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Fluorescence quenching of 2-amino-7-bromofluorene by chloromethanes – static and dynamic model for CCl_4 quenching in polar solvents

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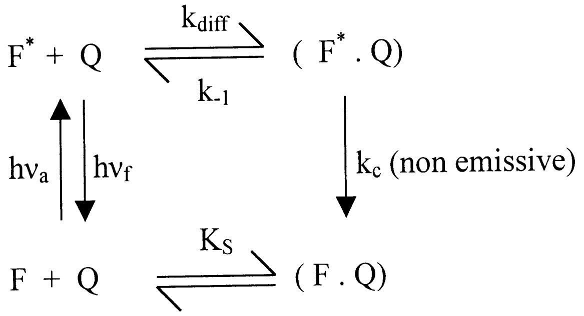
The study of fluorescence quenching of 2-amino-7-bromofluorene (ABF) by chloromethanes (CH_2Cl_2, $CHCl_3$, CCl_4) in various solvents reveals that (i) the quenching constant k_q depends on solvent viscosity for CCl_4 and on solvent polarity for CH_2Cl_2 and $CHCl_3$; (ii) the observed positive deviation in methanol and acetonitrile in the Stern–Volmer plot is due to the presence of a static component in quenching; (iii) the fluorescence quenching is mainly due to the formation of a non-emissive charge transfer complex in the excited state.

Keywords: fluorescence quenching, 2-amino-7-bromofluorene, charge transfer complex

Fluorescence quenching by suitable quenchers has been widely used as one of the common methods for studying the energetics of the excited state. The quenching of aromatic hydrocarbons and their derivatives by haloalkanes has been studied in detail. Among chloromethanes, CCl_4 is known to be a good quencher. In some cases the Stern–Volmer (SV) plots for CCl_4 quenching were found to be non-linear.[9-12,14] In the present study, we investigate the non-linearity of the SV plot in the fluorescence quenching of ABF by CCl_4 in methanol and acetonitrile. The fluorescence quenching rate constants for $CHCl_3$ and CH_2Cl_2 have also been analysed to find out the mechanism of quenching.

The analysis of absorption and fluorescence spectra reveals that: (i) the fluorophore–quencher interaction does not change the absorption and fluorescence spectral properties; (ii) the formation of any emissive exciplex may be discounted; and (iii) there is no observable photochemical reaction between fluorophore and quencher.

The SV plots are linear with the slope K_D in all the systems except for quenching by CCl_4 in methanol and acetonitrile. The SV plots of ABF by CCl_4 in methanol and acetonitrile are shown in Figs 1 and 2. In these solvents, a positive deviation in the SV plot is observed for I_0/I when the concentration of CCl_4 exceeds 0.02 M in methanol and 0.03 M in acetonitrile. The quenching constants (k_q) for the three chloromethanes, determined using the lifetimes of the fluorophore in different solvents, are given in Table 1 along with the dielectric constant and viscosity of the solvents. The kinetics of bimolecular quenching and the presence of static and dynamic quenching can be explained by the following scheme



For the most efficient quencher CCl_4, the value of k_q is close to k_{diff}. In this case $k_c >> k_{-1}$. For $CHCl_3$ and CH_2Cl_2 as quenchers the k_q values generally vary with solvent polarity. This suggests the presence of a charge transfer mechanism for quenching. This is also confirmed by the equation developed by Klein *et al.*[16] for this model

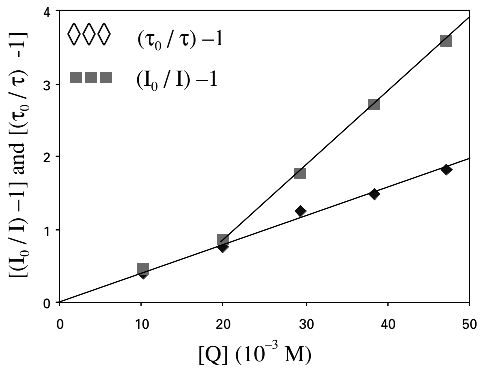


Fig. 1 Stern-Volmer plot of the fluorescence quenching of ABF by CCl_4 in methanol ■ ■ ■ [(I_0/I) – 1] vs [CCl_4] and ◊◊◊ [(τ_0/τ) –1] vs [CCl_4]

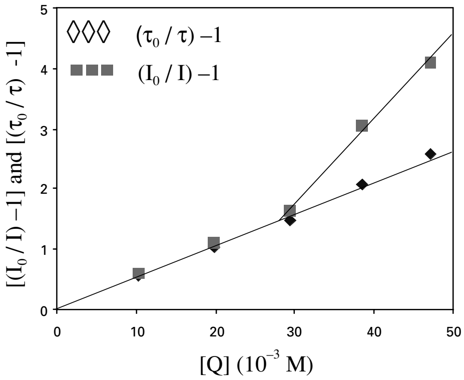


Fig. 2 Stern-Volmer plot of the fluorescence quenching of ABF by CCl_4 in acetonitrile ■ ■ ■ [(I_0/I) – 1] vs [CCl_4] and ◊◊◊ [(τ_0/τ) –1] vs [CCl_4]

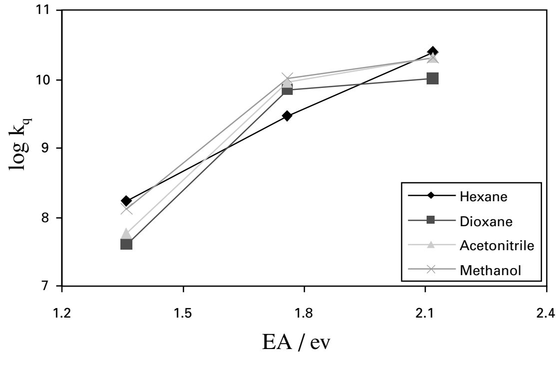


Fig. 3 Plot of EA vs log k_q for ABF fluorescence quenching by chloromethanes.

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Table 1 Singlet state lifetimes and quenching rate constants ($M^{-1}s^{-1}$) for 2-amino-7-bromofluorene in different solvents

No.	Solvent	Dielectric constant (ε)	Viscosity ($M^{-1}s^{-1}$)	k_{diff} ($M^{-1}s^{-1}$) X 10^{10}	Lifetime (ns)	k_q ($M^{-1}s^{-1}$)		
						CCl_4 (10^9)	$CHCl_3$ (10^9)	CH_2Cl_2 (10^6)
1	Hexane	1.89	0.292	3.42	1.33	24.36	2.96	170
2	Dioxane	2.10	1.180	0.847	1.38	10.56	6.88	40.45
3	Acetonitrile	36.0	0.345	2.870	4.62	20.66	9.23	60.32
4	Methanol	32.6	0.545	1.830	4.68	18.66	10.15	132.32

$$\ln k_q \;\alpha\; - [\, (IP - E_A - C - P - E_S)/K_b T \,] \qquad (4)$$

For a constant fluorophore with different quenchers the equation can be reduced to

$$\log k_q = \text{Const} + E_A / (2.303\, k_b\, T) \qquad (5)$$

(k_b is the Boltzman constant, E_A is the electron affinity of the quencher). The expected trend is observed for the plot of log k_q vs EA (Fig. 3). The EA values of chloromethanes are obtained from the literature.[17] The increase of k_q with EA is not linear since curves are levellling off to a diffusion controlled rate constant. The positive deviation observed at high concentration of CCl_4 can be explained by the excited state collision and by ground state complex formation or by transient quenching.

For the ground state complex formation and transient quenching processes the SV equation is

$$(Io / I) - 1 / [Q] = K_1 + K_2\,[Q]. \qquad (12)$$

$K_1 = (K_D + K_S)$ or $(K_D + K_T)$; $K_2 = (K_D \,.\, K_S)$ or $(K_D \,.\, K_T)$ K_S – ground state complex formation constant, K_T - the transient quenching constant and K_D – the dynamic quenching constant.

The plots of $[(I_o/I) - 1]/[Q]$ against [Q] in both solvents were found to be linear. This indicates the presence of a parallel quenching process. If there is transient quenching then a plot of $[(\tau_o/\tau) - 1]$ vs [Q] will not be linear[12] as K_T should rise with $(D\tau)^{1/2}$. As we observed a perfect linear plot of $[(\tau_o/\tau) - 1]$ vs [Q] in both solvents, the transient quenching is ruled out.[12] The K_D values 39.00 (methanol) 54.83 (actetonitrile) were obtained from the slopes of the linear plots $[(\tau_0/\tau) - 1]$ vs [Q]. K_S values 2.52 (methanol) 1.42 (actetonitrile) were estimated from slopes of the plots of $[(I_0/I) - 1]/[Q]$ vs [Q]. The K_S values are found to be less when compared to K_D values. Formation of a ground state complex is often reflected in a small change of absorption spectra of the fluorophore. The reason for no discernable change of absorption spectra in the presence and absence of quenchers may therefore be due to almost similar extinction coefficients (ε) of the fluorophore and the fluorophore-quencher complex. Hence, the positive deviations observed in these two solvents are due to the presence of a small static quenching component in the overall dynamic quenching.

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Techniques used: UV vis spectrophotometry, spectrofluorimetry and picosecond spectrofluorimetry.

References : 18

Table : 2

Table 2: Dynamic and static quenching constants of 2ABF in methanol and acetonitrile solvents.

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References cited in the synopsis

9 W.R. Ware and C. Lewis, *J. Chem. Phys.*, 1972, **57**, 3546.
10 M.S.C. Leite and K. Razi Nagvi, *Chem.Phys.Lett.*, 1969, **4**, 35.
11 P.K. Behra and A.K. Mishra, *J. Photochem Photobiol. A: Chem.*, 1993, **71**, 115–118.
12 P.K. Behra T. Mukerjee, and A.K. Mishra, *J. Lumin.*, 1995, **65**, 131–136.
14 S. Nigam, S.K. Dogra, *Ind. J. Chem.*, 1993, **32A**, 291.
16 J. Klein, V.P. Plazanet and G. Laustrait, *J. Chem. Phys. Physicohem. Biol.*, 1970, **67**, 302.
17 H. Shizuka, *Acc. Chem. Res.*, 1985, **18**, 141.