3B.1 Introduction:

Solute–solvent interactions play a key role in determining the physicochemical properties of solutions, yet our understanding of this subject is far from complete. Rotational diffusion studies of medium sized molecule provide a useful means to probe these interactions [1]. Because of continuous interaction with the neighbouring molecules rotating in a liquid experiences a friction [2]. By modelling this friction using a variety of continuum based theories one can get a better ample insight into the nature of the solute–solvent interactions.

However, the effect of solute-solvent interactions on the rotational motion of a probe molecule in solvent environment has been studied in detail; these interactions are characteristically described as friction to the rotational motion of the probe and can be classified into three types.

1. Short-range repulsive forces which dictate intermolecular dynamics during molecular collisions. These are present in all liquids and lead to viscous dissipation, which is exhaustively described by hydrodynamic theories [1].

2. Long range electrostatic interactions between a probe and polar solvent molecules. As the solute rotates, the induced solvent polarization can lag behind rotation of the probe, producing a torque, which thoroughly reduces the rate of rotational diffusion. This effect, termed as a dielectric friction, occurs from the same type of associated motions of solvent molecules [3-6].

3. Specific solute-solvent interactions, Hydrogen bonding is feasibly the most frequently encountered example of this type. Strong hydrogen bonds will lead to the formation of solute-solvent complexes of well-defined stoichiometry. These new, larger species can stay in solution for reasonably long times and will rotate more slowly than the bare solute. Breaking and formation of hydrogen bonds
arising on time scales faster than the probe rotation will provide a channel for rotational energy dissipation giving rise to further additional friction[1,5,6].

Generally, the friction experienced by the probe in the environment of solvents is purely mechanical or hydrodynamic friction dominated by short range repulsive forces between the molecules. Mechanical friction can be modelled by the hydrodynamic theories. Polar probe in polar solvents experiences dielectric friction in addition to mechanical friction. Dielectric friction can be modelled using the continuum theories of Nee-Zwanzig (NZ) [7] and Vander Zwan Hynes theories (VZH) [5]. Since our understanding of many aspects of solution phase dynamics has grown remarkably in the last decade, it may look amazing that our understanding of friction even in the case of solute rotation is still at qualitative level. To be sure, some aspect of solvent friction can be easily understood in terms of hydrodynamic theories. The wide-ranging approach is to measure the rotational reorientation time of a solute molecule in a solvent experimentally and model using the diffusion based theories of Stokes-Einstein and Debye (SED) [8-10].

A considerable degree of success on the rotational dynamics arises from the Stokes-Einstein-Debye (SED) hydrodynamic theory, which forms the basis of supportive molecular rotations of medium sized molecules in liquid solvents, according to which the rotational reorientation time [6-10] of a solute molecule is proportional to its volume (V), bulk viscosity (\(\eta\)) of the solvent and inversely related to its temperature (T).

\[
\tau_r = \frac{\eta V f C}{kT}
\]  \hspace{1cm} 3B.1
Where, $k$ is the Boltzmann constant, $f$ is the molecular shape factor ($f \geq 1$) and $C$ is a factor ($0 \leq C \leq 1$) which describes the hydrodynamic boundary condition. For a polar molecule in a polar solvent there is no need to correct this relation for dielectric friction. The SED theory explains the rotational diffusion of medium sized molecules precisely when the coupling between the solute and the solvent is purely mechanical or hydrodynamic in nature. This theory associates molecular-level friction with bulk viscosity in such a way as to provide reasonable estimation of the rotation times of molecules in a solution.

The dielectric friction can be modelled using continuum theories of Nee-Zwanzig (NZ) [7], which treats the solute as a point dipole rotating in a spherical cavity. Alavi-Waldeck (AW) [11] model is an extension of the NZ theory, where the solute is treated as a distribution of charges instead of point dipole and the semi empirical approach of Vander Zwan and Hynes (VZH) [5] in which fluorescence Stokes shift of the solute in a given solvent is related to dielectric friction. On the other hand, results of neutral and nonpolar solutes deviate significantly from the hydrodynamic predictions at higher viscosities. These probes rotate much faster than predicted by the SED theory with stick boundary condition and are described by either slip boundary condition or by quasihydrodynamic theories. Slip boundary condition assumes the solute-solvent coupling parameter to be less than unity, contrary to the stick boundary condition. Quasihydrodynamic theories of Gierer and Wirtz (GW)[12], Dote, Kivelson and Schwartz (DKS)[13] and S.R.Inamdar et al [14] attempted to improve upon SED theory by taking into an account, not only the size of the solute but also that of the solvent molecule, there by modifying the boundary conditions. It has been argued that as the size of the solute molecule becomes much
larger than the size of the solvent molecule, the observed reorientation times approach the SED theory with the stick boundary condition.

Based on the above explanation of rotational reorientation dynamics, Red Mega 480 polar probe have been chosen in the present study. The probe used in charged polar solvents with an objective of understanding how the long range charge dipole or dipole-dipole, which influence the rotational dynamics of the probe molecules. Dielectric friction on a rotating solute occurs because of the polar molecule entrenched in a dielectric medium polarizes the surrounding dielectric. As the solute attempts to rotate, the polarization of the medium cannot instantaneously keep in phase with the new orientation of the probe molecule and this lag exerts a retarding force on the probe molecule, giving rise to rotational dielectric friction.

In general, the mechanical and dielectric contributions to the friction are not separable because they are interlinked due to the electro hydrodynamic coupling. However, such a practice has been followed in literature, which allows simple models for the friction coefficients to be used. Mechanical friction can be modelled using the hydrodynamic and quasihydrodynamic theories [12]. Dielectric friction can be modelled using the continuum theories of NZ [7], the AW model [11] which is an extension of the NZ theory, and the semi empirical approach of Van der Zwan–Hynes [5]. Although molecular theories of dielectric friction are available, at present these theories are difficult to apply because they require some knowledge of the intermolecular potential or some other unavailable properties of the solvent. Recent simulations by Kumar and Maroncelli [15] proved that mechanical and dielectric contributions to the friction are indeed not separable in any useful way.
3B.2 Theory:

3B.2.1 Stoke-Einstein-Debye's (SED) theory:

The most accepted model among the several proposed models for the rotational motion is the rotational diffusion model outlined by Debye [10], in which the reorientation is supposed to occur in small angular steps. Due to high frequency collisions, a molecule can rotate through a very small angle before undergoing another reorienting collision. The rotational diffusion equation solved to obtain the rotational correlation time $\tau_r$ with the density function $\rho(\theta, \phi)$ is given by

$$\frac{\partial \rho}{\partial t} = D \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left[ \frac{1}{\sin \theta} \frac{\partial \rho}{\partial x} + \frac{1}{\sin^2 \theta} \frac{\partial^2 \rho}{\partial \phi^2} \right]$$

Where, $D$ is the rotational diffusion coefficient. For spherical particles $\rho$ satisfies the form $C_1(t) Y_{l,m}(\theta, \phi)$ in isotropic liquids, where $Y_{l,m}(\theta, \phi)$ are the Legendre polynomials and the coefficient $C_1(t)$ is fundamentally the same as the correlation function. Substitution of $\rho = C_1(t) Y_{l,m}(\theta, \phi)$ gives an ordinary differential equation for $C$ as

$$\frac{dC_1}{dt} = -Dl(l+1)C_1$$

This implies that the correlation function decays exponentially, $e^{-\eta t}$ and the correlation time is given by $\tau_r = [l (l +1) D]^{-1}$. In fluorescence depolarization experiments, one can estimate the anisotropy decay which is $l=2$ correlation and for this reason $\tau_r = (6D)^{-1}$. The rotational diffusion coefficient of a solute is given by the Stokes-Einstein model [1, 8, 9, 16] as

$$D = \frac{kT}{\xi}$$
where $\xi$ is friction coefficient and $kT$ is thermal energy. It is this friction, which is of great consequence in theoretical as well as experimental studies. A molecule rotating in a liquid experiences friction on account of its continuous interaction with its neighbours and the thirst to understand this inspirational force in carrying the experimental measurements of rotational reorientation in liquids.

### 3B.2.2 Hydrodynamic theory:

Mechanical friction on a rotating solute in solvent is computed employing hydrodynamic theory by treating the solute as a smooth sphere rotating in a continuum fluid [17], which is characterized by a shear viscosity. If ‘$a$’ is the radius of the molecule and ‘$\eta$’ the viscosity of the liquid, then according to Stokes law [8]

$$\xi_h = 8\pi \eta a^3$$  \hspace{1cm} 3B.5

Equation 3B.4 reduces to

$$D_r = \frac{kT}{8\pi \eta a^3} = \frac{kT}{\xi_h}$$  \hspace{1cm} 3B.6

The rotational correlation time $\tau_r$ is given by

$$\tau_r = \frac{1}{6D_r}$$  \hspace{1cm} 3B.7

$$= \frac{\xi_h}{6kT}$$

$$= \frac{\eta V}{kT}$$

Where, $V$ is the molecular volume. The most extensively used SED hydrodynamic equation for the description of rotational dynamics of spherical molecule is given by
\[
\tau_r = \tau_{SED} = \frac{\eta V}{kT} + \tau_0
\]  

3B.8

where, \( \tau_0 \) is the rotational reorientation time at zero viscosity. It is known that spherical approximation entrenched in SED equation is shiny in error and the shape of the probes is however, more important. In reality, the exact shape of the solute molecule need not be spherical and it is essential to include a parameter, which should describe the exact shape of nonspherical probes. Therefore, the equation for nonspherical molecule is proposed by Perrin [18] given as follows,

\[
\tau_r = \frac{\eta V}{kT} (fC)
\]  

3B.9

where \( f \) is referred to as a shape factor and is well specified, \( C \) is the boundary condition parameter reliant strongly on solute, solvent and concentration. The shape of the solute molecule is usually included into the model by treating them as either symmetric or asymmetric ellipsoids. For nonspherical molecules, \( f > 1 \) and the magnitude of deviation of \( f \) from unity describes the degree of the nonspherical nature of the solute molecule. \( C \) specifies the extent of coupling between the solute and the solvent and is known as the boundary condition parameter [19]. In the two limiting cases of hydrodynamic stick and slip for a nonspherical molecule, the value of \( C \) follows the inequality, \( 0 < C \leq 1 \) and the exact value of \( C \) is determined by the axial ratio of the probe. It is observed that the experimentally measured rotational reorientation times of a number of nonpolar solutes [20-32] could be described by the SED theory with slip boundary condition (sub slip behaviour). For homologous series of solvents such as alcohol or alkane, the normalized reorientation times decreased as the size of the solvent is increased. This behaviour known as "size effect" could not
be explained with SED theory. The SED theory takes only the size of the solute molecule into account and not that of the solvent. Quasihydrodynamic theories were developed to look into this aspect as well while in calculating the boundary condition.

3B.2.3 Dielectric friction theories:

When the motion regarding rotations of polar and charged solutes need to be explained, the simple hydrodynamic friction arising out of viscosity of the solvent becomes insufficient. A polar molecule rotating in a polar solvent experiences hindrance due to dielectric friction ($\zeta_{DF}$) in addition to the mechanical ($\zeta_{Mech}$) or hydrodynamic friction. In general, the dielectric and mechanical contributions to the friction are not separable as they are linked due to electrohydrodynamic coupling [11, 13, 15, 33-35]; it is possible to generalize the hydrodynamic treatment by using variable boundary conditions, which incorporates the dielectric solute-solvent coupling in the stress tensor. In spite of this nonseparability, it has been common practice to assume that the total friction experienced by the probe molecule is the sum of mechanical and dielectric friction components.

The research carried out in this field have been used in polar and nonpolar solvents to understand the influence of solute to solvent size ratio and solute shape on the friction experienced by the probe molecule, which in turn enabled us to test the hydrodynamic and quasihydrodynamic theories. The friction experienced by these nonpolar probes is purely mechanical because it is dominated by short-range repulsive forces between the molecules. The second class of studies, however, used probes that are polar and charged in polar solvents with the idea of understanding how the long-range electrostatic interactions between the solute and the solvent, which are charged dipole or dipole–dipole in nature, are influencing the rotational dynamics of the probe molecule. Polar molecule rotating in a polar solvent experiences hindrance due to
dielectric friction ($\xi_{DF}$) in addition to the mechanical ($\xi_{mech}$) or hydrodynamic friction. This extra friction arises because the solvent polarization induced by the polar probe must readjust when the solute tries to move, which is not instantaneous. If we assume that these two kinds of frictions are separable, then the total friction experienced by the rotating probe molecule is given by

$$\xi_{Total} = \xi_{mech} + \xi_{DF}$$  \hspace{1cm} 3B.10

The earliest research into dielectric effects on molecular rotation took place in the theoretical arena. Initial investigations were closely tangled with the theories of dielectric dispersion in pure solvents. The first paper by NZ [7] is to popularize the dielectric friction as related to rotational motion. In the later decades, numerous studies have made to improvements the NZ approach. These have included the “electro hydrodynamic” treatment, which explicitly considered the coupling between the hydrodynamic (viscous) damping and the dielectric friction components. Since the theoretical literature on rotational dielectric friction and especially on the connection between the dielectric relaxations is extensive, only the essential approaches that have most often been considered in experimental investigations of dielectric friction are described in the current study.

3B.2.4 Nee-Zwanzig theory:

Although not the first study, the most prominent early treatment of rotational dielectric friction was made by Nee-Zwanzig (NZ) [7]. These authors examined rotational dynamics of the same solute/solvent model in the “simple continuum” (SC) description i.e., they assumed an Onsager type cavity [33] dipole with dipole moment $\mu$ and radius $a$ embedded in a dielectric continuum with dispersion $\varepsilon(\omega)$. Motion was assumed to be purely diffusive limit. Using a boundary condition value calculation of
the average reaction field, NZ obtained their final result linking the dielectric friction contribution in the spherical cavity as

$$
\tau_{DF}^{NZ} = \frac{\mu^2(\varepsilon_0 + 2)^2(\varepsilon_0 - \varepsilon_\infty)}{9 a^3 kT (2\varepsilon_0 + \varepsilon_\infty)^2} \tau_D
$$

3B.11

Where \(\varepsilon_0, \varepsilon_\infty\) and \(\tau_D\) are the zero-frequency dielectric constant, high frequency dielectric constant and Debye relaxation time of the medium. If one assumes that the mechanical and dielectric components of friction are separable, then

$$
\tau^{obs}_r = \tau_r + \tau_{DF}
$$

3B.12

Therefore, the observed rotational reorientation time \(\tau_r\) is given as the sum of reorientation time calculated using SED hydrodynamic theory and dielectric friction theory.

$$
\tau_r = \frac{\eta V f C}{kT} + \frac{\mu^2 (\varepsilon_0 + 2)^2(\varepsilon_0 - \varepsilon_\infty)}{9 a^3 kT (2\varepsilon_0 + \varepsilon_\infty)^2} \tau_D
$$

3B.13

It is clear from the above equation that for a given solute molecule, the dielectric friction contribution would be significant in a solvent of low \(\varepsilon\) and high \(\tau_D\). However, if the solute is large, the contribution due to dielectric friction becomes small and the relative contribution to the overall reorientation time further diminishes due to a steep increase in the hydrodynamic contribution. Hence, the most pronounced contribution due to dielectric friction could be seen in small molecules with large dipole moments especially in solvents of low \(\varepsilon\) and high \(\tau_D\).

3B.2.5 Vander Zwan-Hynes theory:

The semi empirical method for finding dielectric friction has been proposed by Van der Zwan and Hynes (VZH)[5], which is an improvement over the NZ [7]
model because it provides a recommendation for determining the dielectric friction from the measurements of the response of solute in the solvent of interest. This model relates the dielectric friction experienced by a solute in a solvent to the solvation time $\tau_S$ and the solute Stokes shift, $S$. According to this model the dielectric friction is given by

$$\tau_{DF} = \frac{\mu^2}{(\Delta\mu)^2} \frac{S\tau_S}{6kT}$$

where $\Delta\mu$ is difference in dipole moments of the solute in ground and excited states.

$$S = h\nu_a - h\nu_f$$

$h\nu_a$ and $h\nu_f$ are the energies of the 0-0 transitions of the absorption and fluorescence respectively.

Assuming the separability of the mechanical and dielectric friction components, the rotational reorientation time can be expressed as

$$\tau_{\text{obs}} = \frac{\eta V f C}{kT} + \frac{\mu^2}{(\Delta\mu)^2} \frac{hc\Delta\nu}{6kT} \tau_S$$

where the first term represents the mechanical contribution and second term is dielectric contribution.

**3B.2.6. Alavi and Waldeck theory:**

Alavi and Waldeck (AW) theory is to be considered as a final theory [11, 36-38]. According to this theory, it is the charge distribution of the solute rather than the dipole moment that is used to calculate the friction experienced by the solute molecule. Thus not only the dipole moment of the solute but also the higher order moments contribute significantly to the dielectric friction. In other words, molecules
having no net dipole moment can also experience dielectric friction. The AW theory has been found to be successful when compared to NZ and VHZ theories in modelling the friction experienced by the solutes in nonassociative solvents. The expression for the dielectric friction according to the AW model is given by

$$\tau_{DF} = P \frac{(\varepsilon_0 - 1)}{(2\varepsilon_0 + 1)^2} \tau_D$$

where

$$P = \sum_{j=1}^{N} \sum_{i=1}^{N} L_{\text{max}} \sum_{L} \sum_{M=1}^{L} \frac{(2L + 1)}{(L + 1)} \frac{(L-M)!}{(L+M)!} X$$

$$M^2 q_i q_j \left( \frac{r_i}{r_j} \right)^L \left( \frac{r_j}{r_i} \right)^L P^M_L(\cos \theta_i) P^M_L(\cos \theta_j) \cos M \phi_{ji}$$

Where $P^M_L(x)$ associated Legendre polynomials, "$a$" is the cavity radius, $N$ is the number of partial charges, $q_i$ is the partial charge on atom $i$, whose position is given by $(r_i, \theta_i, \phi_i)$ and $\phi_{ji} = \phi_j - \phi_i$. Although the AW theory also treats solvent as a structure less continuum like the NZ and VHZ theories, it provides a more realistic description of the electronic properties of the solute.

**3B.3. Dielectric friction model:**

The effect of dielectric friction on rotational reorientation times is particularly important in the case of a polar Red Mega 480 dye molecule in polar solvents such as alcohols. Both Hubbard [33-34] and Wolynes [39] and Madden and Kivelson [40] generalized the NZ theory by introducing the orientation tensor of an arbitrary rank. In the zero frequency limits for the friction coefficient both results are comparable to that of NZ. By some adequate assumptions as that the rotation of the solute is slow in comparison with the torque fluctuations, within a dielectric continuum model for the
solvent, the following expression for the dielectric relaxation time $\tau_{DF}$ for second-order ($l = 2$) rotation in solvent with a small dielectric relaxation time $\tau_D$ is given by [39]:

$$\tau_{DF} = \frac{\mu_e^2}{kT a^3} \frac{\varepsilon - 1}{(2\varepsilon + 1)^2} \tau_D \quad \text{3B.18}$$

$$\tau_r = \frac{\eta V f C}{kT} + \frac{\mu_e^2}{kT a^3} \frac{\varepsilon - 1}{(2\varepsilon + 1)^2} \tau_D \quad \text{3B.19}$$

$$\tau_r = \tau_h + \tau_{DF} \quad \text{3B.19}$$

where $\mu_e$ is the dipole moment of Red Mega 480 in the excited state, $\varepsilon$ and $\tau_D$ refer to the dielectric constant and Debye dielectric relaxation time of the solvent, respectively; $a$ is the cavity radius in which the Red Mega 480 rotates and $k$ is the Boltzmann constant.

3B.4. Basic information on dielectric intrinsic relaxation time $\tau_D$:

The Debye theory [10] of the relaxation time $\tau_D$ leads for a rotating probe with the following principle:

$$\tau_D = \frac{4\pi\eta r^3}{kT} \quad \text{3B.20}$$

where $\eta$ viscosity coefficient of the medium and $r$ is radius of the dipolar molecule of the solvent. It follows from that $\tau_D$ is proportional to the volume $V = \frac{4}{3}\pi r^3$ of the polar molecule and to the viscosity $\eta$ of the medium, as experimentally shown [40-42]. Equation 3B.20 is a rough approximation, because it was derived for a simplified model. Equation 3B.20 has been derived under the assumption that we deal with a diluted solution and the polar molecules are of spherical shape and do not
interact as they are separated by a sufficiently large distance. Better approximation is, as shown by Perrin [18, 43] as well as Budo [44-46], an assumption of a molecule as an ellipsoid, in particular an ellipsoid of revolution. In this case three components $\mu_1$, $\mu_2$, $\mu_3$ of the permanent dipole moment along the molecular axes are connected with three relaxation times $\tau_{D1}$, $\tau_{D2}$, $\tau_{D3}$, respectively. When the dipole moment vector is directed along one of the axes of the molecule ($\mu_2 = \mu_3 = 0$), only one relaxation time will be found. If the molecule must be treated as an ellipsoid of revolution then it is necessary to introduce two relaxation times.

Fischer [47-49] has investigated the influence of chain length increase on the relaxation time $\tau_D = \tau_{D1}$ for a series of normal alcohols for infinite dilution in nonpolar benzene by performing measurements of dielectric loss with the calorimetric method [49]. He has found that the direction of the dipole moment is almost perpendicular to the long axis of the molecule and observed similarly [50-56] as in the case of normal ketones and monochlorides only one relaxation time $\tau_D$. Then Cole and Cole [50] by analyzing the results of Slevogt [51] for alcohols have found only a single relaxation time for each alcohol as well. Fischer has found smaller values of $\tau_D$ and increase with the chain length in the case of alcohols due to free rotation of -OH group compared to ketones and monochlorides. Table 3B.3 shows the results of measurements of $\tau_D$ for some alcohols [53, 56] at 298 K.

The measurements of Garg and Smyth [52] confirm the existence of three dielectric dispersion regions in the pure straight chain alcohols. Table 3B.3 shows $\tau_D$ (Debye relaxation time) collected by Dutt and Ghanty [53, 54] for pure n-alcohols. $\tau_D$ was assumed to be single exponential decay given by the longest dielectric relaxation time ($\tau_{DF}$) in alcohol solvents [55] exhibited by probe.
3B.5 Experimental:

3B.5.1 Materials:

Red Mega 480 dye is chosen as a probe molecule to study the solute-solvent interactions by determining their rotational orientation times in series of solvents. The fluorescence anisotropy and lifetime were measured in all chosen solvents. Methanol, ethanol, propanol, butanol, decanol, nonanol, octanol and glycerol, all these solvents are of spectroscopic grade and are of the highest available purity from Aldrich.

3B.5.2 Experimental techniques:

Steady state fluorescence spectra of all the samples were recorded using Fluorescence spectrophotometer (Hitachi, F-7000). Absorption spectra are recorded using Ocean Optics spectrophotometer. Reorientation times of Red Mega 480 are measured using steady state depolarization technique in various spectroscopic grade solvents. Fluorescence life time measurements are made on Time Correlated Single Photon Counting Technique (TCSPC) (Chronos BH Time correlated single photon Counting system) used in our present study.

3B.5.3 Fluorescence anisotropy:

Measurement of fluorescence anisotropy is a powerful tool in physics, chemical, biological research and medical testing. Upon excitation with polarized light the emission from many samples is also polarized. The extent of polarization of the emission is described in terms of the anisotropy $<r>$. Samples exhibiting non zero anisotropies are said to display polarized emission. The origin of anisotropy is the existence of transition moments for absorption and emission that lie along specific directions within the fluorophore structure. When exposed to polarized light, those
fluorophores having their absorption transition moments oriented along the electric vector of the incident light are preferentially excited. Hence, the excited state population is partially oriented. A significant fraction of the excited molecules have their transition moments oriented along the electric vector of the polarized exciting light.

3B.5.4 Anisotropy measurements:

Polarized light striking a fluorescent molecule results in polarized fluorescence. This polarized emission gradually returns to unpolarized fluorescence depending on rotational diffusion and other factors. Anisotropy is directly related to the polarization, and is the ratio of the polarized light component to the total light intensity. With optional polarisers installed in a spectrofluorometer, we define light intensities as:

- $I_{VV}$ is with excitation and emission polarisers mounted vertically.
- $I_{HH}$ is with excitation and emission polarisers mounted horizontally.
- $I_{VH}$ is with excitation polarizer vertical and emission polarizer horizontal.
- $I_{HV}$ is with excitation horizontal and emission polarizer vertical.

The basic setup we used in our present study is called "L-format or Single channel method" (Figure 2.9). Absorption and emission spectra of Red Mega 480 is recorded with different solvents (Figure 3B.1).

Mathematically, anisotropy $\langle r \rangle$ is defined as [16, 31]

$$\langle r \rangle = \frac{I_{HV} - GI_{VH}}{I_{VV} + 2GI_{VH}}$$  \hspace{1cm} 3B.21

where $G$ is called instrument factor and is given by

$$G = \frac{I_{HV}}{I_{HH}}$$
Chapter IIIB: Dielectric Friction Studies of a Laser Dye

Anisotropy provides useful information about the molecular size, shape, local viscosities of a fluorophore's environment, as well as offering insight into changes in molecular sizes of polymers and other macromolecules.

The reorientation time \( \tau_r \) of Red Mega 480 is measured using a steady-state fluorescence depolarization method using the equation

\[
\tau_r = \frac{\tau_f}{\left( \frac{r_0}{<r>} - 1 \right)} \tag{3B.22}
\]

\( r_0, \tau_f \) and \( \tau_r \) are the limiting anisotropy (with respect to glycerol), fluorescence lifetime, and reorientation time, respectively. A Hitachi F-7000 spectrofluorometer was used to measure steady-state anisotropies.

3B.6 Results and discussion:

Experimental data of emission anisotropy \(<r>\), and mean fluorescence lifetime \( \tau_f \), for Red Mega 480 in selected alcohol solvents of different viscosities (\( \eta \)), with solute concentration 5 x 10^{-5} M and the calculated values of total reorientation time \( \tau_r \) is given in Table 3B.2. Graphs are plotted as a function of viscosity (\( \eta \)) and density against the \( \tau_r \) are presented in Figure. 3B.2 and 3B.3. The results of \( \tau_{DF} \) versus \( \eta \) for Red Mega 480 fit fairly well with the straight line in Figure 3B.4. The dielectric friction given by Equation 3B.18 results an additional correction to the sum of rotational relaxation times and product of two quantities \( \frac{\mu_2^2}{kT \alpha^3} \) and \( \frac{\varepsilon-1}{(2\varepsilon+1)\tau_D} \) with the same fluorescent solute and dielectric properties of the solvent respectively. Table 3B.1 contain the values of dipole moments in the excited and ground state dipole moment state for Red Mega 480. Calculated values of \( \tau_{DF} \) are recorded in Table 3B.3.
Figure 3B.3 illustrates the dependencies of $\tau_{DF}$ calculated from Equation 3B.20 as a function of $\eta$ for several alcohols mentioned in Table 3B.3. Linear increase of $\tau_{DF}$ as a function of viscosity $\eta$ is observed. For Red Mega 480 in view of its small dipole moment in the excited state $\mu_e = 5.99$ D (see Table 3B.1) the contribution of the dielectric friction to the total friction is very small due to the fact that the variability range of the parameter of a strongly polar Red Mega 480. Kawski and Bojarski [56], Dutt et al. studied in detail for Nile Red [57]. Most of researchers applied the simplified Lippert–Mataga expression to calculate $\mu_e$, but in the Lippert's theory [58] the polarizability of solute is neglected [59-61]. So, recently we have determined the electric dipole moments in the ground $\mu_g$ and in the excited state $\mu_e$ with five methods (Table 3B.1): solvatochromic, Lippert, Suppan, microscopic polarity $E_N^\tau$ and Mc Rae and we have come to the conclusion that solvatochromic method is the best of the available methods. In all the cases obtained values of excited state and ground state dipole moment is given in Table 3B.1. Figure 3B.4 shows the dependencies of $\tau_{DF}$ versus viscosity $\eta$ (with Onsager radii $a = 4.53$ Å). This in turn leads to more and more distinct difference of $\tau_{DF}$ between particular alcohol solvents. Fluorescence life time measurements of Red Mega 480 dye in butanol and decanol is shown in Figure 3B.5 and 3B.6.

3B.7 Conclusions:

It was concluding from the experimental data of dipole moments in the excited state $\mu_e$ that the rotating polar fluorescent molecule Red Mega 480 in polar solvents like alcohols undergoes not only mechanical friction (hydrodynamic and inertial effects) but also dielectric friction [57, 54, 56, 59-61]. The magnitude of this dielectric friction depends mostly on $\frac{\mu_e^2}{a^3}$. In the case of strongly polar Red Mega 480
molecule in a series of alcohols from methanol (\(\eta=0.54\text{cP}\)) to nonanol (\(\eta=9.12\text{cP}\)) the dielectric relaxation time \(\tau_{DF}\) increases from 3.75ps to 309.91ps i.e. 82-83 times.

The rotating probe molecule experiences more friction as the size of the solute-solvent complexe increases. However, the nature of the function group on the solute molecule plays an important role in forming a stable solute-solvent complex which in turn delays the probe rotation. The weak hydrogen bonds that may also be formed between the carbonyl group of the solute [63] and the hydroxyl groups of the solvent molecules will add further to the slower rotation of the molecule. Dielectric function theories NZ and VZH, which treat the solute as a point dipole, overestimate the dielectric friction contribution, exhibited by Red Mega 480 dye in alcohols.
3B.8 References:


Table 3B.1 Ground-state, Excited state Dipole moment of Red Mega480 dye.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Onsager Cavity radius ‘a’ (Å)</th>
<th>$\mu_g$ (^a) (D)</th>
<th>$\mu_e$ (^b) (D)</th>
<th>$\mu_e$ (^c) (D)</th>
<th>$\mu_e$ (^d) (D)</th>
<th>$\mu_e$ (^f) (D)</th>
<th>$\mu_e$ (^h) (D)</th>
<th>$\mu_e$/$\mu_g$ (^i)</th>
<th>$\Phi$ (^j)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RedMega480</td>
<td>4.53</td>
<td>1.54</td>
<td>5.99</td>
<td>8.97</td>
<td>17.42</td>
<td>58.43</td>
<td>2.95</td>
<td>3.89</td>
<td>1.82 (^0)</td>
</tr>
</tbody>
</table>

1 Debye=3.33564 X 10\(^{-30}\) Cm=10\(^{-18}\) esu cm.

\(^a\) Ground state dipole moment calculated from Equation 3.16

\(^b\) Excited state dipole moment calculated from Equation 3.17 Solvatochromic method,

\(^c\) Excited state dipole moment calculated from Lippert’s Equation 3.11

\(^d\) Excited state dipole moment calculated from Mc Rae’s Equation 3.14

\(^f\) Excited state dipole moment calculated from Suppan’s Equation 3.15

\(^h\) Excited state dipole moment calculated from microscopic solvent polarity function $E_T^S$

\(^i\) Ratio of excited to ground state dipole moments calculated from Equation 3.18

\(^j\) Angle between excited state to ground state dipole moment with solvatochromic data
Table 3B.2 Solvent parameters, anisotropy $<\epsilon>$, fluorescence life time $<\tau_f>$ and reorientation time $\tau_r$ of Red Mega 480 in various alcohol solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Viscosity[62] $\eta$ (cP)</th>
<th>Density[62] $\rho$</th>
<th>$&lt;\epsilon&gt;$</th>
<th>$\tau_f$ (ns)</th>
<th>$\tau_r$ (ps)</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>0.54</td>
<td>0.791</td>
<td>0.1286</td>
<td>0.896</td>
<td>458.5</td>
<td>1.09</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1.07</td>
<td>0.789</td>
<td>0.0757</td>
<td>1.53</td>
<td>380.3</td>
<td>1.05</td>
</tr>
<tr>
<td>Propan-ol</td>
<td>2.04</td>
<td>0.803</td>
<td>0.1096</td>
<td>1.47</td>
<td>595.8</td>
<td>0.95</td>
</tr>
<tr>
<td>Butanol</td>
<td>2.54</td>
<td>0.81</td>
<td>0.1393</td>
<td>1.65</td>
<td>954.5</td>
<td>1.02</td>
</tr>
<tr>
<td>Decanol</td>
<td>8.97</td>
<td>0.829</td>
<td>0.2460</td>
<td>1.75</td>
<td>3212.6</td>
<td>0.97</td>
</tr>
<tr>
<td>Nonanol</td>
<td>9.12</td>
<td>0.827</td>
<td>0.2102</td>
<td>1.59</td>
<td>1967.4</td>
<td>1.01</td>
</tr>
<tr>
<td>Octanol</td>
<td>7.29</td>
<td>0.826</td>
<td>0.2395</td>
<td>1.57</td>
<td>2677.6</td>
<td>1.01</td>
</tr>
</tbody>
</table>

Table 3B.3 Solvent parameters, Dielectric relaxation time of various solvents ($\tau_D$) and Debye dielectric relaxation time ($\tau_{DF}$) of Red Mega 480 in various pure alcohol solvents in the dielectric friction model.

<table>
<thead>
<tr>
<th>SI No</th>
<th>Solvent</th>
<th>Viscosity $\eta$ (cP)</th>
<th>Dielectric constant $\epsilon$</th>
<th>Dielectric relaxation time at 298K $\tau_D$ (ps) [53,56]</th>
<th>$\epsilon - 1 \over (2\epsilon + 1)^2 \tau_D$</th>
<th>$\epsilon - 1 \over (2\epsilon + 1)^2 \tau_{DF}$</th>
<th>$\tau_{DF}$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Methanol</td>
<td>0.54</td>
<td>32.63</td>
<td>55.6</td>
<td>0.0072</td>
<td>0.4003</td>
<td>3.75</td>
</tr>
<tr>
<td>2</td>
<td>Ethanol</td>
<td>1.07</td>
<td>24.30</td>
<td>139.0</td>
<td>0.0095</td>
<td>1.3205</td>
<td>12.39</td>
</tr>
<tr>
<td>3</td>
<td>Propanol</td>
<td>2.04</td>
<td>20.10</td>
<td>362.0</td>
<td>0.0113</td>
<td>4.0725</td>
<td>38.20</td>
</tr>
<tr>
<td>4</td>
<td>Butanol</td>
<td>2.54</td>
<td>17.40</td>
<td>482.0</td>
<td>0.0128</td>
<td>6.1696</td>
<td>57.87</td>
</tr>
<tr>
<td>5</td>
<td>Decanol</td>
<td>8.97</td>
<td>8.00</td>
<td>1639.0</td>
<td>0.0242</td>
<td>39.6638</td>
<td>372.05</td>
</tr>
<tr>
<td>6</td>
<td>Nonanol</td>
<td>9.12</td>
<td>9.00</td>
<td>1495.0</td>
<td>0.0221</td>
<td>33.0395</td>
<td>309.91</td>
</tr>
<tr>
<td>7</td>
<td>Octanol</td>
<td>7.25</td>
<td>10.34</td>
<td>1350.0</td>
<td>0.0199</td>
<td>26.8650</td>
<td>251.99</td>
</tr>
</tbody>
</table>
Figure 3B.1 The typical absorption and fluorescence spectra of Red Mega 480 Dye molecule in ethanol solvent.

Figure 3B.2 Reorientation time of Red Mega 480 dye in various solvents versus Viscosity (mP) (1-Methanol, 2-Ethanol, 3-Propanol, 4-Butanol, 5-Decanol, 6-Nonanol, 7-Octanol)
Figure 3B.3 Reorientation time of Red Mega 480 dye in various solvents versus Density (mP) (1-Methanol, 2-Ethanol, 3-Propanol, 4-Butanol, 5-Decanol, 6-Nonanol, 7-Octanol)

Figure 3B.4 Effect of dielectric friction time of Red Mega 480 dye in various solvents versus Viscosity (mP) (1-Methanol, 2-Ethanol, 3-Propanol, 4-Butanol, 5-Decanol, 6-Nonanol, 7-Octanol)
Figure 3B.5  Life time measurements of Red Mega 480 dye in butanol.
Figure 3B.6 Life time measurements of Red Mega 480 dye in decanol.