Study of Solvent & pH Dependences on Absorption & Fluorescence Spectra of 2-Aminochrysene

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The effect of solvent on the absorption and fluorescence spectra of 2-aminochrysene indicates that it acts as a proton donor to hydrogen accepting solvents and as a proton acceptor to hydrogen donor solvents in the $S_0$ state, whereas proton donor to all solvents in the $S_1$ state. $pK_a(S_0)$ and $pK_a^*(S_1)$ values of various prototropic equilibria in aqueous solutions have been evaluated. Proton-induced fluorescence quenching of 2-aminochrysene in acid solutions is discussed.

The solvent and $pH$ effects on the spectral properties of carbocyclic and heterocyclic amines have been well studied. In general (except when amino group is $\pi$ or $\gamma$ to the tertiary nitrogen atom) it has been found that: (i) depending upon the interaction between the lone pair of nitrogen atom of the amino group and the parent aromatic hydrocarbon, the spectrum of the parent molecule becomes broad and gets red-shifted; (ii) the spectrum of the monocation ($-\text{NH}_2^+$) resembles that of the parent hydrocarbon; (iii) the $-\text{NH}_3^+$ and $-\text{NH}_2$ groups become stronger acids upon excitation; (iv) some of the imino anions are non-fluorescent; and (v) there is no correspondence between the decrease of the fluorescence intensity of the neutral amine and the appearance of its cation at moderate $pH$. The latter has been attributed to the fluorescence-induced quenching of the neutral amine by $H^+$ before $-\text{NH}_3^+$ ion is formed.

The present study was carried out to determine: (i) $pK_a(S_0)$ values, using the Förster cycle method and fluorimetric titration technique for the prototropic equilibria (1-3); and

\begin{align*}
H\text{ChNH}_3^+ & \rightleftharpoons \text{ChNH}_2^+ + H^+ \quad \text{... (1)} \\
\text{ChNH}_2^+ & \rightleftharpoons \text{ChNH}_2 + H^+ \quad \text{... (2)} \\
\text{ChNH}_2 & \rightleftharpoons \text{ChNH}^- + H^+ \quad \text{... (3)}
\end{align*}

(ii) the proton-induced fluorescence quenching rate constant. In addition to this, the effect of solvents on the absorption and fluorescence spectra has been studied.

Materials and Methods

2-Aminochrysene ($\text{ChNH}_2$; K & K Inc) was purified by repeated recrystallisation from methanol. Spectrograde MeOH, AR grade $\text{H}_2\text{SO}_4$ and KOH (all BDH products) were used as such. Acetonitrile (AR, Merck), cyclohexane, dioxane and ethanol were purified by the methods described elsewhere. Triply distilled water was used for the preparation of aqueous solutions. A modified Hammett's acidity scale for solutions using $\text{H}_2\text{SO}_4$-$\text{H}_2\text{O}$ mixtures and Yagil's basicity scale for solutions using KOH-$\text{H}_2\text{O}$ mixtures were used below $pH$ 1 and above $pH$ 13, respectively.

Absorption spectra were recorded on a Shimadzu 190 spectrophotometer, attached to a U135 recorder, and fluorescence measurements were made on a locally fabricated scanning spectrofluorimeter. Excitation and emission monochromators were calibrated with a low pressure mercury lamp from time to time. $pH$ in the range 1-13 were measured on a Toshniwal pH meter, model CL-44A.

Due to poor solubility of $\text{ChNH}_2$ in water, a $10^{-3}M$ stock solution was prepared in 70% (v/v) methanol-$\text{H}_2\text{O}$ mixture. This stock solution (0.14ml) was added to $H_0/pH/H_-$ solution (10ml) just before carrying out the absorptiometric and fluorimetric titrations. Isosbestic point of the respective equilibrium was used as the excitation wavelength. The quantum yields in different solvents were calculated using quinine sulphate in 0.1 $M$ $\text{H}_2\text{SO}_4$ as a standard.

Results and Discussion

Effect of solvents

Table 1 gives the absorption and fluorescence maxima of $\text{ChNH}_2$ in different solvents, along with their intensities. Due to poor solubility of $\text{ChNH}_2$ in water the absorption and fluorescence spectra of saturated solutions of $\text{ChNH}_2$ were recorded. As expected and similar to other aromatic amines, the spectral bands are very broad and are red-shifted as compared to those of the parent molecule in any one particular solvent. As compared to cyclohexane, all the $\lambda_{max}$ in different solvents are red-shifted with increase in solvent polarity but as compared to ether or dioxane, the $\lambda_{max}$ are blue-shifted in alcohols and
Table 1—Absorption and Fluorescence Maxima (nm), Molar Absorptivity (dm$^3$ mol$^{-1}$ cm$^{-1}$) and Fluorescence Quantum Yields of 2-Aminochrysene in Various Solvents and Its Various Prototropic Forms at 298 K

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\lambda_{max}$(nm)</th>
<th>$\varepsilon_{max}$(log)</th>
<th>$\phi_{flu}$(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexane</td>
<td>217</td>
<td>228</td>
<td>243</td>
</tr>
<tr>
<td></td>
<td>(4.40)</td>
<td>(4.51)</td>
<td>(4.33)</td>
</tr>
<tr>
<td>1,4-Dioxane</td>
<td>220</td>
<td>230</td>
<td>242</td>
</tr>
<tr>
<td></td>
<td>(4.38)</td>
<td>(4.44)</td>
<td>(4.32)</td>
</tr>
<tr>
<td>Ether</td>
<td>218.2</td>
<td>229.2</td>
<td>242</td>
</tr>
<tr>
<td></td>
<td>(4.53)</td>
<td>(4.60)</td>
<td>(4.48)</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>218</td>
<td>228.6</td>
<td>242</td>
</tr>
<tr>
<td></td>
<td>(4.49)</td>
<td>(4.55)</td>
<td>(4.42)</td>
</tr>
<tr>
<td>Methanol</td>
<td>218</td>
<td>228.6</td>
<td>242</td>
</tr>
<tr>
<td></td>
<td>(4.49)</td>
<td>(4.52)</td>
<td>(4.38)</td>
</tr>
<tr>
<td>Ethanol</td>
<td>218</td>
<td>227.6</td>
<td>242.5</td>
</tr>
<tr>
<td></td>
<td>(4.49)</td>
<td>(4.49)</td>
<td>(4.38)</td>
</tr>
<tr>
<td>Water (pH 6)</td>
<td>217</td>
<td>225</td>
<td>270</td>
</tr>
<tr>
<td></td>
<td>(4.39)</td>
<td>(4.58)</td>
<td>(5.05)</td>
</tr>
<tr>
<td>$\text{H}_2\text{SO}_4$ ($H_0 = -6$)</td>
<td>215</td>
<td>257.6</td>
<td>267</td>
</tr>
<tr>
<td></td>
<td>(4.58)</td>
<td>(4.86)</td>
<td>(5.05)</td>
</tr>
<tr>
<td>$\text{H}_2\text{SO}_4$ ($H_0 = -10$)</td>
<td>220</td>
<td>267.5</td>
<td>267</td>
</tr>
<tr>
<td></td>
<td>(4.41)</td>
<td>(4.89)</td>
<td>(4.20)</td>
</tr>
<tr>
<td>KOH ($H_0 = -17$)</td>
<td>229</td>
<td>287.5</td>
<td>356</td>
</tr>
<tr>
<td></td>
<td>(4.17)</td>
<td>(4.01)</td>
<td>(3.50)</td>
</tr>
</tbody>
</table>

The absorption and fluorescence spectra of ChNH$_2$ have been studied in the range of $H_0 = -10$ to $H_0 = -17$. The absorption and fluorescence spectra of different prototropic species of ChNH$_2$ are depicted in Figs 1 and 2 and the data are recorded in Table 1. Between $pH$ 13 and 2, the long wavelength absorption band is not well-defined (as mentioned earlier, due to poor solubility in water) but the other two bands appear at 272 and 215 nm. Between $pH$ 3 and $H_0 = -7$, all the bands water, the blue-shift being maximal in water, whereas a continuous red-shift is noticed in the fluorescence maxima under the above environments.

Besides the dispersive interactions between the solute and the solvent molecules, the amino group in ChNH$_2$ acts as a proton donor in ether, dioxane and acetonitrile. It acts as a proton acceptor in alcohols and water in the ground state but is a better proton donor in the $S_1$ state. These results further indicate that in the $S_1$ state the availability of the lone pair is markedly reduced by a greater charge transfer interaction of the lone pair of the amino group with the ring, consistent with the earlier reports for amino compounds$^{17-22}$. The continuous decrease in the fluorescence quantum yield (Table 1) of ChNH$_2$ with the increase in the polarity or hydrogen bonding capacity of solvents suggests that stronger interactions with the solvents lead to increase in the rate of radiationless processes.

Effect of pH

The absorption and fluorescence spectra of ChNH$_2$ have been studied in the range of $H_0 = -10$ to $H_0 = -17$. The absorption and fluorescence spectra of different prototropic species of ChNH$_2$ are depicted in Figs 1 and 2 and the data are recorded in Table 1. Between $pH$ 13 and 2, the long wavelength absorption band is not well-defined (as mentioned earlier, due to poor solubility in water) but the other two bands appear at 272 and 215 nm. Between $pH$ 3 and $H_0 = -7$, all the bands...
are blue-shifted, structured and resemble those of the parent chrysene molecule and thus can be assigned to the monocation (ChNH$_3^+$) formed by the protonation of the amino group. At $H_0$ more negative than −7, all the bands are red-shifted and remain structured except the 265 nm band. This could possibly be due to the dication formed by the protonation of the ring carbon atom, as observed in case of chrysene. The $pK_a$ value for the dication-monocation equilibrium could not be determined because the change is not maximum even at the highest acidity studied, but $pK_a(1)$ is expected to be less than −8. This value is much less than that for the protonation of chrysene ($pK_a = −1.6$) and could be due to the positive charge already existing on the molecule which makes the ring less basic. The $pK_a(2)$ for the cation-neutral molecule is found to be 2.4. In basic solutions at $H_0 = 14$, all the bands are red-shifted and this could be attributed to the formation of monoanion, by the deprotonation of amino group. The $pK_a(3)$ for the neutral-anion is found to be 16.2.

From the study of the fluorescence spectra, three species can be assigned: the dication in the range of $H_0$ = 8 to −10; the monocation in the range $H_0$ = 3 to $H_0$ = 7; and the neutral species in the range $pH$ 12 to $H_0$ = 2. Similar to some aromatic amines, imino anion does not fluoresce in highly basic solution. The $pK_a$ values at 298 K are calculated with the help of the Forster cycle method using Eq. (4).

$$pK_a^* = pK_a - 2.1 \times 10^{-3} (\tilde{v}_A - \tilde{v}_0)$$

where $\tilde{v}_A$ and $\tilde{v}_0$ are the band maxima (the O−O transition is used wherever it can be located) of the acid and its conjugate base, respectively. The values calculated using Eq. (4) and the absorption, fluorescence and average of absorption and fluorescence maxima, are given in Table 2. In the case of the dication-monocation equilibrium, only $\Delta pK_a^*$ (= $pK_a^* - pK_a$) values are given as it is difficult to calculate $pK_a(1)$ from absorptiometry. The $\Delta pK_a^*$ values indicate that the ring carbon atom of the hydrocarbon becomes more basic upon excitation, which agrees with the earlier report.

The $pK_a^*$ values are also calculated for various equilibria from the fluorimetric titration curves shown in Fig. 3. The data are compiled in Table 2. The fluorimetric titration curve for monocation-neutral equilibrium is similar to the other aromatic amines in the sense that proton-induced fluorescence quenching of neutral amine is observed before protonation. Thus the $pK_a^*(2)$ value has been calculated from the formation curve of ChNH$_3^+$ rather than from the decrease in intensity curve of ChNH$_2$. This value may not be very much different from the value obtained from time-dependent fluorimetry. The difference between the values of $pK_a^*(2)$ obtained using absorption and fluorescence data respectively could be due to the difference in the solvent relaxation in the two states and the use of band maxima rather than the O−O bands.

**Fluorescence quenching**

Proton-induced fluorescence quenching has been regarded as due to (i) deactivation of fluorescence intensity of aromatic amines by proton transfer reactions in $S_1$ state (by Förster), (ii) ring protonation (by Weller), (iii) the formation of the stoichiometric complex in the $S_1$ (by Schulman et al.) and (iv) intramolecular charge transfer structure (by Shizuka et al.). The last model seems to

![Fig. 3](image-url)

**Table 2—Values of $pK_a$ and $pK_a^*$ for Various Prototropic Equilibria of 2-Aminochrysene**

<table>
<thead>
<tr>
<th>Equilibria</th>
<th>$pK_a$</th>
<th>$pK_a^*(ab)$</th>
<th>$pK_a^*(fl)$</th>
<th>$pK_a^*(av)$</th>
<th>$pK_a^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dication⇌Monocation</td>
<td>—</td>
<td>1.22*</td>
<td>2.68*</td>
<td>1.93*</td>
<td>—</td>
</tr>
<tr>
<td>Monocation⇌Neutral</td>
<td>2.4</td>
<td>−3.56</td>
<td>−5.25</td>
<td>−4.40</td>
<td>−2.9</td>
</tr>
<tr>
<td>Neutral⇌Anion</td>
<td>16.4</td>
<td>11.34</td>
<td>—</td>
<td>—</td>
<td>12.4</td>
</tr>
</tbody>
</table>

*Only $\Delta pK_a^*$ values are indicated for this equilibrium.*
be probable and acceptable.\(^\text{35}\) Under the conditions that the life-time of ChNH\(_3^+\) is large and the concentration of proton is small, the kinetic model for the proton-induced fluorescence quenching, proposed by Shizuka \textit{et al.}\(^\text{36}\), can be simplified to the simple Stern-Volmer reaction, given by Eq. (5).

\[
\frac{\Phi_0}{\Phi} = 1 + k_q \tau [H^+] \quad \cdots \quad (5)
\]

where \(\Phi_0\) and \(\Phi\) are the fluorescence efficiencies of neutral amine in the absence and presence of fluorescence quenching respectively, \(\tau\) is the life-time of the \(S_1\) state and \(k_q\) is the proton-induced fluorescence quenching rate constant. The plot of \((\Phi_0/\Phi - 1)\) versus \([H^+]\) is linear (Fig. 4) with a slope of \(8.7 \text{ dm}^3\text{mol}^{-1}s^{-1}\), which is equal to \(k_q \tau\). The life-time of ChNH\(_2\), calculated using Strickler and Berg's relation, is found to be \(2.2 \times 10^{-9}\) s. The value of \(k_q\) thus obtained is \(4.1 \times 10^9\text{dm}^3\text{mol}^{-1}s^{-1}\). This value is within the same order of magnitude \((10^8-10^9\text{dm}^3\text{mol}^{-1}s^{-1})\) as observed for other amino compounds and indicates that electrophilic protonation occurs at one of the carbon atoms of the aromatic ring of the molecule.

The decrease in the fluorescence efficiency of the neutral molecule at \(pH > 10\) is due to the formation of imino anion, which appears to be non-fluorescent probably due to edge effect\(^\text{16}\) and the participation of some new steric factors arising out of a non-promoting out-of-plane model as suggested by Valyer and Weber\(^\text{37}\).

\textbf{Acknowledgement}

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\textbf{References}

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