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Fluorescence Quenching of Some Aromatic Amines by *p*-chloranil in Benzene and Methanol

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An attempt has been made to obtain the fluorescence quenching spectra of some aromatic amines (aniline, *p*-toluidine, *p*-anisidine and *p*-chloraniline) using *p*-chloranil as a quencher in two different solvents. The stern-Volmer constants for all the quenching processes have been plotted. Stoke's shift, ionization potential, electron affinity and the solvent parameter (Z) have been calculated.

Key Words: Fluorescence quenching, *p*-chloranil, aromatic amines, Stern-Volmer plot, Stoke's shift, Ionization potential, Electron affinity, Solvent parameter.

INTRODUCTION

The tendency to attract fluorescer and quencher is greater when they collide and their attraction depends on their polar and polarizability properties. Some degree of charge transfer is involved in their tendency to attract each other. This attraction leads to the formation of complexes between the excited fluorescer and the quencher and these complexes, formed in the excited state, are known as exciplexes[1–3].

Quantum considerations show that molecules with heavy atoms quench fluorescence dissociating exciplexes *via* the triplet state.

$$A \xrightarrow{h\nu} {}'A^* + Q \quad ({}'AQ)^* \quad {}^3A + Q \quad A + Q$$

The quantum of charge transfer is large where heavy atoms are absent and exciplexes degrade by light emission. Their lifetime is longer, and therefore dissociation generally occurs through ion-pair complexes.

$${}'A \xrightarrow{h\nu} {}'A^* + Q \quad {}'(AQ)^* \quad {}'(A^{\pm} \ldots . Q^{\pm}) \quad {}'A + Q$$

It is the solvent which plays a vital role in the formation of ion-pair complexes.

Taniguchi *et al.*[4] reported that the method of the nsec laser photolysis and conductivity measurement appears quite suitable for the detection of ion radicals of even small concentrations in a solvent which is not very polar.

Mataga[5] suggests that electron transfer reaction occurs not only in the ground state but also in its various excited states when the ion radicals have low energy excited levels.

There is a recent report of fluorescence studies of the charge transfer complex of some substituted benzenes and naphthalene with chloranil by Nupur *et al.*[6] Ayad *et*

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al.[7] have studied fluorescence quenching of 7-dimethyl amino-4-methyl coumarin (DMC) and pyrene using *p*-chloranil and picric acid as acceptors.

We intend to show that *p*-chloranil is an effective quencher of amines using benzene and methanol as solvents.

EXPERIMENTAL

AR grade sample (*p*-chloranil) was recrystallised from glacial acetic acid. Its purity was checked by determining its melting point (290°C). All the aromatic amines (aniline, *p*-toluidine, *p*-anisidine and *p*-chloroaniline) and the solvents (benzene and methanol) were purified by standard methods. The solutions were not degassed. The fluorescence spectra of amines (fluorescers) were measured by the spectrofluorometer with JASCO model FP-550. It operates with a 150 W xenon lamp as the light source. The absorption spectra of the amines were measured by a spectrophotometer JASCO-UVIDEC-650.

RESULTS AND DISCUSSION

The fluorescence-quenching spectrum of aniline in benzene without *p*-chloranil and at different levels of concentration of the quencher has been shown in Fig 1. Light at the wavelength of 295 nm was trained to excite the fluorescers in the solutions. But the wavelength at which the fluorescers in the various solutions were excited differ and they have been given in Table-2 as λ_{abs}. The fluorescence quenching spectra of the other aromatic amines in the solvents benzene and methanol are similar; the exception is the position of the λ_{flu} of the complex.

$\left(\frac{I_n}{I}-1\right)$ values for different concentrations of the quencher (*p*-chloranil) in benzene and methanol have been given in Table-1. The quenching ratios $\left(\frac{I_n}{I}-1\right)$ were plotted against quencher concentration (Q) in benzene and methanol and they have been shown in Figs. 2 and 3 respectively.

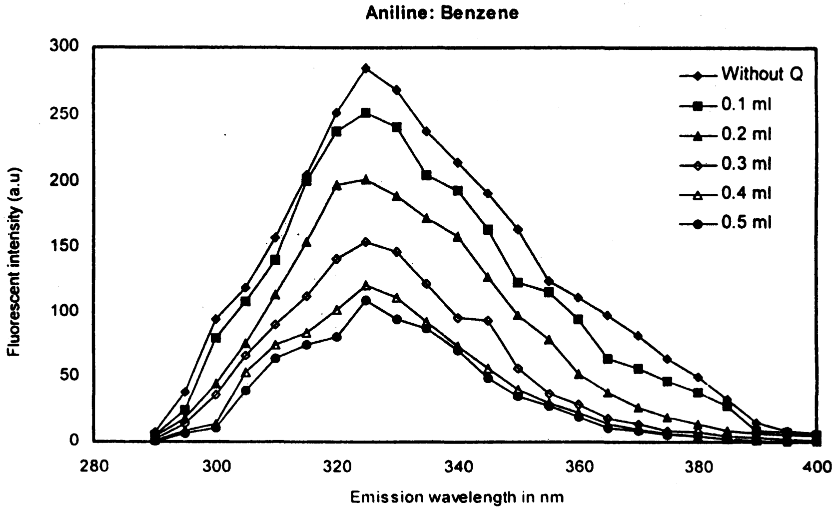

Fig. 1. Fluorescence quenching spectrum of aniline in benzene

TABLE-1

FLUORESCENT INTENSITY RATIOS $\left(\frac{I_0}{I} - 1\right)$ OF AMINES AT DIFFERENT QUENCHER CONCENTRATIONS IN BENZENE AND METHANOL

Solvents	[Q] in 10^{-5} M/L	Aniline	*p*-Toluidine	*p*-Anisidine	*p*-Chloroaniline
Benzene	2	0.13	0.10	0.07	0.25
	4	0.41	0.32	0.25	0.58
	6	0.85	0.50	0.56	0.89
	8	1.22	0.78	0.80	1.26
	10	1.59	1.13	1.06	1.70
Methanol	2	0.13	0.17	0.25	0.14
	4	0.39	0.60	0.47	0.30
	6	0.65	1.08	0.77	0.56
	8	0.85	1.60	0.92	0.81
	10	1.16	2.18	1.33	1.04

TABLE-2

IONIZATION POTENTIAL, ELECTRON AFFINITY, STOKE'S SHIFT AND SOLVENT PARAMETER VALUES OF THE COMPLEXES IN BENZENE AND METHANOL

Solvents	Amines	λ_{CT} (nm)	$h\nu_{CT}$ (ev)	I_D (ev)	E_A (ev)	λ_{abs} (nm)	λ_{flu} (nm)	Stoke's shift $\Delta\nu$ (cm^{-1})	Solvent parameter (kcal/mol) (z)
Benzene	Aniline	530	2.333	8.1666	1.818	295	325	3129	53.943
	p-Toluidine	575	2.150	7.938	2.005	305	336	3025	49.721
	p-Anisidine	590	2.096	7.870	2.061	289	335	4752	48.457
	p-Chloroaniline	528	2.342	8.177	1.809	301	340	3811	54.147
Methanol	Aniline	537	2.302	8.128	1.849	299	335	3594	53.240
	p-Toluidine	587	2.106	7.883	2.050	300	347	4515	48.240
	p-Anisidine	595	2.078	7.848	2.079	300	361	5633	48.050
	p-Chloroaniline	532	2.324	8.155	1.827	291	347	5546	48.665

Regression analysis for Stern-Volmer plot (Figs. 2 and 3) has been carried out and the slope of the Stern-Volmer plot gives the Stern-Volmer constant K_{SV}. Ionization potential (I_D), electron affinity (E_A), Stoke's shift ($\Delta\nu$) and solvent

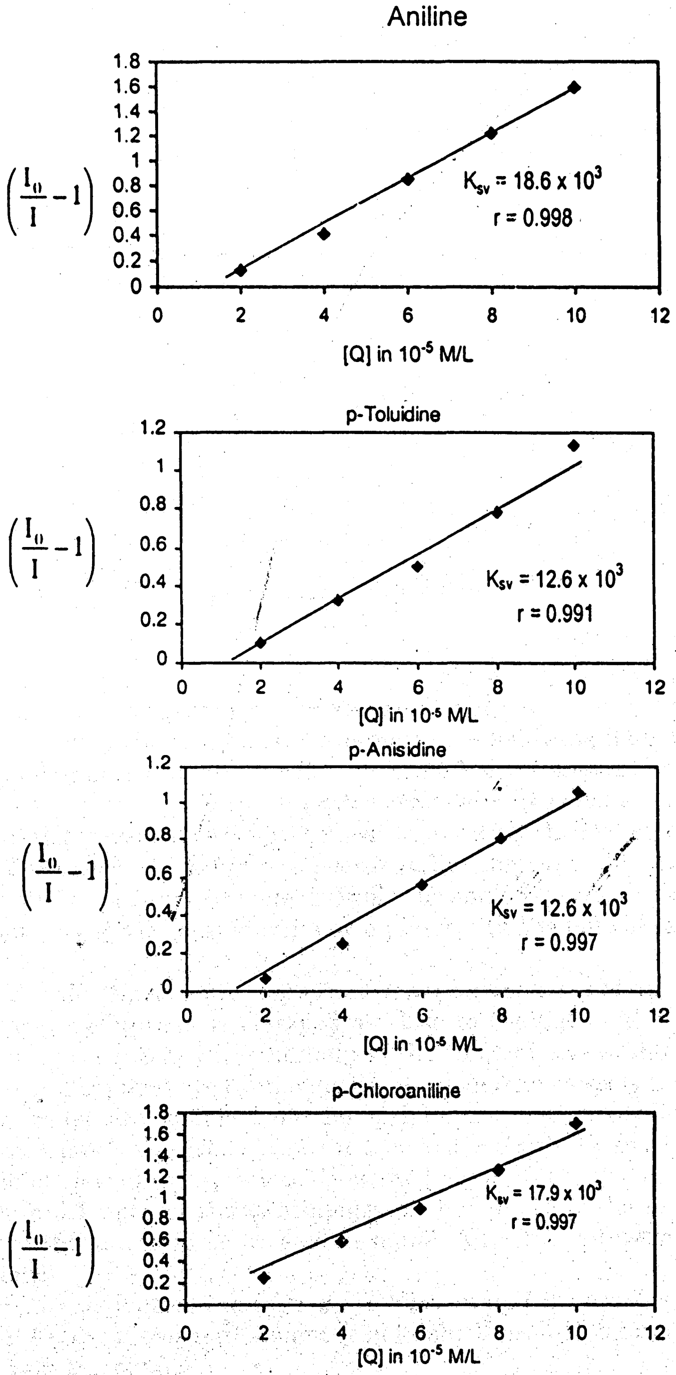

Fig. 2. Stern-Volmer plot of $\left(\frac{I_0}{I}-1\right)$ against Q $\left(\frac{M}{L}\right)$ for the amines in benzene

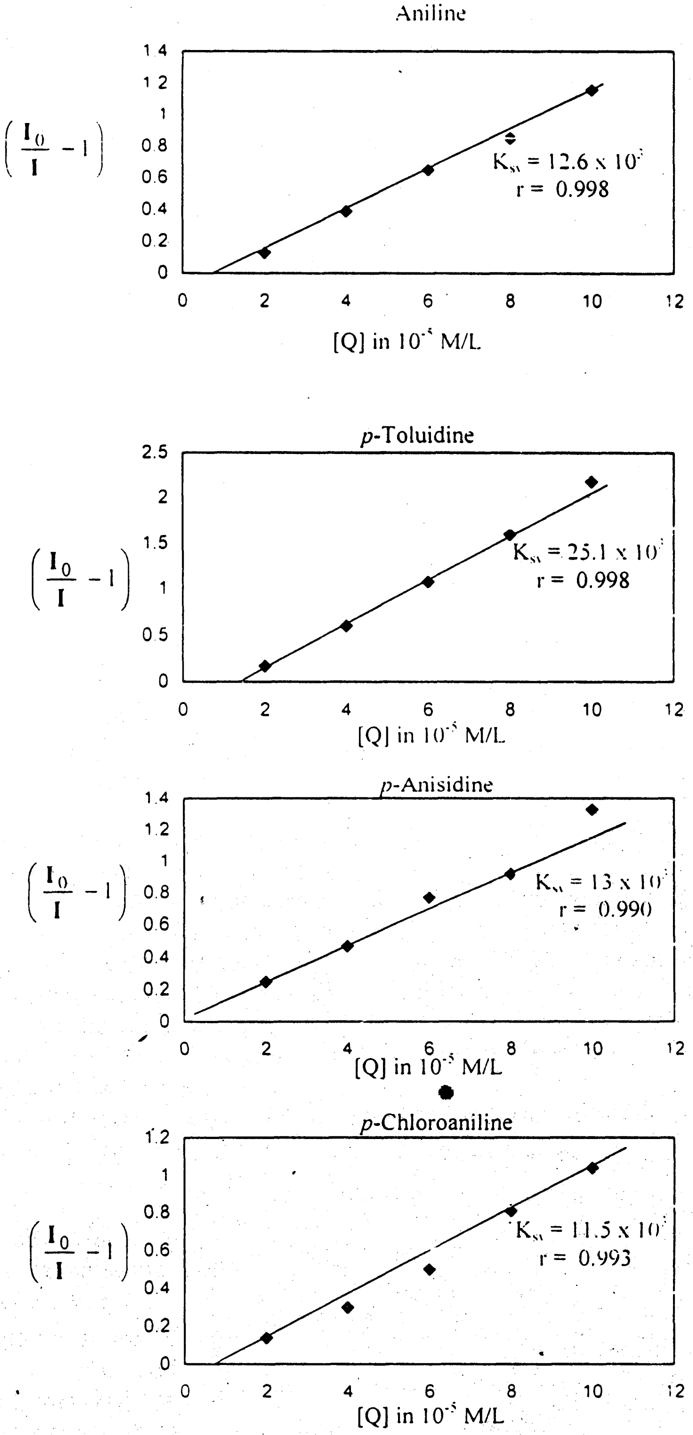

Fig. 3. Stern-Volmer plot of $\left(\frac{I_0}{I}-1\right)$ against $Q\left(\frac{M}{L}\right)$ for the amines in methanol

parameter (Z) have been calculated and the resultant values have been presented in Table-2. The Stern-Volmer constants plotted for all the quenching processes are linear and the regression analysis of all the curves correlates well. The regression coefficient (r) for all the curves is about 0.99. The linearity of the plotted Stern-Volmer constants leads to the conclusion that:

(a) only one quenching mechanism is operative, and

(b) quenching is bimolecular.

It is not possible to record the fluorescence spectrum of *p*-chloranil as *p*-chloranil does not fluoresce. *p*-Chloranil can therefore be used only as a quencher. It could be seen from Fig. 1 that florescent intensity values decrease if the quencher concentration increases. Similar results were obtained for all the other fluorescers in the solvents benzene and methanol.

Experiments at the 10^{-5} level of concentration of the quencher have shown that the addition of chloranil does not modify the absorption spectrum in the ground state. Table-2 reveals that the $h\nu_{CT}$ values are in the order:

p-Chloraniline > Aniline > *p*-Toluidine > *p*-Anisidine

Dwivedi and Banger[8] in their work on aromatic hydrocarbon donors with DDQ with chloroform have observed that the λ_{CT} value decreases with an increase in the ionization potential of the donor and the results of our study are in agreement with theirs. It can be said, based on a scrutiny of Table-2, that the increased ionization potential of the donor and the electron affinity of the acceptor increases the efficiency of the quencher where the mechanism of quenching is charge transfer.

Conclusion

The Stern-Volmer constants for all the quenching processes were determined by studies of fluorescence quenching of aromatic amines by *p*-chloranil using benzene and methanol as solvents. These constants are linear, when plotted, for all the quenching processes and the regression analysis of all the curves leads to the conclusion that *p*-chloranil is one of the best quenchers for aromatic amines.

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