Fluorescence quenching of a few aromatic amines by inorganic anions

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Inorganic anions-induced fluorescence quenching of seven aromatic amines has been studied up to 0.1M concentration. The fluorescence intensities of all the aromatic amines (except aniline) remain unaffected when Cl⁻ and SCN⁻ are used as quenchers, whereas sufficient decrease in the fluorescence intensities is noticed when Br⁻ and I⁻ are used as quenchers. Based on the results obtained in the case of aniline, the fluorescence quenching efficiency of the anions can be ordered as: SCN⁻ < Br⁻ < I⁻. Observed results cannot be explained completely either by spin-orbit coupling interaction or by charge transfer mechanism, although the latter seems to be more appropriate as log $k_q$ cannot be correlated with the spin-orbit coupling constants of the quencher atom when aniline is considered.

In a recent study¹ carried out to find out whether simple aromatic amines can be used as probe molecules for investigating the micellar properties, we have found that the fluorescence quantum yield of 2-aminonaphthalene (2-AN) decreases with the increase in cetyltrimethylammonium bromide (CTAB) concentration¹, whereas the fluorescence quantum yields of aniline (AB), 9-aminophenanthrene (9-AP), 1-aminopyrene (1-APy), 2- and 6-aminochrysene (2-6-AC) and 3-aminofluoranthene (3-AF) increase under similar conditions. On the other hand, the fluorescence quantum yields of all the aromatic amines increase in sodium dodecyl sulphate (SDS) and cetyltrimethylammonium chloride (CTAC) micelles². The fluorescence intensities of the aromatic amines decrease when KBr and KI are added to CTAC and CTAB. This means that Cl⁻ ion is not effective in quenching the fluorescence intensity, but Br⁻ and I⁻ ions do so in the case of the aromatic amines.

It is well established that the fluorescence of the neutral molecules or their monocations is quenched by the inorganic anions³−¹⁷. In order to get any meaningful results about the fluorescence characteristics of these aromatic amines in ionic micelles, the data should be examined carefully since inorganic ions themselves are good fluorescence quenchers. In the present study the quenching rate constants of some aromatic amines by the inorganic ions have been calculated and the results obtained have been examined with a view to finding whether the fluorescence quenching by inorganic ions follows the charge transfer mechanism or heavy atom effect.

Materials and Methods

2-AN was obtained from Riedel de Haen AG Seelz Hannover, crystallized first from ethanol and then sublimed in vacuo. AB was obtained from S.D. Fine Chemicals and was purified by distilling it in vacuo. 9-AP, 1-APy, 3-AF and 6-AC were procured from Aldrich Chemical Company, whereas 2-AC was obtained from ICN Pharmaceuticals. All these compounds were crystallized from 95% ethanol except 9-AP, which was crystallized from benzene. The purity of these compounds was checked on the basis of their m.p., absorption spectral data and getting similar fluorescence spectra when excited at different wavelengths. Triply distilled water was used for preparing the solutions. Analytical grade NaOH, orthophosphoric acid, NaCl, NaBr, NaSCN, NaI and Na₂SO₄ were used as such. pH of 9 ± 0.5 was maintained by adding appropriate amounts of orthophosphoric acid and NaOH solutions because it has been found that this phosphate buffer does not quench the fluorescence intensity of the fluorophore¹⁸.

The absorption spectra were recorded on a 190 UV Shimadzu spectrophotometer, fitted with a 135U chart recorder. The fluorescence intensities were measured using a scanning spectrophotometer, the details of which are available elsewhere¹⁹. The fluorescence intensities of aromatic amines in the presence of different quencher concentrations were measured at the respective fluorescence band maxima. The stock solutions of aromatic amines were prepared in methanol; the final amount of methanol present in the solution was
not more than 2% (v/v), except in the case of 2-AC and 6-AC where it was 20%. The concentration of the fluorophore was kept 2 × 10^{-5} M. pH values of the solutions were measured with a Toshniwal digital pH meter model CL 46.

Fluorescence lifetimes of the compounds were recorded on time correlated, single photon counting nanosecond spectrophotometer, supplied by Applied Photophysics Limited, London (model SP-70/80). The electronic processing equipment and the multichannel analyser were supplied by Ortec and Norland respectively. The software for deconvolution, supplied by APB, was used for calculating the fluorescence lifetimes. In all the cases, a single exponential decay was observed. The data have been compiled in Table 1.

Cyclic voltammetric studies were made with a PAR model 370 polarographic analyser utilising the thred electrode configuration of a Pt(BAS) working electrode, a platinum mesh counter electrode and an Ag/AgCl electrode as the reference electrode. Tetrabutylammonium perchlorate (TBAP) was used as the supporting electrode. The solvents used were acetonitrile, water, tetrahydrofuran and dichloromethane. An RE 0074 model XY recorder was used to record current-voltage-output. Half-wave potentials were measured as the average of cathodic and anodic peak potentials.

Results and Discussion

Absorption spectra of aromatic amines (2 × 10^{-5} M) were recorded in the presence of various inorganic anions at concentrations varying from 0 to 0.1 M. In all the experiments, the ionic strength of the solution was maintained at 0.1 M with the addition of Na_{2}SO_{4}, as Na^{+} and SO_{4}^{2-} do not quench the fluorescence intensities of these molecules^{18,20}. No change was observed in the band maxima or in the spectral profile which indicated that no complex was formed between the aromatic amine and the inorganic anion in the ground state.

Fluorescence quenching of the aromatic amines (1A*) by Br^- and I^- occurred without any change in the fluorescence spectrum; Cl^- ions did not quench the fluorescence intensity of any of the aromatic amines even up to 0.5 M (NaCl). SCN^- decreased the fluorescence intensity of only AB in this range of concentration. There was no effect of cation on the fluorescence quenching, e.g., use of potassium salts resulted in the fluorescence quenching to the same extent as that in the presence of sodium salts. No new fluorescence band was observed at the expense of fluorescence intensity of the aromatic amine. This indicates that no excimer or exciplex is formed during the quenching experiments.

In each case, a Stern-Volmer plot of I/I_0 versus X^- gave a straight line, where I and I_0 denote the relative fluorescence intensities and \( \tau \) and \( \tau_0 \) are the fluorescence lifetimes in the presence and absence of X^- respectively.

\[
\frac{I}{I_0} = 1 + k_q \tau_0 [X^-] = 1 + K_{sv} [X^-] \quad \ldots (1)
\]

To establish whether the fluorescence quenching is of static or of dynamic nature, lifetimes of

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \tau_0 ) (ns)</th>
<th>( E^* ) (eV)</th>
<th>( \log k_q )</th>
<th>( \Delta G'_{RW} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AB</td>
<td>3.2^a</td>
<td>4.10</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2-AN</td>
<td>21.65</td>
<td>3.72</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9-AP</td>
<td>13.11</td>
<td>3.28</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1-APy</td>
<td>6.95</td>
<td>3.12</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2-AC</td>
<td>10.57^b</td>
<td>3.06</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6-AC</td>
<td>10.42^b</td>
<td>3.06</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3-AF</td>
<td>12.14</td>
<td>2.80</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>E(X^-/X)</td>
<td></td>
<td></td>
<td>1.5</td>
<td>5.59</td>
</tr>
<tr>
<td>E(CCTS)</td>
<td></td>
<td></td>
<td>5.59</td>
<td>6.24</td>
</tr>
</tbody>
</table>

a = methanol
b = 20% methanol (v/v)
2-AN and 2-AC were measured in presence of different concentrations of $I^-$. Stern-Volmer plots of $\tau/\tau_0$ versus $[I^-]$ gave a straight line in each case. The values of $k_q$ obtained are $4.25 \times 10^8$ and $2.4 \times 10^8$ M$^{-1}$ s$^{-1}$ for 2-AN and 2-AC respectively. These are in agreement with those obtained from steady-state measurements. Thus, it can be concluded that fluorescence quenching is occurring by a dynamic mechanism and similar behaviour can be assumed for other fluorophores and quencher combinations as all the fluorophores are of similar nature. The values of $k_q$ for X$^-$ can be calculated from the Stern-Volmer constants $K_{sv}/\tau_0$. The values of $k_qE_{1/2}$ (the electronic 0-0 transition energy) of the aromatic amines, $E(X^-/X)$ (the oxidation potential of the donor anion $X^-$), $E(CTTS)$ (the transition energy for charge transfer to solvent of $X^-$) are compiled in Table 1.

It is clear from the data in Table 1 that the values of $k_q$ for Br$^-$ and I$^-$ ions decrease with increase in oxidation potential and also with the decrease in first excited singlet state energy of the aromatic amines. Value of $k_q$ for quenching the fluorescence intensity of AB by SCN$^-$ is less than that for Br$^-$, even though oxidation potential of SCN$^-$ is less than that of Br$^-$. A similar behaviour is also expected for other amines when SCN$^-$ is used as the quencher because decrease in the fluorescence intensity has not been observed for other aromatic amines when SCN$^-$ is used as quencher up to 0.1 M concentration.

The values of $k_q$ observed from the above results can be explained with the help of electron transfer mechanism as shown below:

\[
\begin{align*}
1A^* + 1X^- & \rightarrow 1A^- + 1X^* \quad k_1 \quad \text{diffusion} \quad k_2 \\
1A^- + 1X^* & \rightarrow 2A^- + 2X^* \quad k_2 \quad \text{degradation} \quad k_3 \\
1A^- + 1X^- & \rightarrow 2A^- + 2X^- \quad k_3 \\
\end{align*}
\]

where ($1A^*$ .... $1X^-$) is a collision complex, formed by diffusion of excited fluorophore and quencher molecules and ($2A^- + 2X^*$) is a radical ion pair obtained by the transfer of electron from quencher to aromatic amine. Equation (3) can be derived using the steady state approximation.

\[
k_q = \frac{k_1}{1 + \frac{k_2}{k_1} \left( \frac{k_3}{k_2} + 1 \right)} \quad \cdots (3)
\]

The free energy change $\Delta G$ (in eV) involved in the electron transfer process can be calculated from Eqs (4) and (5).

\[
\Delta G_{RW} = E(X^-/X) - E_{1/2} - E_{1/2} - 4.7 \quad \cdots (5)
\]

\[
\Delta G_{TH} = E(CTTS) - E_{1/2} - E_{1/2} - 4.7 \quad \cdots (5)
\]

given by Rehm and Weller$^{21}$ and by Treinin and Hayon$^{22}$ respectively. $E_{1/2}$ for the aromatic amines could not be determined because the reduction potentials for these molecules are less than $-2.5\text{V}$, because the solvents like tetrahydrofuran start getting reduced below this voltage. This seems to be in the right direction because the reduction potentials of naphthalene, 1-methoxynaphthalene, phenanthrene and pyrene are 2.25, 2.32, 2.22 and 2.45V respectively$^{13}$. Since amino group is a better electron donor, the reduction potentials of the aromatic amines will be greater than those of their parent hydrocarbons. Since the values of $E_{1/2}$ for these amines are not known, the quantities $\Delta G_{RW}$ and $\Delta G_{TH}$ have been defined as,

\[
\Delta G'_{RW} = \Delta G_{RW} + E_{1/2} = E(X^-/X) - E_{1/2} \quad \cdots (6)
\]

\[
\Delta G'_{TH} = \Delta G_{TH} + E_{1/2} = E(CTTS) - E_{1/2} - 4.7 \quad \cdots (7)
\]

The values of $\Delta G'_{RW}$ along with log$k_q$ values for different quencher-fluorophore combinations are compiled in Table 1. $\Delta G'_{TH}$ can also be calculated similarly.

Qualitatively, it is clear from the results that the electron transfer mechanism is operative in the fluorescence quenching, i.e., if we go from CI$^-$ to I$^-$, $k_q$ increases. Quantitatively, the results seem to be more complex and cannot be explained by simple electron transfer mechanism. If the electron transfer is the rate determining step, $\Delta G$ (and so $\Delta G'$) will be acting as thermodynamic barrier for electron transfer. If $k_3$ is assumed to be much faster than $k_2$, Eq. (3) will reduce to,

\[
k_q = \frac{k_1}{k_2} \quad \cdots (8)
\]

and will become Eq. (10) after combining with Eq. (9), where $A_0$ is the frequency factor.

\[
k_2 = A_0 e^{-\Delta G/RT} \quad \cdots (9)
\]

\[
k_q = \frac{k_1}{k_2} A_0 e^{-\Delta G/RT} \quad \cdots (10)
\]

Assuming that the $E_{1/2}$ values for the aromatic amines are equal to those of their parent hydrocarbons, $\Delta G$ values observed for 2-AN, 9-AP and 1-APy with I$^-$ as quencher are $-0.07$, $+0.34$ and $0.73$ eV respectively. These values of $\Delta G$ indicate that $k_q$ for the above mentioned aromatic amines should be approximately $10^{11}$, $10^4$ and $10^{-2}$ M$^{-1}$ s$^{-1}$ respectively, whereas the values of $k_q$ observed in our case are much larger for positive $\Delta G$ (or $\Delta G'$). Thus, the electron transfer me-
chanism is unable to explain quantitatively the quenching kinetics observed in the present case, although qualitatively it seems to explain the results.

The other possible mechanism which can explain the fluorescence quenching rate constant is based on the heavy atom effect\(^6\), which depends upon the spin-orbit coupling constant of the quencher, i.e., some power of the nuclear charge of the perturbing atom\(^23\). Although data are not extensive (AB and three quenchers only), there is no correlation between log \(k_q\) and spin-orbit coupling constant of the quencher. It can thus be concluded that the results cannot be explained simply on the basis of heavy atom effect. The different behaviour\(^13\) of SCN\(^-\) may be due to the resonance structures \(S = C = N - \rightarrow \bar{S} = C \equiv N\). The ion SCN\(^-\) is known to be ambidentate.

In the absence of a clear cut mechanism for fluorescence quenching in these systems, it may be proposed that a quantum mechanical coupling of higher lying electron transfer states, which can induce radiationless transitions from first excited singlet state of aromatic amines to other electronic states, is predominant in these cases also as earlier proposed and confirmed by Watkins\(^8\)–\(^10\) and Shizuka et al.\(^12\)–\(^14\) in some other cases. As stated by them\(^9\)–\(^11\), this mechanism involves the coming together of fluorophore and the quencher to form a loose associate, whose binding energy is much less than \(k_b T\) and the loose complex formed is non-fluorescent. In the absence of any other evidence, it may be proposed that this loose complex may produce the molecules in the triplet state by intersystem crossing or decay to ground state by internal conversion. The reaction scheme can be represented by Scheme 1,

\[
\begin{align*}
\text{A}^* + \text{X}^- \xrightarrow{k_1} & \text{A}^* \cdots \cdots \cdot \text{X}^- \\
\text{A}^* \cdots \cdots \cdot \text{X}^- \xrightarrow{k_b} & \text{A}^* - \text{X}^- \\
\text{A}^* \cdots \cdots \cdot \text{X}^- \xrightarrow{k_i} & \text{A}^* - \text{X}^- \\
\end{align*}
\]

Scheme 1

where \(k_b\) and \(k_i\) are the rate constants for the internal conversion and intersystem crossing respectively. From our results it is very difficult to predict whether \(1\text{A}^* ... \text{X}^-\) will decay to \(\text{A}...\text{X}^-\) or \(3\text{A}^* + \text{X}^-,\) that is whether \(k_b > k_i\) or \(k_i > k_b\) although the existence of latter is more likely.

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References