

Influence of Nitrobenzene and Acetonitrile in *p*-Chloroaniline and 1,4-dioxane

S. BAKKIALAKSHMI*, B. SHANTHI†, R. SANTHI‡ and D. CHANDRAKALA**

Department of Physics, Annamalai University, Annamalai Nagar-608 002, India

An attempt has been made to obtain the fluorescence quenching spectra of *p*-chloroaniline using nitrobenzene and acetonitrile, as quenchers in 1,4-dioxane. The concentration of fluorescer solution was kept constant (0.01 m) in each experiment, by adding fixed aliquot of stock solutions prepared in the solvent. Quenchers (nitrobenzene and acetonitrile) in the respective solvent was added to the above solution in small volumes (0.1–0.5 mL) and the fluorescent intensities were measured. The Stern-Volmer constants for all quenching processes were plotted. Regression analysis for Stern-Volmer plot was carried out. Regression coefficient and the Stern-Volmer constant were calculated. Stoke's shift, ionization potential, electron affinity and the solvent parameter were also calculated.

Key Words: Fluorescence quenching, Nitrobenzene, Acetonitrile, *p*-Chloroaniline, Stern-Volmer plot, Stoke's shift, Ionization potential, Electron affinity, Solvent parameter.

INTRODUCTION

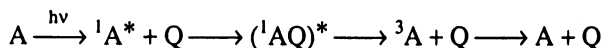
Any reduction in the intensity of fluorescence is called fluorescence quenching. Quenching can also be caused by non-radiation loss of energy from the excited molecules. Quenching processes may take place either in the ground state or in the excited state. The quenching process taking place in the ground state is called static quenching, while the process taking place in the excited state is called dynamic quenching. In solutions, the major energy deactivation process occurs by collisional energy transfer through excited state complex. Research in this area has been stimulated by Mulliken's theory of charge transfer interaction¹. Although some exciplexes do show their characteristic emission bands usually at longer wavelengths than the fluorophore fluorescence, if not so always, since direct observation of non-fluorescent exciplex is not possible, information about their formation can only be inferred^{2,3}. There are convincing evidences for the important role of charge and electron transfer processes in the formation and

† Centralized Instrumentation and Service Laboratory (CISL), Annamalai University, Annamalainagar-608 002, India.

‡Mahendra Engineering College, Mahendrapuri, Namakkal (Dt)-637 503, India.

**Arcot Sri Mahalakshmi Women's College, Villapakkam, Arcot (TK), Vellore 632 521, India.

decay of many exciplex species. When the rate of formation of excited state collisional quenching is extremely large, it can approach the diffusion limiting value, within the frame work of diffusive model of dynamics, there have been many approaches to the problem of quenching, the most familiar being that of Smoluchowski⁴⁻⁷. Molecules with heavy atoms act as quenchers by exiplex mechanism. Quantum considerations show that they quench the fluorescence by the dissociation of exciplexes *via* a triplet state.



Fluorescence quenching of some aromatic amines by *p*-chloranil in benzene and methanol was studied earlier⁸.

EXPERIMENTAL

AR grade samples (nitrobenzene and acetonitrile) were distilled and used. Boiling points are 210°C/760 mm Hg and 81–82°C/760 mm Hg respectively. The aromatic amine (*p*-chloroaniline) and solvent 1,4-dioxane were purified by standard methods. The fluorescence spectra of fluoreshpore were measured with JASCO model FP 550 spectrofluorometer, operating with 150 W xenon lamp as light source. The absorption spectra of donor (amine) were measured using a JASCO-Uvidec-650 spectrophotometer.

RESULTS AND DISCUSSION

The fluorescence quenching spectrum of *p*-chloroaniline in 1,4-dioxane without the quenchers (nitrobenzene and acetonitrile) and with various concentrations of the quenchers (nitrobenzene and acetonitrile) have been shown in Figs. 1 and 2.

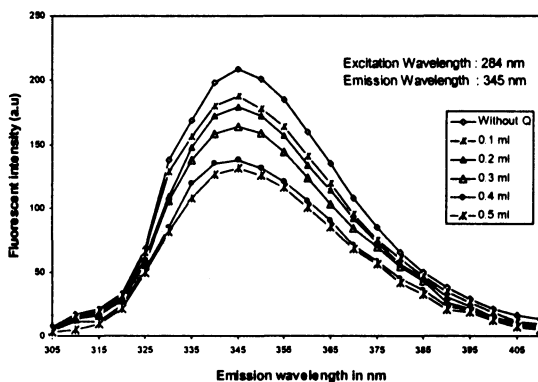


Fig. 1. Fluorescence quenching spectrum of *p*-chloroaniline in 1,4-dioxane with the quencher nitrobenzene

$[I_0/I]$ values for different concentrations of the quenchers (nitrobenzene and acetonitrile) were calculated (Table-1). The quenching ratios $[I_0/I]$ were plotted against quencher concentration $[Q]$ and the plots are shown in Fig. 3.

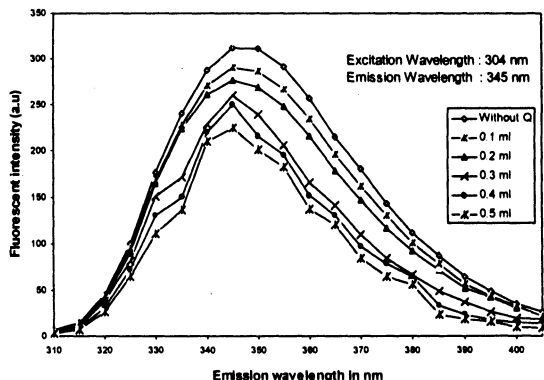
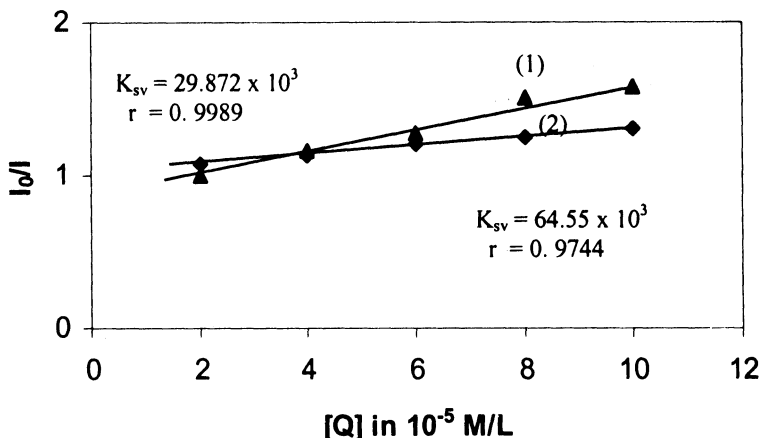


Fig. 2. Fluorescence quenching spectrum of *p*-chloroaniline in 1,4-dioxane with the quencher acetonitrile



1. *p*-chloroaniline-nitrobenzene-1,4-dioxane, 2. *p*-chloroaniline-acetonitrile-1,4-dioxane

Fig. 3. Fluorescent intensity ratio *p*-chloroaniline with nitrobenzene and acetonitrile at different concentrations in 1,4-dioxane

TABLE-I
FLUORESCENT INTENSITY RATIOS OF *p*-CHLOROANILINE AT DIFFERENT CONCENTRATIONS IN 1,4-DIOXANE

Solvent	[Q] in 10 ⁻⁵ M/L	[I ₀ /I]	
		Nitrobenzene	Acetonitrile
1,4-Dioxane	2	1.11	1.07
	4	1.16	1.13
	6	1.27	1.20
	8	1.51	1.24
	10	1.58	1.31

Regression analysis for Stern-Volmer plot has been carried out and the values of regression coefficient (r) and the slope are given in the corresponding figures. The slope of the Stern-Volmer plot gives the Stern-Volmer constant (K_{sv}).

The Stern-Volmer plots for the quenching processes are linear and the regression analyses of all the curves are in good correlation. The linearity of Stern-Volmer plot shows:

(a) Only one quenching mechanism is operative and (b) Quenching is bimolecular.

Absorption spectrum of *p*-chloroaniline in the solvent 1,4-dioxane is not affected by the addition of quenchers in the concentration range used in fluorescence quenching experiment. This reveals that there is no complex formation or association of *p*-chloroaniline with the quencher in the ground state and the quenching occurs only due to the interaction of excited *p*-chloroaniline and the quenchers, hence the quenching is not static but dynamic in nature.

Stoke's shift, ionization potential, electron affinity and the solvent parameter are calculated and presented in Table-2. It could be noted that among the two quenchers, acetonitrile is better quencher for *p*-chloroaniline as compared to nitrobenzene.

TABLE-2
ENERGY, IONIZATION POTENTIAL, ELECTRON AFFINITY, STOKE'S SHIFT AND SOLVENT PARAMETER VALUES OF THE COMPLEXES IN 1,4-DIOXANE

Solvent	Fluorophore	Quenchers	λ_{CT} (eV)	HV _{CT} (eV)	I _D (eV)	E _A (eV)	λ_{abs} (nm)	λ_{flu} (nm)	Stoke's shift ($\Delta\nu$) (cm ⁻¹)	Solvent parameters (kcal/ mol) (z)
1,4-Dioxane	<i>p</i> -Chloroaniline	Nitrobenzene	608	2.0434	7.8043	2.1154	284	345	6225	47.0230
		Acetonitrile	612	2.0300	7.7875	2.1297	304	345	6909	46.7157

Conclusion

Fluorescence quenching studies of *p*-chloroaniline by nitrobenzene and acetonitrile in 1,4-dioxane have been successfully carried out. The Stern-Volmer constants for the quenching processes have been determined. The Stern-Volmer plots for the quenching processes are linear and the regression analysis of all the curves gives a very good correlation. It is concluded that among the two quenchers, acetonitrile is one of the best quenchers while nitrobenzene is one of the poor quenchers for *p*-chloroaniline.

REFERENCES

1. R.S. Mulliken, *J. Am. Chem. Soc.*, **72**, 600 (1950); **74**, 811 (1952).
2. A.E.W. Knight and B.K. Selinger, *Chem. Phys. Lett.*, **10**, 43 (1971).
3. R.J. McDonald and B.K. Selinger, *Aust. J. Chem.*, **24**, 1797 (1971).
4. M. Smoluchowski, *J. Chem. Phys.*, **92**, 129 (1917).
5. R.M. Noyes, *J. Am. Chem. Soc.*, **79**, 551 (1957).
6. A. Weller, *J. Chem. Phys.*, **13**, 335 (1957).
7. U.M. Gosel, *Prog. React. Kinet.*, **13**, 63 (1984).
8. S. Bakkialakshmi, B. Shanthi and S. Deepa, *Asian J. Chem.*, **15**, 1367 (2003).