hence k<sub>q</sub> values are restricted by the electron affinity of the quencher when they are lesser than the diffusion-controlled limit. When k<sub>q</sub> equals k<sub>diff</sub>, it becomes independent of EA.

A. The effect of solvent



At the extreme efficient diffusion limited quenching, when F\* and Q come close to each other to within the collision cross-section to form the encounter complex, the emission is quenched rapidly and non-emissive excited complex (F\*.Q) would not form completely. The encounter complex is not appreciably affected by solvent polarity when k<sub>q</sub> is close to k<sub>diff</sub> and quenching is diffusion limiting. k<sub>q</sub> becomes dependent on solvent viscosity.

It is clearly seen that k<sub>q</sub> of 2PAN and 4PAN with CCl<sub>4</sub> and CHCl<sub>3</sub> (Table 1) are large in least viscous hexane and less in most viscous dioxane with no effect of on solvent polarity. But as discussed the rate of formation

and decay of a non-emissive exciplex is determined by the rate constant of diffusion ( $k_{diff}$ ), back diffusion ( $k_{-1}$ ) and intrinsic quenching constant ( $k_c$ ). Complete non-emissive exciplex formation with proper geometry for optical overlap and proper orientation of solvent cage necessarily mean that overall quenching ( $k_q$ ) should be much less than  $k_{diff}$ . Only in such case, a clear effect of solvent polarity is expected to be observed. On the other hand, if  $k_q$  is very close to  $k_{diff}$ , a complete formation of exciplex may not take place before quenching occurs. Then quenching could be diffusion limiting and the effect of solvent viscosity should be more pronounced than the effect of solvent polarity. So the variation of  $\log k_q$  is according to solvent viscosity for  $CCl_4$  and  $CHCl_3$ .

ie., Hexane > Acetonitrile > Methanol > Dioxane.

$k_q$  shows a diversified trend with no clear-cut variation with solvent polarity and viscosity for  $CH_2Cl_2$ . In this case, the interactions between  $F^*$  and Q remains CT type, but the excited state complex is an intermediate state between the pure encounter complex (viscosity dependent) and completely formed exciplex (polarity dependent) and called as intermediate donor-acceptor complex.

#### IV. CONCLUSION

Stern-Volmer quenching curves for 2-Phenoxyaniline are linear and quenching is dynamic in all solvents.  $k_q$  values are large with  $CCl_4$  and  $CHCl_3$  and close to diffusion rate constant ( $k_{diff}$ ), where as for  $CH_2Cl_2$  they are less. Low value for  $CH_2Cl_2$  is due to the formation of non-emissive exciplex. Results reveal that (i) quenching is diffusion controlled with the efficient quenchers  $CCl_4$  and  $CHCl_3$  (ii) quenching involves the formation of exciplex between donor and acceptor in the excited state with 2-Phenoxyaniline as electron donor and chloromethanes as electron acceptors.

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