Solvent Dependency of Azobenzene Thermal Relaxation

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Problem
Azobenzenes are a class of organic dyes that are commonly used as optical switches, photoconverting between cis and trans isomers.

Due to their biocompatibility, there is growing interest in using these dyes as in vivo optical triggers.¹ ² However, this transition is complicated by solvent dependency.

Background
Disperse Red 1 (DR1) is a commonly used azo switch that thermally relaxes very quickly (t₁/₂ = 0.4 s, in tetrahydrofuran, THF).

DR1 is insoluble in water, so we previously incorporated it into an acrylic acid co-polymer, to facilitate aqueous applications.³

Despite switching in THF, methanol (MeOH) and N,N-dimethylformamide (DMF), the polymer showed no switching in water.

Slowly adding water to a THF solution of the polymer, we were able to show that the switching was quenched.

Broadly Soluble Azobenzenes
We synthesized and screened a series of azobenzenes, looking for solubility in many solvents. The two compounds at right are soluble in all of the below solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dielectric Constant</th>
<th>Polarity</th>
<th>Hydrogen Bonding</th>
<th>Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>80</td>
<td>Polar</td>
<td>42.3</td>
<td>Protic</td>
</tr>
<tr>
<td>MeOH</td>
<td>36</td>
<td>Polar</td>
<td>11.3</td>
<td>Aprotic</td>
</tr>
<tr>
<td>DMF</td>
<td>33</td>
<td>Nonpolar</td>
<td>22.3</td>
<td>Protic</td>
</tr>
<tr>
<td>Acetone</td>
<td>21</td>
<td>Nonpolar</td>
<td>7</td>
<td>Aprotic</td>
</tr>
<tr>
<td>THF</td>
<td>7.5</td>
<td>Nonpolar</td>
<td>8</td>
<td>Aprotic</td>
</tr>
</tbody>
</table>

Table of solvent properties, with selected solvents having a broad range of characteristics.⁴

UV Vis Kinetics
Due to a dramatic change in absorptivity between cis and trans conformations, it is possible to monitor molecular states optically.

By observing the transmission of a solution over time, it is possible to determine the rate at which cis molecules relax to the trans position.

Laser Measurements
When the cis to trans conversion happens too quickly to monitor with UV Vis, pump-probe frequency modulation may be used.

The laser table setup for the frequency domain pump-probe experiments.

Effect of Solvent
Our measurements show that the half-lives of the dye in different solvents relate most directly to the hydrogen bonding character of the solvent.

Additionally, the magnitude of the response decreases dramatically in protic solvents (MeOH and water).

There is currently disagreement in the scientific community as to the mechanism of isomerization in azo dyes.⁵

Our next step is to use this data to revisit this problem, hopefully being able to further explain azo dye conformational changes.

Acknowledgements

References:
4) http://en.wikipedia.org/wiki/Solvent