CHAPTER 2

SOLVENT-SOLUTE INTERACTIONS

2.1 INTRODUCTION

The photophysical and photochemical properties of a dye molecule are determined by the nature and the energy of its electronically excited states. The spectra of the dye in the gas phase is different from that in solution. This is due to the intermolecular interaction between the dye and the solvent molecules. This electrostatic interaction between solute and solvent molecules, known as "solvation", is of considerable importance in photophysics and photochemistry.

When a dye molecule is dissolved in a solvent, the dye molecule is surrounded by solvent molecules. These solvent molecules arrange themselves around the dye molecule in such a way as to minimize the energy of the system. The dye molecule undergoes interactions with these solvent molecules and attains thermal equilibrium. This results in a lowering of the ground state energy level of the dye molecule in the solution with respect to the ground state energy level in the vapour state and the magnitude of the shift depends upon the magnitude of the solute-solvent interaction. The dye molecules on excitation reorient themselves to conform to the new electronic distribution of the excited molecules. The excitation process of the dye molecule is instantaneous (<10^{-15} sec)[17]. The solvent cage rearrangement or relaxation takes place rapidly (10^{-11} sec) compared to the fluorescence lifetimes which are around
$10^{-9} - 10^{-8}$ second. The solvent molecules reorient themselves and lower the excited nonequilibrium state (called the Franck-Condon excited state) to an equilibrium excited state. The magnitude of the energy lowering depends upon the excited state solute-solvent interactions. The radiative emission process takes place to the Franck-Condon ground state, which then relaxes non-radiatively to the equilibrium ground state in around $10^{-11}$ sec. Thus the emission spectra have a bathochromic shift with respect to the absorption spectra (the Stokes shift).

Figure 2.1 Energy level diagram of a ground state molecule (M) and an excited molecule (M*) in vacuum and in a solvent.

Figure 2.1 represents the Stokes shifts of the electronic transitions. Here S stands for the solvation shell which surrounds the molecule M. "r" refers to a relaxed state; "fc" to a Franck-Condon state. A molecule M
which does not change its geometry on excitation to \( M^* \) has no Stokes shift in vacuum i.e., the electronic transitions coincide in absorption (a) and fluorescence (f). If the stable excited state geometry differs from that of the ground state, nuclear relaxation will take place leading to the state \( (M_r^*) \) and emission \( (f') \) will bring the molecule to a Franck-Condon ground state \( M_{fc} \). In solution, all molecules have an additional Stokes shift due to the different solvation energies of the ground state \( (E_{sg}) \) and the excited state \( (E_{se}) \) \([17]\).

The shifts in absorption and emission spectra of the dye solution are caused by the dielectric interactions which are long range in nature and also by specific interactions which are of short range.

2.2 DIELECTRIC INTERACTIONS

There are three dielectric interactions resulting from nonspecific solute-solvent dipole interactions. They must be distinguished from specific interactions such as hydrogen bonding. These three dielectric interactions can be described as follows:

i. Dipole-dipole interactions between the dye molecule and solvent molecules. These dipoles are permanent and the solute molecule has a different dipole moment in the excited state compared to its ground state.

ii. Dipole-induced dipole interaction, which occur even when the solute or solvent molecule has zero dipole moment.
iii. Induced dipole-induced dipole interactions, which cause a general red shift and depend upon the refractive index of the solvent.

2.2.1 The dipole-dipole interactions

The solute dipole moment $\mu_s$ produces an electric field proportional to $\mu_s/r^3$ at a distance $r$ from the dipole centre [17]. This field produces an orientation of the solvent dipoles $\mu_s$ which give in return a reaction field $R$ at the centre of the solute molecule of radius $a$, given by,

$$R = \left( \frac{\mu_s}{a^3} \right) (f(D) - f(n^2)) \quad (2.1)$$

where $D$ is the static dielectric constant and $n$ is the refractive index of the solvent. The functions $f(D)$ and $f(n^2)$ are the "Onsager polarity functions" which are used in general for the simple description of electrostatic solute-solvent interactions [17] and are given by,

$$f(D) = \frac{2(D-1)}{2D+1} \quad \text{and} \quad f(n^2) = \frac{2(n^2-1)}{2n^2+1} \quad (2.2)$$

The static dielectric constant $D$ and the refractive index $n$ are the macroscopic, observable quantities which are related to the polarity of the medium. The relationship between these macroscopic quantities and the microscopic properties $\mu_s$ and $\alpha_s$ of the solvent molecules comes out in its clearest form in the equations of Clausius-Mossoti and Debye

$$\phi(n^2) = \frac{(n^2-1)}{(n^2+2)} = \frac{(4N\alpha_s\pi)}{(3M_s)} \quad (2.3)$$
(Clausius-Mossotti)
\[
\phi(D) = \frac{(D-1)}{(D+2)} = \frac{(4N_6\delta_s \pi)}{(3M_s)} \left( \frac{\alpha_s + \mu_s^2/kT}{(\text{Debye})} \right)
\]

where \( \delta_s \) and \( M_s \) are the density and the molecular weight of the solvent respectively.

From the Equations (2.2-2.4) an expression relating \( \Delta f \) and \( \mu_s \) can be written as

\[
\Delta f = \frac{[8\pi\delta_s x + 3M_s (x+1)] 8\pi\delta_s}{[4\pi\delta_s x + 3M_s] [4\pi\delta_s + 3M_s]}
\]

where \( x = \left( \frac{\alpha_s + \mu_s^2}{kT} \right) \)

\( \Delta f = \text{dipole factor} = (f(D) - f(n^2)) \)

For a solvatochromic shift the observation pertains to the difference of solvation energy between a relaxed initial state (e.g. of dipole moment \( \mu_g \) in absorption) and a FC final state (\( \mu_e \) in absorption). The solvent dipoles cannot reorient during the electronic transition and the reaction field \( R \) remains unchanged. The energy spent in polarizing the solvent around the solute dipole is therefore also unchanged and cancels out between the ground and excited state solvation energies. The solvatochromic shift due to the dipole-dipole interaction is then

\[
(\Delta E_{ge}) = -\mu_g (\mu_e - \mu_g) a^{-3} \left( f(D) - f(n^2) \right)
\]

In the case of a luminescence emission the states (g and e) are simply inverted, and the solvatochromic shift is

\[
(\Delta E_{eg}) = -\mu_e (\mu_g - \mu_e) a^{-3} \left( f(D) - f(n^2) \right)
\]
2.2.2 Solvent Dipole-induced solute dipole interactions

This is the interaction between the total dipole moment $\mu_M$ of the solute molecule and the induced dipole moments in the polarizable solvent; the reaction field is now $R = (\mu_M/a^3)f(n^2)$ and the stabilization energy in the polarized solvent is,

$$E_s = -(\mu_M^2/a^3)f(n^2) \quad (2.8)$$

Since the induction polarization of the solvent involves only the motion of electrons (and not the reorientation of the nuclear framework) it is able to follow the excitation process so that the FC and relaxed states of the solvent are identical. The total solvation energy in each electronic state of the solute is then the stabilization energy given above less the energy spent in polarizing the solvent. The solvatochromic shift due to the dipole-induced dipole interactions is therefore,

$$\Delta E_{ge} = -(\mu_e^2 - \mu_g^2)/2a^3 \Delta f(n^2) \quad (2.9)$$

In the absence of a solute permanent dipole moment no orientation of the solvent dipole can take place. However, the random motion of the solvent dipoles around the non-polar but polarizable solute can yield small, fluctuating electric fields which will produce an induced dipole moment in the solute molecule. This interaction has been called the "solvent Stark effect" and is a rather small effect which can be neglected in most cases [18].
2.2.3 Induced dipole-induced dipole interactions

The interaction of two non-polar, polarizable particles is the "dispersion interaction" which results from the fluctuations of their instantaneous dipoles [17]. Although the average dipole moment of a non-polar molecule is zero, the instantaneous dipole moment is finite and produces an instantaneous induced dipole in a nearby polarizable molecule. The solvatochromic shift which results from the change in the polarizability of the solute molecule between the ground and excited states is given by,

$$\Delta E_{ge} = -(a_e-a_g)a^{-3} C \Delta f(n^2) \quad (2.10)$$

2.3 SPECIFIC INTERACTIONS

The specific interactions are due to hydrogen bonding, complex and exciplex formation etc. The complex or exciplex formation usually leads to large changes in the shape of spectral bands. Specific interactions in general, and hydrogen bonding in particular, must be distinguished from the nonspecific, dielectric solute-solvent interactions: a specific association implies a fixed stoichiometry (usually 1:1) of the interacting molecules, as well as a fixed geometry (bond length, bond angle), whereas even the dipole-dipole interactions which are the strongest nonspecific intermolecular forces concern unspecified numbers of freely moving molecules.

Hydrogen bonding can have considerable solvatochromic effects which are observed as deviations from the dielectric solvatochromic plot, specifically from the \((f(D) - f(n^2))\) plot since hydrogen bonding solvents are invariably polar. These deviations which are called
the hydrogen-bonding anomaly is defined here as the difference in energy between the electronic transition measured in the hydrogen-bonding solvent and non-hydrogen bonding solvent of the same dielectric polarity function \( f(D) \).

### 2.3.1 Hydrogen bonding

This is a bimolecular association which generally occurs between two electronegative atoms (e.g., O, N or S atoms) with the hydrogen atom. Mataga et al. [19-21] have observed that pyridine which is non-fluorescent in benzene exhibits higher absorption and considerable fluorescence in alcohols. This was attributed to the hydrogen bonding between the oxygen atom of alcohol and the nitrogen atom of pyridine as shown in Figure 2.2. They also observed that the intensity of absorption and fluorescence increased with the hydrogen bond donating capacity of the donor.

![Figure 2.2: H-Bonding between pyridine and ethanol](image)

**Figure 2.2** H-Bonding between pyridine and ethanol

In pyridine, the non-bonded n electron (of sp\(^2\) character) is localized on the nitrogen atom. The non-bonding orbital is in the plane of the molecule but pointing away from it. The \( \pi \) electron orbital is in the transverse plane of the molecule and hence, in general, there is very little overlap between the n orbital and the \( \pi \) orbital. When pyridine undergoes H bonding with ethanol the lone pair electrons of the oxygen atom in ethanol repel the lone pair...
electron on the nitrogen atom because of their proximity. This repulsion pushes these electrons of the nitrogen atom towards the nitrogen atom but out of the molecular plane and thus in effect reduces the non-bonding character of the \( sp^2 \) electrons of the nitrogen atom. It thus becomes possible now for these non-bonding \( sp^2 \) electrons to move into vacant orbitals of the \( \pi \) electron system, thus enhancing the ring current. Such intramolecular charge transfer processes generally helps in increasing the absorption and emission characteristics of the molecule [19].

In such intramolecular charge transfer processes, the migration of charge in the excited state may be higher or lower than in the ground state. Whenever charge transfer occurs, the corresponding state is stabilized, i.e., the energy level is lowered. When the charge transfer is greater in the excited state than in the ground state, lowering of the excited state energy level is greater than the ground state level. That is, the spectra will be red shifted in a H- bonding association compared to a solvent where H-bonding is absent.

2.4 SOLVATOCHROMIC SHIFTS

Excluding specific associations such as hydrogen bonding, all the other interactions described in the earlier sections represent dielectric or nonspecific solute-solvent interactions, and if they are assumed to be independent the total solvation energy is given by their sum. Each term is a product of two factors which represent separately the "solute polarity" and the "solvent polarity". The dipole-dipole interaction term and the solvent Stark effect are related to the solvent polarity function \([f(D)-f(n^2)]\).
The solvatochromic shifts of dipolar molecules in a series of polar solvents of similar refractive index result from the dipole-dipole interaction only. The dipole-dipole effect is by far the most important contribution to the solvatochromic shifts of polar molecules and it has been used extensively for the estimation of excited state dipole moments [22].

The \( f(D) \) solvatochromic plot (strictly speaking the \( f(D) - f(n^2) \) plot at constant refractive index \( n \)) has been widely used for the estimation of excited state dipole moments although it does include the angle \( \omega \) between the ground state dipole vector \( \mu_g \) and the charge transfer vector \( \mu_e - \mu_g = \Delta \mu_{ge} \) (for absorption spectra); or the angle between the excited state dipole vector \( \mu_e \) and the reverse charge transfer vector \( \mu_g - \mu_e = \Delta \mu_{eg} = -\Delta \mu_{ge} \) in the case of luminescence spectra. These simple solvatochromic shift equations apply to both absorption and fluorescence spectra, and they should of course give the same result for the excited state dipole moment \( \mu_e \) provided these dipole moments do not change between the FC and relaxed states i.e. \( \mu_e(\text{relaxed}) = \mu_e(\text{FC}) \) and \( \mu_g(\text{relaxed}) = \mu_g(\text{FC}) \) [17].

This assumption is equivalent to assuming that the initial and final state molecular geometries are similar. Important exceptions are encountered in a few cases, of which the twisted intramolecular charge transfer (TICT) states of some flexible molecules are the best examples [17].

Assuming that in FC and relaxed states, the dipole moments are equal, the simple dipole-dipole interaction solvatochromic shift equations
\[ \Delta E = -\mu_g \cdot \Delta \mu_{ge} a^{-3} \Delta f(D) \quad (\text{absorption}) \quad (2.11) \]

and

\[ \Delta E = -\mu_e \cdot \Delta \mu_{eg} a^{-3} \Delta f(D) \quad (\text{emission}) \quad (2.12) \]

can be combined together in the "Lippert Method" [23]. In this method, the energy difference between the fluorescence band and the first absorption band is plotted against the solvent polarity function \( f(D) \) in a series of solvents of the same refractive index \( n \). This energy gap is then given by,

\[ \Delta E_{\text{flu-abs}} = - (\Delta \mu_{ge})^2 a^{-3} \Delta f(D) \quad (2.13) \]

and this depends only on the absolute magnitude of the charge transfer dipole moment \( \Delta \mu_{ge} \).

Mataga et al. [21] have given a detailed theory on the influence of the solvent on the spectra of the solute molecule. They have shown that in the absence of H-bonding effects, the shifts produced in the absorption and emission spectra of the solute due to the interaction between the solute dipole and the solvent dipole is far more important than other interactions such as the dipole - induced dipole interaction.

Mataga has shown that in cases where solute dipole-solvent dipole interactions are important and when H-bonding effects are absent one can expect an approximate linear variation of the Stokes shift with the dipole factor.

\[ \nu_a - \nu_f = \left[ \frac{2(D-1)}{(2D+1)} - \frac{2(n^2-1)}{(2n^2+1)} \right] \frac{(\mu_e - \mu_g)^2}{a^3hc} \quad (2.14) \]
where $V_f$ - fluorescence peak in wave number
$\nu_a$ - absorption peak in wave number
$D$ - dielectric constant of solvent
$n$ - refractive index of solvent
$\mu_g$ - dipole moment of the solute in the ground state
$\mu_e$ - dipole moment of the solute in the excited state
$a$ - Onsager's cavity radius

The term in the square bracket in the above expression is called the dipole factor $\Delta f$.

Table 2.1 gives a few examples of excited state dipole moments obtained from solvatochromic shifts [24]. The large dipole moment of the exciplex formed by anthracene and N,N-dimethylaniline (DMA) confirms the high CT nature of this complex which resembles an ion pair; this agrees with the fact that complete charge separation takes place in highly polar solvents, so there can be no doubt that the dipole moment must be close to that of an ion pair prior to separation. Intramolecular charge transfer [24] provides further proof of the general validity of the solvatochromic shift methods for the measurement of excited state dipole moments. The TICT state of DMABN is an example of total charge separation within a formally conjugated molecule. The solvatochromic shift measurements have been important for the dipole moment determinations of these states.

The solute molecule's polarizability has not been included explicitly in the solvatochromic shift equations, but these equations are in principle valid as long as the "dipole moments" ($\mu_g$, $\mu_e$) are total dipole moments, that is they are the sum of the solute's permanent and induced
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<th>$\mu_d$ (Debye)</th>
<th>Transition</th>
<th>$\mu_e$ (Debye)</th>
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<td></td>
<td></td>
<td>$S_1-S_0$</td>
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<tr>
<td>DMABN</td>
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<td>$S_0-S_1$</td>
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<td></td>
<td>TICT</td>
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<td>$S_0-S_1$</td>
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</tr>
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<td>$S_0-S_1$</td>
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<tr>
<td></td>
<td></td>
<td>($\pi-\pi^*$)</td>
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</tr>
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</table>

NAS - (4-N,N'-dimethylamino -4'-nitrostilbene)
DMABN - (4-N,N'-dimethylamino benzonitrile)
moments. The solute molecule's polarizability is then included in the form of the induced dipole moment. The change in polarizability between the ground and excited state is also included only implicitly in the dipole-dipole solute-solvent interaction equations since the "excited state dipole moments" $\mu_e$ must be seen as the sum of the permanent and induced dipole moments. The solute molecule's polarizability is then included in the form of the induced dipole moment.

2.5 THERMOCHROMIC SHIFTS

The shifts of absorption and emission spectra as a function of the temperature $T$ of a solvent are known as thermochromic shifts. The thermochromic effects result from the temperature dependence of the solvent polarity functions $f(D)$ and $f(n^2)$ and it can be expressed simply as follows [17]:

$$\frac{\delta E}{\delta T} = -\frac{\mu_g \mu_{ge}}{a^3} \frac{\delta}{\delta T} (f(D) - f(n^2)) - \frac{\mu_e^2 - \mu_g^2}{2a^3} \frac{\delta}{\delta T} f(n^2) \quad (2.15)$$

The $f(n^2)$ function varies with $T$ only because the solvent density varies with $T$. On the other hand, the temperature dependence of the solvent dipole orientation polarity $(f(D) - f(n^2))$ is quite complex and is best taken in the empirical form [25]

$$\chi = -d \frac{(\log D)}{dT} \quad (2.16)$$

for the dielectric constant, from which the polarity function itself can be calculated.

In most cases thermochromic shifts are small compared to solvatochromic effects. The exceptionally large
Thermochromic shifts of the fluorescence spectra of 4-dimethylamino 4-nitrostilbene and of DMABN are related to their very large excited state dipole moments of around 20 Debye due to their TICT conformations [24].

Thermochromic shifts are important because they provide a means to determine excited state dipole moments in single solvents. In solvatochromic shift methods it is assumed that the dipole moments $\mu_g$ and $\mu_e$ are solvent independent molecular properties, and this assumption may not be valid in some cases. In particular, the charge transfer character of some exciplexes may be solvent dependent, such that the dipole moment increases with solvent polarity as polar solvents promote charge separation [26].

2.6 SUMMARY

Solvatochromic and thermochromic shifts must be considered as experimental manifestation of the influence of the medium on the energy states of molecules. These are fundamental experimental observations which are of importance for the photophysical and photochemical properties of these molecules in various environments. On the basis of such observations it is possible to find correlations with various solvent and solute properties such as electron distribution of electronically excited molecules, distinction between n-$\pi^*$ and $\pi-\pi^*$ states, the charge transfer character of such states and of exciplexes. Thus studies of solvatochromic and thermochromic shifts have assumed great importance.