Solvent Effect on Fluorescence Quenching of Anthracene by Acrylonitrile

N. SELVARAJAN & V. RAMAKRISHNAN*

Department of Chemistry, Indian Institute of Technology, Madras 600036

Received 20 October 1978; revised and accepted 5 July 1979

The quenching of anthracene by acrylonitrile is more efficient in protic solvents than in aprotic solvents. In either case the quenching increases with increase in polarity and decreases with viscosity. A linear relationship between fluorescence quenching constant \( k_q \) and solvent polarity parameter, \( Z \)-value has been observed. The results indicate the intermediary of a reversible exciplex in fluorescence quenching.

### Materials and Methods

Anthracene was purified by co-distillation with ethylene glycol and subsequent recrystallization from toluene. Acrylonitrile was purified by the method described in literature. Solvents were purified by standard methods. The instrument used and the methods employed are as described earlier. Irradiations were done at 365 nm with 3.5 ml of solutions in 1 cm cells (\( \sim 35^\circ \text{C} \)).

### Results and Discussion

The fluorescence of anthracene (A) was quenched by added acrylonitrile (AN). As irradiation resulted in rapid reaction leading to 1 : 1 adduct formation, the zero time fluorescence intensities were carefully measured and fluorescence quenching constants \( k_q \) determined. The fluorescence quenching was consistent with the Stern-Volmer equation

\[
\frac{F_0}{F} = 1 + k_q \tau [\text{AN}]
\]

### Table 1 — Data on Fluorescence Quenching of Anthracene by Acrylonitrile in Various Solvents

<table>
<thead>
<tr>
<th>Solvents</th>
<th>( k_q \times 10^4 ) (M(^{-1})sec(^{-1}))</th>
<th>( \tau ) (sec)</th>
<th>( k_q \times 10^{-7} ) (M(^{-1})sec(^{-1}))</th>
<th>( k_{diss} \times 10^{-1} ) (M(^{-1})sec(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>6.60</td>
<td>4.2</td>
<td>1.93</td>
<td>0.19</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>19.88</td>
<td>5.5</td>
<td>5.06</td>
<td>0.23</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>16.64</td>
<td>5.7</td>
<td>2.92</td>
<td>1.32</td>
</tr>
<tr>
<td>Methanol</td>
<td>19.05</td>
<td>5.5</td>
<td>3.54</td>
<td>0.54</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>14.38</td>
<td>6.0</td>
<td>2.40</td>
<td>0.38</td>
</tr>
<tr>
<td>Isobutanol</td>
<td>20.97</td>
<td>5.5</td>
<td>3.81</td>
<td>—</td>
</tr>
<tr>
<td>tert.-Butanol</td>
<td>10.01</td>
<td>6.0</td>
<td>1.67</td>
<td>0.20</td>
</tr>
<tr>
<td>Benzyl alcohol</td>
<td>18.03</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

where \( \tau \) is the life-time of the first excited singlet state of anthracene. \( k_q \tau \) values were obtained from the plot of \( F_0/F \) vs [AN]. \( \tau \) values were taken from the literature. The values of \( k_q \), \( \tau \), \( k_{diss} \) and \( k_q \tau \) are listed in Table 1.

In this particular system, the fluorescence quenching can be attributed only to the formation of an exciplex between \( \text{A}^* \) and AN. The most direct proof of the exciplex formation is the observation of the characteristic exciplex emission. But in several cases exciplexes are non-emissive in nature and in such cases the existence of exciplexes is inferred from other evidences. In this case also the exciplex is non-emissive. The \( k_q \) values are large. \( k_q \tau \) values are uniformly high in polar aprotic solvents suggesting a specific type of solvent-solute interaction and charge transfer nature of the interaction between \( \text{A}^* \) and AN is certainly indicated. Hence the solvent sensitivity definitely points out to exciplex formation. A simple collision mechanism cannot explain such a specific solvent effect. The low \( k_q \) values are about one thousandth of the diffusion-control values. It is necessary to explain this. The low \( k_q \) values may be due to the reversibility of the exciplex formation. The exciplex is weak and consequently dissociation of \( \text{A}^* \ldots \text{AN} \) to give back \( \text{A}^* + \text{AN} \) can have a high rate constant. Although \( k_q \) is close to \( k_{diss} \), the high value of \( k_q \) can lower \( k_q \). (Scheme 1).
The fluorescence quenching was studied in solvents with different physical properties. The observed $k_q$ decreases in the following order: isobutanol > n-butanol > methanol > isopropanol > tert-butanol > acetonitrile > benzene.

The viscosity of the solvents follows the sequence: acetonitrile < methanol < benzene < ethanol < acetic acid < n-propanol < isopropanol < n-butanol < tert-butanol.

The dielectric constant varies as acetonitrile > methanol > n-propanol > isopropanol > n-butanol > acetic acid > benzene.

Kosower's solvent polarity parameter $Z$ decreases as methanol > acetic acid > n-propanol > tert-butanol > acetonitrile > benzene.

It is quite clear that the fluorescence quenching constant decreases in the order of Kosower's solvent polarity parameter $Z$ value. In the present system quenching is found to be maximum in alcoholic solvents, less in acetonitrile and the least in non-polar aprotic solvents. With few exceptions the observed trend in fluorescence quenching parallels the trend in $Z$-value of the solvent. As the $Z$ value of the solvent increases the value of the quenching constant also increases.

The dielectric constant, viscosity and refractive index taken individually are not capable of explaining the observed trend. It is the $Z$-factor which determines the magnitude of quenching. The quenching is more efficient in protic solvents and among the protic solvents quenching decreases as viscosity of the medium increases. It is only in such cases effect of viscosity is felt. The exciplex is weak. Hence specific interaction with the solvent is likely to enhance its stability. Protic solvents are involved in hydrogen bonding with the AN moiety of the exciplex. It has been noted that the photoaddition of AN to anthracene proceeds faster in protic solvents and when H$^+$ is added the rate is further enhanced. Scheme 1 explains the results.

\[
\begin{align*}
A & \xrightarrow{h_v} ^1A^* \quad \text{365nm} \\
^1A^* & \xrightarrow{k_1} A + h\nu \\
^1A^* & \xrightarrow{k_2} A \\
^1A^* & \xrightarrow{k_3} ^3A^* \\
^1A^* + AN & \xrightarrow{k_4} \text{Exciplex} \\
k_4 & \xrightarrow{k_5} A^+ \cdots \cdots AN^- \\
\text{Exciplex} & \xrightarrow{k_6} 1:1 \text{ adduct} \\
\text{Exciplex} & \xrightarrow{k_7} A + AN
\end{align*}
\]

Scheme 1

According to Scheme 1 $F_0/F = 1 + k_q [\text{AN}]$

where $k_q = \frac{k_4(k_5 + k_6 + k_7)}{k_4 + k_5 + k_6 + k_7}$

Acknowledgement

The authors wish to thank the CSIR, New Delhi for financial support.

References