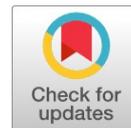


Analysis of 2-Phenoxyaniline Fluorescence Quenching by Chloromethanes

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).

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

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.

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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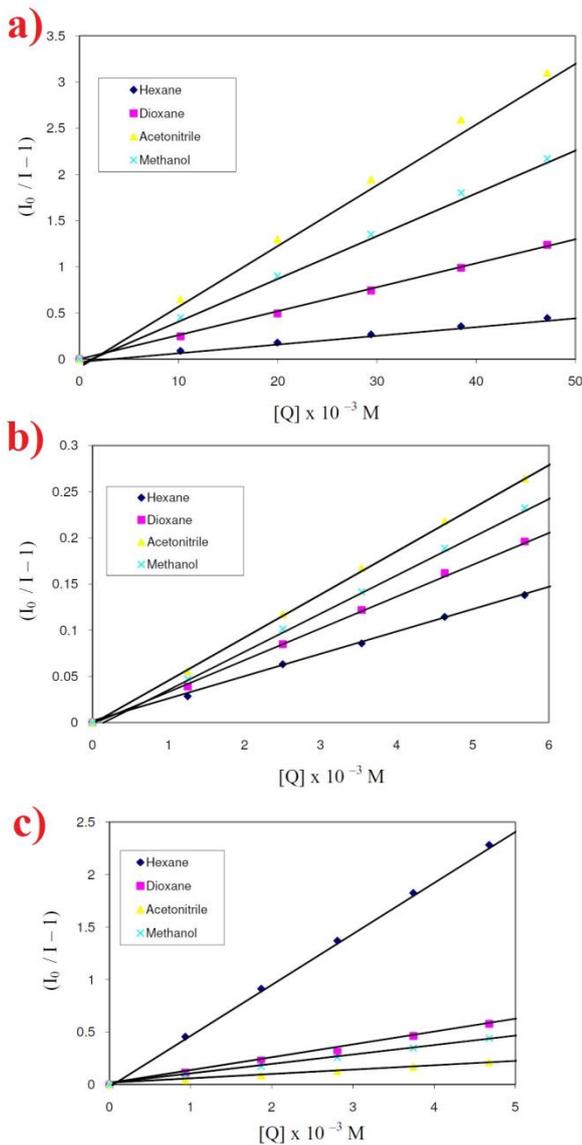
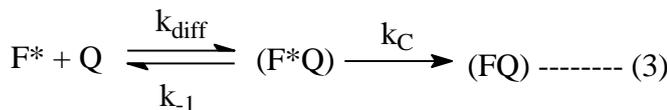


Fig.1. Stern – Volmer plot of 2PAN fluorescence quenching by chloromethanes in different solvents (a) CCl₄, (b) CHCl₃ and (c) CH₂Cl₂

Table 1. The k_q values for 2PAN and 4PAN fluorescence quenching in different solvents with k_{diff} and ε values of solvents

Solvent	τ ₀ (ns)		ε	k _{diff} (10 ¹⁰ M ⁻¹ s ⁻¹)	k _q (M ⁻¹ s ⁻¹)					
	2PAN	4PAN			2PAN			4PAN		
					CH ₂ Cl ₂ (10 ⁹)	CHCl ₃ (10 ⁹)	CCl ₄ (10 ⁹)	CH ₂ Cl ₂ (10 ⁹)	CHCl ₃ (10 ⁹)	CCl ₄ (10 ⁹)
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 CCl₄ and CHCl₃ k_q values are large and close to k_{diff} values of solvents and less for CH₂Cl₂. A kinetic scheme is shown by eqn (3).



Under steady state conditions, equation 4 can be 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_q (obs) is independent of solvent viscosity. If the exciplex is polar, solvent polarity will stabilize the exciplex (reduces k₋₁) thereby increasing k_q[20].
- (iii) If $k_c = k_{-1}$, then k_q (obs) is less than k_{diff} and solvent polarity or viscosity has no effect.

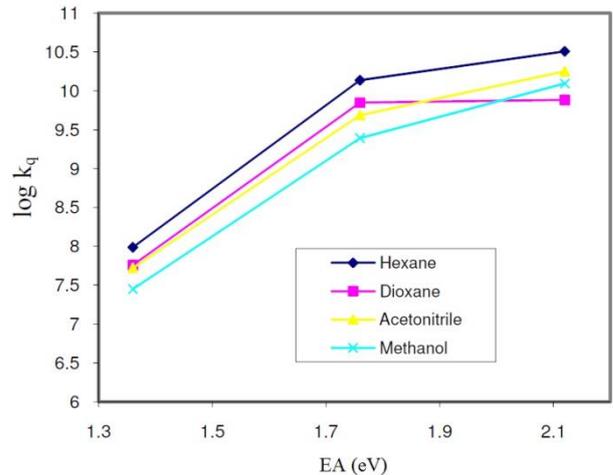
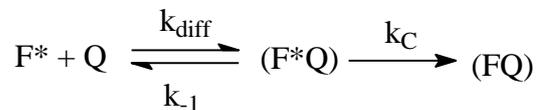


Fig. 2. Plot of EA Vs log k_q for 2PAN fluorescence quenching by chloromethanes in different solvents.

Figure 2 displays a graph of log k_q values of 2-PAN in each solvent against electron affinity (EA) of chloromethanes obtained from literature [21]. There is a rise of log k_q, 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_q values are restricted by the electron affinity of the quencher when they are lesser than the diffusion-controlled limit. When k_q equals k_{diff}, 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_q is close to k_{diff} and quenching is diffusion limiting. k_q becomes dependent on solvent viscosity. It is clearly seen that k_q of 2PAN and 4PAN with CCl₄ and CHCl₃ (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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