CHAPTER IV

ROTATIONAL DYNAMICS OF NONPOLAR AND POLAR PROBES
IV. ROTATIONAL DYNAMICS OF NONPOLAR AND POLAR PROBES

IV.1. INTRODUCTION

Quest to understand the nature of solute-solvent interaction has been a great deal of interest in physico-chemical processes because of the importance of these interactions in determining properties such as chemical reaction yield and kinetic or the ability to isolate one compound from another. Interactions between the solutes and their surrounding solvent molecules are difficult to resolve because, unlike in solids, the spatial relationship between the molecules in liquids are not fixed on time scales that can be accessed using structural measurements such as X-ray diffraction or multidimensional NMR spectrometry. Intermolecular interactions in the liquid phase are more complex than those in gas phase due to their characteristic strength, the property that gives rise to the liquid phase and at the same time prevents a simple statistical description of collisional interactions from providing adequate insight [1].

Despite almost more than three decades of continuous investigation, the details of solute-solvent interactions, particularly in polar solvent systems, remain to be understood in detail. Most investigations of intermolecular interactions in solution have used a “probe” molecule present at low concentration in neat or binary solvent systems. Typically, a short pulse of light is shone to establish some non-equilibrium condition in the ensemble of probe molecules, with the object of the experiment being to monitor the return to equilibrium. Such studies have included fluorescence lifetime, molecular reorientation [2-28], vibrational relaxation [29-41] and time-dependent fluorescence Stokes shift [42-51] measurements. Of these, molecular reorientation of molecules in solution has been an important experimental and theoretical concept for probing the nature of liquids and the interactions of solvents with molecules. This has proven to be among the most useful because
of the combined generality of the effect and the well-developed theoretical framework for the interpretation of the experimental data [52-57]. Though, the effect of solute-solvent interactions on the rotational motion of a probe molecule in solution has been extensively studied, these interactions are generally described as friction to the rotational motion of the probe and can be classified into three types. The first category includes short-range repulsive forces, which dominate intermolecular dynamics during molecular collisions. These are present in all liquids and lead to viscous dissipation, which is well described by hydrodynamic theories [1]. The second category includes long-range electrostatic interactions between a charged or dipolar probe and polar solvent molecules. As the solute turns, the induced solvent polarization can lag behind rotation of the probe, creating a torque, which systematically reduces the rate of rotational diffusion. This effect, termed dielectric friction, arises from the same type of correlated motions of solvent molecules, which are responsible for the time dependent Stokes shift (TDSS) [58, 59] dynamics of fluorescent probes [60, 61]. The third category includes specific solute-solvent interactions. Hydrogen bonding is probably the most frequently encountered example of this kind. Strong hydrogen bonds will lead to the formation of solute-solvent complexes of well-defined stochiometry. These new, larger species can persist in solution for fairly long times and will rotate more slowly than the bare solute. Formation and breakage of H bonds occurring on time scales faster than the probe rotation will provide a channel for rotational energy dissipation giving rise to additional friction.

The theoretical interest in the study of rotational reorientation kinetics of molecules in liquids arises from the fact that it provides information about the intermolecular interaction in the condensed phase. However, the theoretical
modeling of molecular reorientation in liquids and its correlation with experimental data is still far from satisfactory. So far, two kinds of approaches have been employed in understanding the rotational dynamics. In the first approach, binary collision approximation has been used to explain the rotational dynamics. With this approach, kinetic theory model for rotational relaxation has been employed by Widom, Rider and Fixman, and Chandler [62-64] for rough sphere fluids and by Evans et al. [65-67] for smooth convex bodies. Evans model along with Enskog equation for viscosity has been employed to express rotational reorientation time ($\tau_r$) as a function of the solvent viscosity. However, explaining rotational dynamics from such a molecular point of view is severely constrained on account of multibody interaction in a fluid. For real systems the quantitative predictions can be made about the variation of $\tau_r$ with solvent viscosity. The second, is the macroscopic approach of understanding the rotational dynamics, where the solvent is assumed to be a structureless continuum and the rotational motion of solutes is considered Markovian or diffusional. A considerable degree of success on the rotational dynamics arises from the Stokes-Einstein-Debye (SED) hydrodynamic theory, which forms the basis of understanding molecular rotations of medium sized molecules (few hundred $\text{Å}^3$ volumes) in liquids [52, 68, 69], according to which the rotational reorientation time ($\tau_r$) of a solute molecule is proportional to its volume ($V$), bulk viscosity ($\eta$) of the solvent and inversely related to its temperature ($T$).

The SED theory has been found to describe the rotational dynamics of medium sized molecules fairly well when the coupling between the solute and solvent is purely mechanical or hydrodynamic in nature. It has been reported that the SED model correctly predicts the linear dependence of the rotational
reorientation times on the solvent viscosity for polar and cationic dyes dissolved in polar and non-polar solvents [70-84] that have been interpreted using dielectric fiction theories. The dielectric friction can be modeled using continuum theories of Nee-Zwanzig (NZ) [85], which treats the solute as a point dipole rotating in a spherical cavity. Alavi-Waldeck (AW) [86, 87] model is an extension of the NZ theory where the solute is treated as a distribution of charges instead of point dipole and the semiempirical approach of van der Zwan and Hynes (ZH) [60] in which fluorescence Stokes shift of the solute in a given solvent is related to dielectric friction. On the other hand, the results of neutral and nonpolar solutes deviate significantly from the hydrodynamic predictions at higher viscosities [88-101]. 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 [55] assumes the solute-solvent coupling parameter to be less than unity, contrary to the stick boundary condition. Quasihydrodynamic theories of Gierer and Wirtz (GW) [102] and Dote, Kivelson and Schwartz (DKS) [103] attempt to improve upon SED theory by taking into consideration not only the size of the solute but also that of the solvent molecule, thereby modifying the boundary conditions. It has been argued [92, 93] 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 description of rotational reorientation dynamics, two kinds of solutes categorized as nonpolar and polar has been chosen in the present study. In the first case, where the nonpolar probes embedded in polar or nonpolar solvents to examine the influence of solute to solvent size ratio and
the shape of the solute on the friction experienced by the probe molecule which in turn enables us to test the validity of hydrodynamic and quasihydrodynamic theories. The friction experienced by these probes is purely hydrodynamic or mechanical in nature since it is dominated by short-range repulsive forces. In the latter case of studies, however, polar probes used in charged polar solvents with an intention of understanding how the long-range electrostatic interactions between the solute and the solvent, which are charge-dipole or dipole-dipole in nature, influence the rotational dynamics of the probe molecules. Dielectric friction on a rotating solute arises because of the polar molecule entrenched in a dielectric medium polarizes the surrounding dielectric. As the solute tries 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.

IV.2. THEORETICAL BACKGROUND

Among many proposed models for the rotational motion, the most commonly employed is the rotational diffusion model outlined by Debye [52], in which the reorientation is assumed to occur in small angular steps. On account of 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 $\tau_r$ of the density function $\rho(\theta, \phi)$ is given by

$$\frac{\partial \rho}{\partial t} = D \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left[ \frac{1}{\sin \theta} \frac{\partial \rho}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2 \rho}{\partial \phi^2} \right]$$  \hspace{1cm} (4.1)

where $D$ is the rotational diffusion coefficient. For spherical particles $\rho$ satisfies the form $C_i(t) Y_{i,m}(\theta, \phi)$ in isotropic liquids, where $Y_{i,m}(\theta, \phi)$ are the Legendre
polynomials and the coefficient $C_1(t)$ is essentially 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

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

(4.2)

This implies that the correlation function decays exponentially, $e^{-t/\tau}$ and the correlation time $\tau_i = \left[l(l+1)D\right]^{-1}$. In fluorescence depolarization experiments, one measures the anisotropy decay which is $l=2$ correlation and hence $\tau_r = (6D)^{-1}$.

The rotational diffusion coefficient of a solute is given by the Stokes-Einstein model [1] as

$$D = \frac{kT}{\zeta}$$

(4.3)

where $\zeta$ is the friction coefficient and $kT$ is the thermal energy. It is this friction, which is of great importance in theoretical as well as experimental studies. A molecule rotating in liquid experiences friction on account of its continuous interaction with its neighbors and the desire to understand has been a motivating force in carrying the experimental measurements of rotational reorientation in liquids.

IV.2.1. 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, 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 [68]
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\[ \zeta = 8\pi a^3 \eta \]  \hspace{1cm} (4.4)

Eqn. (4.3) reduces to

\[ D = \frac{kT}{8\pi \eta a^3} \]  \hspace{1cm} (4.5)

The rotational correlation time \((\tau_r)\) is given by

\[ \tau_r = \frac{1}{6D} = \frac{\zeta}{6kT} \]  \hspace{1cm} (4.6)

Substitution of Eqn. (4.4) in (4.6) gives

\[ \tau_r = \frac{\eta V}{kT} \]  \hspace{1cm} (4.7)

where \(V\) is the molecular volume. The most widely used SED hydrodynamic equation for the description of rotational dynamics of spherical molecule is given by

\[ \tau_r = \frac{\eta V}{kT} + \tau_0 \]  \hspace{1cm} (4.8)

where \(\tau_0\) is the rotational reorientation time at zero viscosity. It is known that spherical approximation embedded in SED equation is glossy 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 necessary to include a parameter, which should describe the exact shape of nonspherical probes. Hence, the equation for nonspherical molecule is proposed by Perrin [53] given as follows

\[ \tau_r = \frac{\eta V}{kT} (fC) \]  \hspace{1cm} (4.9)

where \(f\) is referred to as a shape factor and is well specified, \(C\) is the boundary condition parameter dependent strongly on solute, solvent and concentration. The shapes of the solute molecules are usually incorporated 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. \( C \), signifies the extent of coupling between the solute and the solvent and is known as the boundary condition parameter [55]. 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 [88-101] could be described by the SED theory with slip boundary condition (subslip behavior). For homologous series of solvents such as alcohols or alkanes, the normalized reorientation times decreased as the size of the solvent is increased. In other words, the reorientation times did not scale linearly with solvent viscosity. This behavior known as “size effect” could not be explained with the SED theory. The SED theory takes only the size of the solute molecule into consideration and not that of the solvent. Quasihydrodynamic theories were developed to look into this aspect as well while calculating the boundary condition.

IV.2.2. Quasihydrodynamic Theory

While the SED hydrodynamic theory takes only the size of the solute molecule into account, one need to focus by taking the size of the solute as well as solvent molecules into consideration. Quasihydrodynamic theories take into consideration not only the size of the solute but also that of the solvent molecule and modify the boundary condition accordingly. To explain such
observed size effects, two quasihydrodynamic theories by Gierer and Wirtz (GW) and Dote, Kivelson and Schwartz (DKS) were developed.

**IV.2.2.1. The Gierer and Wirtz Theory**

The first and the relatively old theory proposed by Gierer and Wirtz (GW) [102] in 1953, takes into account both the size of the solute as well as that of the solvent while calculating the boundary condition. This theory visualizes the solvent to be made up of concentric shells of spherical particles surrounding the spherical probe molecule at the center. Each shell moves at a constant angular velocity and the velocity of successive shells decreases with the distance from the surface of the probe molecule, as though the flow between the shells is laminar. As the shell number increases, i.e., at large distances, the angular velocity vanishes. The angular velocity $\omega_1$ of the first solvation shell is related to the angular velocity $\omega_0$ of the probe molecule by means of a sticking factor $\sigma$.

$$\omega_1 = \sigma \omega_0$$

(4.10)

When, $\sigma = 1$, it gives the stick boundary condition and $\sigma$ is related to the ratio of the solute to solvent size, and is given by

$$\sigma = \left[ 1 + 6 \left( \frac{V_s}{V_p} \right)^{1/3} C_0 \right]^{-1}$$

(4.11)

where

$$C_0 = \left[ \frac{6(V_s/V_p)^{1/3}}{1 + 2(V_s/V_p)^{1/3}} \right] + \left[ \frac{1}{1 + 4(V_s/V_p)^{1/3}} \right]^{-1}$$

(4.12)

$V_s$ and $V_p$ are the volumes of the solvent and probe, respectively. The expression for $C_{GW}$ is given by
\[ C_{GW} = \sigma C_0 \]  

(4.13)

C in Eqn. (4.9) should be replaced with \( C_{GW} \) obtained from Eqn. (4.13) for calculating the reorientation times with GW theory. When the ratio \( V_J / V_P \) is very small \( C_{GW} \) reduces to unity and the SED equation with stick boundary condition is obtained.

**IV.2.2.2. The Dote-Kivelson-Schwartz Theory**

Although, the GW theory successfully predicts the observed size effects in a qualitative way, it could not explain the faster rotation of nonpolar probes in alcohols as compared to alkanes. Hence, the second quasihydrodynamic theory, which is relatively new, was proposed by Dote, Kivelson and Schwartz (DKS) [103], in 1981. The DKS theory not only takes into consideration the relative sizes of the solvent and the probe but also the cavities or free spaces created by the solvent around the probe molecule. If the size of the solute is comparable to the free spaces in the solvents, the coupling between the solute and the solvent will become weak, which results in reduced friction experienced by the probe molecule. According to DKS theory the solute-solvent coupling parameter, \( C_{DKS} \) is given by

\[ C_{DKS} = (1 + \gamma / \phi)^{-1} \]  

(4.14)

where \( \gamma / \phi \) is the ratio of the free volume available for the solvent to the effective size of the solute molecule, with

\[ \gamma = \frac{\Delta V}{V_p} \left[ 4 \left( \frac{V_P}{V_s} \right)^{2/3} + 1 \right], \]  

(4.15)

and \( \phi \) is the ratio of the reorientation time predicted by slip hydrodynamics to the stick prediction for the sphere of same volume. \( \Delta V \) is the smallest volume of free space per solvent molecule and some discretion must be applied while
calculating this term \([84, 96, 104]\). It is empirically related to the solvent viscosity, the Hilderbrand-Batchinsky parameter \(B\) and the isothermal compressibility \(k_T\) of the liquid by

\[
\Delta V = Bk_T \eta k_T .
\]

Since the Frenkel hole theory and the Hilderbrand treatment of solvent viscosity were developed for regular solutions [96], Eqn. (4.16) may not be a valid measure of the free space per solvent molecule for associative solvents like alcohols and polyalcohols. Hence, for alcohols \(\Delta V\) is calculated using

\[
\Delta V = V_m - V_s
\]

where \(V_m\) is the solvent molar volume divided by the Avagadro number.

**IV.2.3. Dielectric Friction Theories**

When the motion concerning rotations of polar and charged solutes need to be described, the simple hydrodynamic friction arising out of viscosity of the solvent becomes inadequate. A polar molecule rotating in a polar solvent experiences hindrance due to dielectric friction (\(\zeta_{DF}\)) in addition to the mechanical (\(\zeta_M\)) or hydrodynamic friction. In general, the dielectric and mechanical contributions to the friction are not separable as they are linked due to electrohydrodynamic coupling [103, 105-109]. It is possible to generalize the hydrodynamic treatment by using a variable boundary condition, which incorporates the dielectric solute-solvent coupling in the stress tensor. Despite 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, i.e.,

$$\zeta_{\text{Total}} = \zeta_M + \zeta_{DF}.$$  \hfill (4.18)

Mechanical friction can be modeled using both hydrodynamic \[52\] and quasi-hydrodynamic \[102, 103\] theories, whereas, dielectric friction is modeled using continuum theories.

The earliest research into dielectric effects on molecular rotation took place in the theoretical arena. Initial investigations were closely intertwined with the theories of dielectric dispersion in pure solvents \[110-112\]. The first paper to popularize the dielectric friction as related to rotational motion was an article by Nee and Zwanzig in 1970 \[85\]. In the latter decades, a number of studies have criticized and made improvements to the Nee-Zwanzig approach \[60, 86, 87, 107, 108, 113-120\]. These have included the “electrohydrodynamic” 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 present study.

**IV.2.3.1. The Nee-Zwanzig Theory**

Although not the first study, the most influential early treatment of rotational dielectric friction was made by Nee and Zwanzig (NZ) \[85\]. 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
dipole with dipole moment \( \mu \) and radius \( a \) embedded in a dielectric continuum with dispersion \( \varepsilon(\omega) \). Motion was assumed to be in the purely diffusive (or Smoluchowski) limit. Using a boundary condition value calculation of the average reaction field, Nee and Zwanzig obtained their final result linking the dielectric friction contribution in the spherical cavity as

\[
\tau_{DF}^{NZ} = \frac{\mu^2}{9a^3kT}\left(\frac{\varepsilon_0 + 2}{(2\varepsilon_0 + \varepsilon_\infty)^2}\right)\tau_D
\]

(4.19)

where \( \varepsilon_0, \varepsilon_\infty \) and \( \tau_D \) are the zero-frequency dielectric constant, high-frequency dielectric constant and Debye relaxation time of the solvent, respectively.

If one assumes that the mechanical and dielectric components of friction are separable, then

\[
\tau_{\text{obs}} = \tau_r + \tau_{DF}.
\]

(4.20)

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

\[
\tau_{\text{obs}} = \frac{\eta VfC}{kT} + \frac{\mu^2}{9a^3kT}\left(\frac{\varepsilon_0 + 2}{(2\varepsilon_0 + \varepsilon_\infty)^2}\right)\tau_D.
\]

(4.21)

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 step increase in the hydrodynamic contribution. Hence, the most pronounced contribution due to dielectric friction
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could be seen in small molecules with large dipole moments especially in solvents of low $\varepsilon$ and large $\tau_D$.

IV.2.3.2. The van der Zwan-Hynes Theory

The semiempirical method for finding dielectric friction has been proposed by van der Zwan and Hynes (ZH) [60], which is an improvement over the Nee and Zwanzig model because it provides a prescription for determining the dielectric friction from the measurements of the response of the 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

$$\tau_{DF} = \frac{\mu^2 S \tau_s}{(\Delta \mu)^2 6kT} \quad (4.22)$$

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

$$S = h\nu_a - h\nu_f \quad (4.23)$$

$h\nu_a$ and $h\nu_f$ are the energies of the 0-0 transitions for absorption and fluorescence, respectively. The solvation time is approximately related to the solvent longitudinal relaxation time, $\tau_L = \tau_D(\varepsilon_\infty/\varepsilon_0)$ and is relatively independent of the solute properties. Hence $\tau_L$ can be used in place of $\tau_s$ in Eqn. (4.22).

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

$$\tau_{r,obs} = \frac{\eta V C}{kT} + \frac{\mu^2}{(\Delta \mu)^2} \frac{hc \Delta \nu}{6kT} \tau_s \quad (4.24)$$
where the first term represents the mechanical contribution and the second the dielectric contribution.

IV.2.3.3. The Alavi and Waldeck Theory

The final theory to be considered is due to Alavi and Waldeck (AW) [86, 87]. 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 contributes 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 ZH theories in modeling the friction experienced by the solutes in nonassociative solvents [121]. The expression for the dielectric friction according to the AW model is given by

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

(4.25)

where

$$P = \frac{4}{3akT} \sum_{j=1}^{N} \sum_{i=1}^{L} \sum_{m=1}^{L} \left( \frac{2L + 1}{L + 1} \right) \left( \frac{L - M}{L + M} \right) \times$$

$$M^2 q_i \left( \frac{r_i}{a} \right)^L \left( \frac{r_j}{a} \right)^L P_L^M (\cos \theta_i) P_L^M (\cos \theta_j) \cos M \phi_{ij}$$

(4.26)

where $P_L^M (x)$ are the 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 $\phi_{ij} = \phi_j - \phi_i$. Although the AW theory also treats solvent as a structureless continuum like the NZ and ZH theories, it provides a more realistic description of the electronic properties of the solute.
IV.3. EFFECTIVE ROTOR SHAPE

The rotational motion of a molecule in solution is rarely consistent with the behavior expected of a spherical probe molecule. To elucidate the intrinsically anisotropic nature of the molecular motion, the time-dependent fluorescence anisotropy, $r(t)$ is defined as [122]

$$r(t) = \frac{I_\parallel(t) - I_\perp(t)}{I_\parallel(t) + 2I_\perp(t)}$$

where $I_\parallel(t)$ and $I_\perp(t)$ are the components of fluorescence intensity, parallel and perpendicular to the polarization of the excitation radiation, respectively.

The expressions for $I_\parallel(t)$ and $I_\perp(t)$ are given by

$$I_\parallel(t) = \frac{(1/3)f(t)[1 + 2r(t)]}{I(t)}$$  \hspace{1cm} (4.28)$$

$$I_\perp(t) = \frac{(1/3)f(t)[1 - r(t)]}{I(t)}$$  \hspace{1cm} (4.29)

where $f(t)$ is the decay of fluorescence. The fluorescence intensity $I(\theta, t)$ at any arbitrary orientation $\theta$ with respect to the polarization of the excitation radiation is given by [123]

$$I(\theta, t) = \frac{(1/3)f(t)[1 + (3\cos^2 \theta - 1) r(t)]}{I(t)}$$  \hspace{1cm} (4.30)

Eqn. (4.30) reduces to Eqns. (4.28) and (4.29) when $\theta$ is $0^0$ and $90^0$, respectively. When, $\theta = 54.7^0$ which is known as the ‘magic angle’, the fluorescence is totally depolarized and $I(t)$ becomes $f(t)$, the decay of fluorescence.

The expression for the limiting anisotropy or zero-time anisotropy $r_0$ is given by [122]

$$r_0 = \left(\frac{2}{5}\right)\left[\frac{3\cos^2 \gamma - 1}{2}\right]$$  \hspace{1cm} (4.31)
where $\gamma$ is the angle between the absorption and emission dipoles. $r_0$ can have a value of 0.4 if the absorption and emission dipoles are parallel and −0.2 if they are perpendicular.

The expression for $r(t)$ of an asymmetric rotor contains at the most five exponentials and is given by [1]

$$r(t) = \frac{6}{5} \left[ \sum_{i=1}^{3} c_i \exp(-t/\tau_i) + \left( \frac{F + G}{4} \right) \exp(-[6D - 2\Delta]t) + \left( \frac{F - G}{4} \right) \exp(-[6D + 2\Delta]t) \right]$$

(4.32)

where $D = (D_1 + D_2 + D_3)/3$ is the mean-diffusion coefficient and $D_1$, $D_2$ and $D_3$ are the diffusion coefficients along the three principal axes, respectively.

$$\Delta = (D_1^2 + D_2^2 + D_3^2 - D_1 D_2 - D_1 D_3 - D_2 D_3)^{1/2}$$

$$c_i = \alpha_i \alpha_i \varepsilon_i \varepsilon_i; (ijk) = (123), (231), \text{ or } (312)$$

$\alpha_1, \alpha_2, \alpha_3$ are the direction cosines of the absorbing dipole with respect to principal axes of rotation and $\varepsilon_1, \varepsilon_2, \varepsilon_3$ are the corresponding direction cosines of the emitting dipole.

$$\tau_i = 1/3(D + D_i)$$

$$F = \sum_{i=1}^{3} \alpha_i^2 \varepsilon_i^2 - \frac{1}{3}$$

$$G\Delta = \sum_{i=1}^{3} D_i (\alpha_i^2 \varepsilon_i^2 + \alpha_j^2 \varepsilon_j^2 + \alpha_k^2 \varepsilon_k^2) - D; \quad i \neq j \neq k \neq i$$

Eqn. (4.32) can be readily simplified by assuming certain symmetry properties for the molecule and it is also assumed that the absorption and emission dipoles are parallel.
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IV.3.1. Spherical Rotor

In this case $D_1 = D_2 = D_3 = D$ and

$$r(t) = \frac{2}{5} \exp(-6Dt) \quad (4.33)$$

Thus the rotational motion is isotropic with a rotational-correlation time

$$\tau_r = \frac{1}{6D} \quad (4.34)$$

IV.3.2. Symmetric Rotor

For a molecule that possesses an axis of symmetry, such as an ellipsoid of revolution

$$D_1 = D_l \text{ and } D_2 = D_3 = D_\perp$$

If the transition dipole is parallel to the symmetric axis

$$r(t) = \frac{2}{5} \exp(-6D_l t) \quad (4.35)$$

When the transition dipole is perpendicular to the symmetric axis ($\theta = 90^0$), $r(t)$ has a double-exponential of the form

$$r(t) = \frac{2}{5} \left[ \frac{1}{4} \exp(-6D_\perp t) + \frac{3}{4} \exp(-(2D_\perp + 4D_l)t) \right] \quad (4.36)$$

The physical basis of Eqns. (4.35) and (4.36) is that when the transition dipole is parallel to the symmetry axis only motions perpendicular to that axis (i.e., tumbling) will reorient the dipole, whereas, if the transition dipole is perpendicular to the symmetry axis both tumbling and spinning will change the dipole orientation.

IV.3.3. Asymmetric Rotor

When the transition moment is parallel to the symmetry axis, Eqn. (4.32) reduces to
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\[ r(t) = \frac{2}{5} \left[ \frac{1}{2} + \frac{3}{4} (D - D_1) / \Delta \right] \exp(-6D + 2\Delta t) \\
+ \left[ \frac{1}{2} - \frac{3}{4} (D - D_1) / \Delta \right] \exp(-6D - 2\Delta t) \]  \hspace{1cm} (4.37)

Although, according to theory, the \( r(t) \) of an asymmetric ellipsoid can decay with five correlation times, usually only one correlation time is observed experimentally and the reason for this will be discussed in the subsequent section. Under such conditions the reorientation time is given by \([22, 84]\)

\[ \tau_r = \frac{6}{5 \rho_0} \left[ \cos^2 \beta \sin^2 \beta + \frac{F + G}{3(D + D_1)} + \frac{F - G}{4(6D - 2\Delta)} \right] \]  \hspace{1cm} (4.38)

where \( \beta \) is the angle between the transition moment and the symmetry axis of the molecule. The above equation is obtained under the assumption that the transition dipole lies in the xy-plane. Eqn. (4.38) gets further simplified if the transition dipole lies along the symmetry axis and is given by

\[ \tau_r = \frac{1}{12} \left[ \frac{4D_1 + D_2 + D_3}{D_1D_2 + D_2D_3 + D_3D_1} \right] \]  \hspace{1cm} (4.39)

In order to use the Eqns. (4.33) to (4.39) it is necessary to evaluate the principal diffusion coefficients of the molecule. These are calculated via the rotational friction coefficients \( \zeta_r \). Hence Eqn. (4.3) in general form is given by

\[ D_i = \frac{kT}{\zeta_i} \]  \hspace{1cm} (4.40)

The standard procedure for calculating the rotational friction coefficients is to (i) approximate the molecule as a smooth ellipsoidal body immersed in a continuum fluid; (ii) write the Navier-Stokes hydrodynamic equations for the velocity field of the fluid relative to the body; (iii) linearize these equations by assuming slow, steady rotation of the body; (iv) impose appropriate boundary
conditions for the velocity field at the surface of the body; and (v) solve these equations for the total hydrodynamic torque on the body. This procedure has been simplified because tabulated values of axial ratios are readily available in literature. Hu and Zwanzig [55] calculated friction coefficients for symmetric ellipsoids (prolate or oblate) as a function of axial ratios, both with stick and slip boundary conditions. Youngren and Acrivos [56] calculated friction coefficients for an asymmetric ellipsoid with slip boundary condition, which were later, modified by Sension and Hochstrasser [124]. The friction coefficients with stick boundary condition are obtained from the tables of Small and Isenberg [125] for an asymmetric ellipsoid.

IV.4. REVIEW OF LITERATURE

The first direct experimental observation of the orientational relaxation of molecules in a liquid environment using picosecond laser pulses employing a polar laser dye rhodamine-6G (Rh6G) as a probe was carried out by Eisenthal and Drexhage [126]. The method consisted of exciting a fraction of the molecules dissolved in a liquid to a higher electronic state with a picosecond pulse and then probing at later times with a greatly attenuated picosecond pulse. The sample solution of Rh6G was excited using 530 nm light pulses. The measured lifetime of the excited molecules was considerably longer than the orientational relaxation of the probe molecules. For these reasons the decay of the measured dichroism depends only on the reorientation time of the ground-state molecules. To relate experimental measurements to the orientational relaxation time they also calculated the absorption of parallel and perpendicular components of the probe at various times after excitation. The distribution function used to calculate the time dependence of the dichroism
was obtained by a solution of the rotational diffusion equation assuming that
the diffusion constant is a scalar. In this way they found the orientational
relaxation time of Rh6G in ethylene glycol to be $6.5\pm0.5\times10^{-10}$ sec. Since then
a large number of experiments have been carried out to determine orientational
relaxation of various probe molecules in different environments.

In a subsequent paper by Chuang and Eisenthal [70], orientational
relaxation of Rh6G using picosecond light pulses was measured in a series of
normal alcohols, ethylene glycol, chloroform and formamide. The rotation of
Rh6G in linear alcohols viz., decanol and undecanol, deviated remarkably from
the linear viscosity dependence and was attributed to the fact that solvent
molecules having greater linear dimension than the solute molecule and
therefore, the hydrodynamic model could not expected to be adequate. The
deviation of results in ethylene glycol was due to the extensive solvent-solvent
aggregation by hydrogen bonding interactions, which form polymeric network
and is probably responsible for the high viscosity of the liquids, relative to the
linear alcohols that contain only one hydroxy group for hydrogen bonding.
Finally, it was concluded that this molecule being isotropic with regard to
rotational diffusion, it followed Stokes-Einstein diffusion without significant
effects due to hydrogen bonding. Porter et al. [73] used
tetrachlorotetraiodofluorescein and Rh6G to study the rotational diffusion times
in series of low viscosity, hydrogen-bonding solvents by picosecond time-
resolved fluorescence depolarization spectroscopy. Steady-state measurements
of both the dyes were used to obtain the results of comparable accuracy to the
kinetic technique. Data from both techniques indicated that Stoke-Einstein
behavior holds at low viscosities, but for higher viscosity solvents rotation
times are longer than predicted.
The experimental study of viscosity dependence of reorientational times of small molecules ($V=38 \text{ Å}^3$ to $73 \text{ Å}^3$) in liquids was carried out and discussed in the light of the hydrodynamic slip model by Bauer et al. [127]. The experimental viscosity dependence in aqueous solutions of these molecules was found to lie in between the predictions of slip and stick models. The authors concluded that hydrodynamics with slip boundary conditions could successfully predict the reorientation times of most of the small molecules in the absence of strong solute-solvent interactions. And in the presence of these interactions, the reorientation times are longer than the slip prediction.

Fleming et al. [71] for the first time reported the time dependent fluorescence depolarization measurements extending to the picosecond regime by using streak camera and optical multichannel analyzer detection for the fluorescein dye derivatives (eosin and rose bengal). These dyes rotate in polar solvents as if their volume is at least double that of the free molecule because of solvent attachment. This effect was apparently the major cause of the breakdown of the literal Einstein hydrodynamic model for rotation of such relatively small molecules in solution. The solvent attachment also very likely reduces the effect of molecular shape on rotational depolarization, causing these molecules to behave more like spheres than their molecular structure would imply. In addition, unlike most fluorescence probe experiments on nanosecond time scales applied to the study of macromolecular structure, these authors also observed a theoretical value of 0.4 for the polarization anisotropy at zero time.

A picosecond time dependent fluorescence depolarization experiment to study the rotational diffusion of neutral probe BBOT ($V=385 \text{ Å}^3$) in cyclohexane and ethanol has also been carried out by Fleming et al. [128]. The
measured rotational correlation times were $180\pm30$ ps and $210\pm30$ ps respectively, in cyclohexane and ethanol which were in good agreement with those predicted from hydrodynamics with slip boundary condition and contradictory to their previous results for the probes rose bengal [71] and DODCI [72], and of Chuang and Eisenthal [70] and Porter et al. [73] for Rh6G. The results demonstrated that slip boundary conditions were appropriate for the rotational diffusion of the prolate neutral molecule BBOT in both the solvents. They attributed this due to the rapid solvent exchange rate that are comparable with the time scale of the elementary rotations of the molecule. On the other hand for oblate or prolate molecules with the transition moment perpendicular to the symmetry axis, the initial decay of the time dependent fluorescence depolarization will be very rapid.

The rotational relaxation of rose bengal in protic and aprotic solvents in the lowest excited singlet state was studied by Spears and Cramer [75]. The observed orientational decay for the dipolar aprotic solvents and the alcohols, agree with the values predicted by Stokes-Einstein equation. In the latter solvents, volume and shape corrections were made for attachment of the alcohol to the two anion sites of the dye molecule. The solvent N-methylformamide, however, showed rose bengal reorienting much faster than the alcohols and followed the Stokes-Einstein equation with stick boundary condition. A solvent torque model in which the solvent interaction at each anion site of rose bengal controls the deviations from an expected slip boundary condition, was also proposed by the authors.

Millar et al. [76] used picosecond pulses (0.6-2.5 ps duration) from a passively mode-locked and cavity-dumped dye laser to study the molecular reorientation of cresyl violet in liquids. They obtained the dipole correlation
function from the decay of the induced dichroism. The results when compared with hydrodynamics gave a good agreement with the stick boundary condition, and predict the effective shape of cresyl violet in the liquid. Von Jena and Lessing [78] studied subnanosecond transient-dichroism experiments, to investigate the rotational diffusion of several dyes in solution. Dyes and solvents were chosen in a way to obtain information on the influence of size, shape and hydrogen-bonding abilities either of the solute or the solvent molecules. They observed slow orientational relaxation of di-anionic xanthene dyes in alcohols, while oblate cationic dyes rotated faster in spite of their comparable size. The rotational diffusion times for alcohol solutions exceeded the theoretical values except for prolate molecules. For a solute molecule with internal mobility the rotational diffusion exhibits a partial slip behavior. They showed that the deviations from the Debye-Einstein model are restricted to alcohols since for other solvents either with or without strong hydrogen-bonding abilities the experimental values agree with the hydrodynamic model including the stick-boundary condition. Experiments on erythrosine B revealed the influence of size and shape of the attached solvent molecules.

Rice and Kenney-Wallace used three xanthene dyes, namely Rh6G, fluorescein and eosin-Y in several n-alcohols, ethylene glycol and glycerol following the fluorescence depolarization using a single photon counting technique [77]. The results on reorientational motion of these dyes in most of the cases were found to be similar as in the previous studies by Chuang and Eisenthal [54] and Lessing et al. [78] for Rh6G. A saturation effect in the higher viscosity fluids since the rotational relaxation times are up to 50 times faster than those predicted by low viscosity data and hydrodynamic theory was found. The fastest rotational relaxation times are described as associated with
neutral or non-interactive molecules, and hence, the smaller solute-solvent interaction energy, deviating away from the hydrodynamic stick boundary condition. Waldeck et al. [88] have studied the rotational relaxation of 1,4-diphenyl-1,3-butadiene (DPB) in dilute alkane solution using pump-probe technique. The motion of DPB ($V=205 \text{ Å}^3$) in tetradecane was well described by hydrodynamics with a slip boundary condition which is reasonable for an uncharged nonpolar molecule in a nonpolar solvent as observed in previous reports.

The rotational diffusion behavior of tetracene ($V=210 \text{ Å}^3$) in ethylene glycol and $n$-dodecanol by fluorescence depolarization spectroscopy was reported by Sanders and Wirth [2]. It was observed that tetracene exhibits much faster reorientation in its molecular plane in ethylene glycol than in dodecanol. This suggests that the solvation structure, in addition to solute geometry, influences the relative values of the diffusion constants. Templeton et al. [3] described the reorientational dynamics in polar fluids of resorufin, a rigid aromatic probe molecule, whose anionic site permits several specific intermolecular interactions to be investigated. They used a technique reported for first time with difference-frequency multiple modulation picosecond absorption spectroscopy, to study the ground-state dynamics of resorufin in a series of protic alcohols, aprotic fluids, and the binary system of propanol-water. The reorientation time in alcohols was found to be well described by SED equation with stick boundary conditions, whereas the data in acetonitrile, DMF and DMSO show faster reorientation times and quite different behavior from hydrodynamic expectations, even if slip boundary conditions were invoked in the analysis. Finally, resorufin in formamide, water and water/propanol systems showed considerable deviation from the pattern.
established in the alcohols. A model was also proposed in which the lifetime of the local and site-specific intermolecular interaction between resorufin and its nearest-neighbor solvent molecules is compared to the cooperative relaxation time of the overall three-dimensional or two-dimensional network of solvent interactions typical of hydrogen-bonded system. It was concluded that both long-wavelength hydrodynamic effects and the nature and behavior of the first solvation shell influenced the rotational dynamics.

Philips et al. [90] used a picosecond time-resolved fluorescence depolarization spectroscopy to measure the rotational reorientation times of Rh6G and \( p \)-terphenyl (PTP) as a function of solvent viscosity. The viscosity in this method was varied either by changing the solvent or by changing the pressure in a single solvent. The experimental observations on PTP demonstrated that uncharged, intermediate sized molecules are adequately described by the SED equation. Only subtle deviation from the SED behavior is observed when either the solvent or the pressure is varied. The improvement in fitting experimental data using SED and GW models argued that the finite size of the solvent molecules and the free space in the liquid, influence the dynamics of the rotational motion. Discrepancies between the predictions of these models and the experimental data also suggested that other properties might also become important, particularly for the case of associated liquids under pressure. The trend predicted by the dielectric friction model explains the dramatic difference in the behavior of the charged Rh6G molecule compared to that of the neutral PTP molecule. This model also explains the changes in the rotational reorientation times of Rh6G in isoviscous solutions, thereby elucidating the cause of deviations from SED behavior. The rotational diffusion dynamics of Rhodamine-640 (Rh640) in series of normal aliphatic alcohols,
methanol through \( n \)-decanol is studied by Deal Cruz and Blanchard [129]. The reorientation data indicate close association of the solute with several solvent molecules and follow super-stick behavior. This suggested that the solute-solvent interaction is greater than the predication of modified SED model.

A study of the rotational diffusion of stilbene (\( V=180 \ \text{Å}^3 \)) in alkane and alcohol solutions by Courtney et al., [91] revealed that the rotational reorientation time of stilbene in alkanes followed slip limit whereas in alcohols a faster rotation than slip hydrodynamics was noted. The authors attributed subslip behavior in alcohols to the association of alcohol molecules in forming supramolecular structure. Later Kim et al. [130] studied the reorientation times of stilbene in alcohols, which are consistent with incomplete solvation in the initial state for alcohols larger than ethanol and with stabilization of the polar transition state by rapid components of the solvent dielectric response in all alcohols. The combination of these two effects leads to a progressive decrease in apparent barrier height with increasing size of alcohol.

A study of rotational diffusion by Ben Amotz and Scott [131] for the nonpolar solutes \( p \)-terphenyl (\( V=224 \ \text{Å}^3 \)), \( p \)-quaterphenyl (\( V=296 \ \text{Å}^3 \)) and 9, 10-diphenylantrancene (\( V=312 \ \text{Å}^3 \)) has been carried out in \( n \)-alkane and \( n \)-alcohol solvents. The observed microscopic frictional coefficients approximate the prediction of slip hydrodynamics is alkanes. Substantially lower friction is found in \( n \)-alcohols of comparable viscosity. These differences have been interpreted as an indication of nonhydrodynamic behavior in the microscopic rotational friction. Later, Ben-Amotz and Drake [92] experimentally measured rotational diffusion times of large (rigid) and neutral molecule \( N,N' \)-bis(2,5-di-tert-butylphenyl)-3,4,9,10-perylene dicarboxamide (BTBP) in series of alcohols and alkanes. SED hydrodynamic theory quantitatively described the
rotational anisotropy decay of this large molecule, both in alkane and alcohol solvents. This behavior stands in marked contrast to that of smaller neutral solutes, which have been found to rotate faster than predicted and to have a different viscosity dependence in alcohol than in alkane solvents. The slip hydrodynamic predictions were in poor agreement with the experiment. They also observed the diffusion of BTBP very close to stick predictions both in alcohols and alkanes and argued this due to its larger size than solvent molecules.

In a subsequent paper by Roy and Doraiswamy [93], the rotational reorientation times of substituted quaterphenyl and quinquephenyl molecules (neutral and nonpolar) of volumes ranging from 325 to 639 Å³ have been measured in a series of n-alkanes, n-nitriles and n-alcohols, by picosecond fluorescence depolarization technique. A transition towards the stick hydrodynamic limit with increase in solute size was evident in the chosen set of solute probes. It is observed that the DKS model agrees with experimental data in both solvents up to a solute radius of ~4.5 Å but fails beyond that. The GW model is seen to be adequate only for very small molecules. Thus, the ability of the quasihydrodynamic microfriction models to show a transition from microscopic to macroscopic behavior with increase in solute size is observed.

Rotational diffusion kinetics of large, neutral, triphenodioxazines dyes, with radii from 3.9 to 5.2 Å, were studied in chloroform using fluorescence polarization anisotropy technique with pulsed excitation at 532 nm by Justus et al. [132], modeling them as prolate and oblate ellipsoids. The experimentally observed fluorescence depolarization kinetics is compared with rotational diffusion kinetics based on the SED hydrodynamic continuum model with stick and slip boundary condition. The two prolate models yield fluorescence
anisotropy decay time, nearly the same in the slip limit than in the stick limit. Nevertheless, prolate model indicated the use of stick boundary condition rather than slip for calculating the orientational relaxation times of these large rigid molecules. Blanchard [12] studied the rotational diffusion behavior of the monocation methylene blue, for several alcohols, nitriles and water. Interpretation of these data in the framework of SED model showed that the solvent attachment scheme to be a good agreement with experimental results. In this study significant discrepancies between the SED model and experiment were noted.

Dutt et al. [81] measured fluorescence lifetimes and rotational reorientation times of four structurally similar dye molecules-three monocations: cresyl violet, nile blue and oxazine 720 and one neutral but polar: nile red by picosecond time-resolved fluorescence depolarization spectroscopy using single-photon counting technique, in a number of solvents, which included a wide range of alcohols, other hydrogen-bonding liquids and a few aprotic solvents. The rotational reorientation of the dye probes (oblate ellipsoids) sought to be explained in terms of SED theory and dielectric friction. The rotational behavior of all the four dyes in amides and aprotic solvents was reasonably well explained in terms of the simple stick hydrodynamic model with the molecular volume obtained by using measured rotational reorientation time in water. They also included the friction contribution due to dielectric properties of the solvent to describe the rotational reorientation dynamics in alcohols. The rotational dynamics of all the four dyes in amides and aprotic solvents is satisfactorily described by the hydrodynamic friction and that in \(n\)-alcohols needed the inclusion of dielectric friction contribution. It is also seen that a significant deviation of the observed
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rotational reorientation times of charged dye molecules from the predictions of the simple hydrodynamic picture which was ascribed to the neglect of the dielectric friction contribution, the magnitude of which is evaluated from macroscopic dielectric parameters, like $\varepsilon$ and $\tau_D$. This investigation confirmed that the dielectric friction concept is adequate to describe the rotational dynamics of dipolar solutes in polar solvents reasonably.

Simon and Thompson [133] have analyzed the rotational dynamics of oxazine 725 in alcohols in terms of dielectric friction theories. A commonly used continuum theory expression for evaluating the dielectric friction constant is found to be inconsistent with the static spectroscopic data. However, the model developed by van der Zwan and Hynes, which connects the dielectric friction to time-dependent solvation dynamics, results in qualitative agreement with the data obtained from static spectroscopy. It was concluded that using this model, an accurate measure of the contribution of dielectric friction to the rotational dynamics could be calculated. A work by Alavi and co-workers [82] on rotational diffusion of three structurally similar phenoxazine dyes namely resorufin, resorufamine and oxazine, which possess distinct electrical properties was studied in isopropanol at different temperatures. These results were also analyzed for other polar solvents in terms of continuum theories of rotational dielectric friction. It was found that a continuum based theory can account for the observed rotational relaxation dynamics, but only with realistic modeling of the solute charge distribution (not a point dipole), and by accounting for both frequency and wave vector dependences of the solvent dielectric properties.

Kim and Hochstrasser [134], studied the rotational diffusion of fluorene ($V=160 \, \text{Å}^3$) to measure fluorescence anisotropy using a time-correlated single
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photon-counting apparatus. The measured rotational relaxation times in various alcohol solvents were compared with hydrodynamic predictions for prolate spheroidal and asymmetric ellipsoidal shapes in the stick and slip limits. The anisotropy calculations for the prolate spheroid and the asymmetric ellipsoid made remarkably different predictions of the rotational relaxation times. It was found that the fluorene molecule rotates significantly faster than slip hydrodynamic limit, which was attributed to the strong hydrogen-bonding association among the alcohol solvent molecules. Also, the observed slight nonlinearity in the $\tau$ vs. $\eta$ plots was ascribed to the hydrophobicity increasing with solvent chain length. Moog et al. [135] studied the rotational dynamics of Coumarin 102 (Cl02) in pure decalin and pure trifluoroethanol (TFE), and of a 1:1 C102:TFE complex in decalin, using time-resolved fluorescence anisotropy measurements. The rotation of Cl02 in decalin followed the SED hydrodynamic model with slip boundary conditions in 1:1 complex. The reduced rotation time, $\tau_c/\eta$ of Cl02 in pure TFE is significantly longer than its value in pure decalin but is indistinguishable from that of the complex in decalin. The results suggested that the rotation of Cl02 in TFE can be interpreted as the rotation of a 1:1 C102:TFE complex following the hydrodynamic model with slip boundary condition.

Molecular rotational reorientation times of three solutes of similar size and shape (nile red, neutral nile blue and cationic nile blue) dissolved in alcohol and alkane solvents were investigated using time-resolved fluorescence depolarization studies by Williams et al. [94]. A universal correlation is found between reorientation time, solvent viscosity and solute volume for solutes dissolved in alkanes, while strongly interacting solutes experience relatively enhanced friction, and nonpolar solutes dissolved in alcohols experience
reduced friction that is approximately consistent with slip hydrodynamics prediction. Imeshev and Khundkar [18] studied the rotational correlation time of the dipolar $p,p'$-cyano thiomethyl diphenylacetylene that varies linearly with the emission Stokes shift in 1-propanol. Such effect was not observed in nonpolar (pentane, hexadecane) or fast polar (methanol, acetonitrile) solvents. It was opined that the dielectric friction in the different local environments experienced by the probe and the inhomogeneities persist on time scale much longer than the solvation time.

The $\tau$, of rose bengal as a function of viscosity using picosecond time-resolved fluorescence depolarization spectroscopy was studied by Srivastava and Doraiswamy [17]. The variation of viscosity has been effected in two different ways-using different solvents and different compositions of aqueous binary mixtures. The SED hydrodynamic theory is found to reasonably and satisfactorily explain the rotational diffusion of rose bengal in amides and aprotic solvents, however, the dielectric friction model provides a better appreciation of its motion in normal alcohols. This dielectric friction model is used to explain the nonhydrodynamic profile of $\tau$ vs. $\eta$ of rose bengal in $t$-butanol-water binary mixture. They also pointed out the dual values of $\tau$, at isoviscous points corresponding to the two different compositions of HMPA in water based on different degrees of solvation ($H_2O+HMPA$) moieties at the oxygen sites of rose bengal. Nevertheless, the boundary condition model does not satisfactorily explain the rotational dynamics of rose bengal in binary mixtures in view of the fact that a well determined $\tau$, for it in water is not available.

Backer et al. [136] investigated the rotational dynamics of perylene and tetra-tertiary butylperylene using time-resolved fluorescence anisotropy
experiments. In the polarized fluorescence decay traces, the preexponential factors in the anisotropy decay are linked over a series of n-alcohols while the rotational correlation times over two excitation wavelengths. The anisotropy decay of perylene was analyzed using biexponential decay law with a fast in-plane and a slower out-of-plane rotation. It was also found that upon substituting perylene systematically by four tertiary butyl groups the two rotational correlation times become equal, resulting in monoexponential anisotropy decay. The high ratio between the two diffusion coefficients indicates that these molecules can be modeled as disk and not as an oblate ellipsoid of revolution. The experimentally obtained rotational correlation times are close to the theoretically predicted values, indicating stick boundary condition.

Rasimas and Blanchard [137] have studied carminic acid in primary aliphatic alcohols and water to develop an understanding of its dynamic properties. The fluorescence response exhibited biexponential decay and was attributed to emission from two stable conformers of carminic acid. The reorientation behavior of carminic acid is sensitive to the chemical identity of the solvent. This dynamical response is predicted by SED equation with a sticking boundary condition for water, methanol, ethanol and 1-propanol. In higher alcohols, carminic acid reorientation follows SED behavior in the slip limit. This shows that as the size of the solvent molecules increases, the frictional interactions between the probe and its surroundings appear to decrease.

The photophysical properties of 2,9-di-n-pentyl-5,6,11,12-tetraazo-5,6,11,12-tetracarboxy-bis-n-heptadecylimide (P5-17) in solution were investigated as a function of concentration by Biasutti et al. [19]. The rotational
dynamics of P5-17 and its aggregates were investigated using steady-state and time-resolved fluorescence anisotropy measurements. From the global analysis of the polarized decay traces, it was found that for both monomer and aggregate, the anisotropy decay was found to describe by a monoexponential decay law. The rotational correlation time for the monomer is linked over two excitation wavelengths corresponding to $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_n$ transitions. For the aggregate, the excitation and emission dipoles were perpendicular and a fast fluorescence depolarization was observed. The correlation time for the monomer (0.22 ns) was also attributed to the free three-dimensional rotation while the fast depolarization observed for the aggregates is explained by the fast energy transfer between the molecules in the aggregates.

Fluorescence anisotropy of two neutral and nonpolar molecules, 2,5,8,11-tetra-tert-butylperylene (TP) and 2,5,10,13-tetra-tert-butylterrylene (TT), in series of alcohols and alkanes was reported by Backer et al. [20]. The authors globally analyzed the polarized fluorescence decay traces at different excitation wavelengths by modeling TP and TT as oblate ellipsoids with essentially identical rotational correlation times. They showed that these molecules couldn’t be seen as prolate or as spherical molecules, but as oblate ellipsoids with two indistinguishable rotational correlation times. The rotational correlation times of TP and TT were proportional to the viscosity for each solvent series and rotation for both the probes were found to be faster in alcohols than in alkanes. This effect is more pronounced for TP than for TT, indicating that the SED equation is not valid at a molecular scale.

A molecular dynamic study of the friction experienced by the dye molecule resorufamine rotating in a polar solvent is performed by Kumikova et al. [138]. They tested the validity of simple continuum theories of dielectric
friction and found that Alavi-Waldeck theory gave reasonable results for the zero frequency dielectric coefficients while the NZ theory required an unphysically small cavity radius. They also suggested a procedure for evaluating the time dependent friction kernal from torques and angular velocities, which enables the contributions to the friction from the van der Waals and Coulomb forces separately. This study showed that electrostatic interactions could enhance the friction by at least two physical mechanisms. First contribution to the friction, arises solely from retardation of the solvent reaction field and the second from local structural changes of the solvent, which were driven by the electrostatic field, i.e., a change in the local viscosity. Harms et al. [139] studied the picosecond time-correlated single-photon counting to measure the fluorescence anisotropy decays of tyrosine and the tyrosine-alanine and tyrosine-leucine dipeptides. After excitation of tyrosine at 287 nm two emitting species were observed, one at 303 nm with a lifetime of 3.3 ns and another at 340 nm with a lifetime of 360 ps. The rotational correlation time of tyrosine at 303 nm is 38 ps in water at pH 7 and depends linearly on viscosity with a slope 44 ps/cP, consistent with Stokes-Einstein-Debye theory. The rotational correlation times of tyrosine, tyrosine-alanine and tyrosine-leucine dipeptides increased linearly with the van der Waals volumes. However, rotational relaxation is somewhat faster than expected from SED theory with stick boundary condition.

Horng et al. [21] have measured the fluorescence anisotropy of Coumarin 153 (C153) in different solvents. Rotational correlation times were observed to be longer in polar solvents than in nonpolar solvents of similar viscosity. They examined this difference in the context of theories of dielectric friction, which relate the extra friction in polar solute/solvent systems to long-
range dipole-dipole interactions. In polar aprotic solvents, solvation data indicated that dielectric friction effects should be rather modest (10-20% of the total friction). It is found that there is clear correlation between dielectric friction predictions and the observed solute-solvent coupling in these solvents. However, in normal alcohol solvents the effects of dielectric friction are predicted to be large and well beyond the scatter in the experimental data. Also there was no evidence of such an important dielectric friction contribution observed in these solvents, in spite of the fact that long-time components of the solvation dynamics do appear to be present in the rotational friction.

The rotational diffusion of 9,10-disubstituted anthracenes in various solvents was studied by Hartman et al. [22]. A systematic variation of the anthracene functionalities by the influence of the electrostatic properties of the solute-solvent frictional coupling was investigated. The approach in this work was to measure the orientational correlation function of anthracenes, which have been derived in a manner so that the influence of electrostatic interactions on the frictional coupling between the solute and solvent can be evaluated. These derivatives were chosen so that the size and shape of the anthracene do not change significantly, but its electrostatic characteristics do change. They apply these in view of the success of extended charge distribution model in describing the frictional coupling and found similar trend to that observed in the other systems, however, it has been applied in this work to other functional groups (Cl and CN). For simple solvents (toluene, benzonitrile and DMSO), the extended charge distribution model provided a reasonable estimate for the observed relaxation times. By contrast, point source models were seen to be in qualitative error, e.g., dicyanoanthracene experienced the most friction even though it has no dipole moment. Also the cavity radii needed to fit the data
were somewhat larger for Cl than one would expect from the van der Waals considerations alone. In benzyl alcohol solvent the modeling is not successful, and it remained unclear if this resulted from a failure of the mechanical friction, the dielectric friction or both. These results supported the validity of an electrostatic treatment of the interaction of functionalized solute molecule with the solvent. Data from this and previous work, suggest a simple addition of the frictional coupling with functional groups. Later study by Laitinen et al. [23] estimated the effect of dielectric friction on the rotational correlation times of three cationic cyanine dyes. Dielectric corrections were evaluated by using SED hydrodynamic model including the dielectric friction for DiIC2, DiIC6 and DiIC14 in different n-alcohol solutions at room temperature. The dielectric corrections were applied to cis and trans conformations of the cyanine dyes. For the trans conformations, which were found more stable than cis conformations, the dielectric model seemed to be more properly suited. For DiIC14, the Stokes-Einstein model and van der Waals volumes gave results, in good agreement, but for DiIC2 and DiIC6 the van der Waals volumes were clearly smaller than those of the Stokes-Einstein model. The use of ZH model for the data of DiIC2 in trans conformation and found that the dielectric friction constants greatly increased when going from shorter alcohols (ethanol) to longer alcohols (decanol). The obtained dielectric friction constants were smaller (by a factor of 9) when the excited state dipole moment was evaluated from the experimental Lippert-Mataga method than when the value was obtained by using the dipole moment from the ab initio calculations.

In the subsequent work, Dutt et al. [84] studied the rotational dynamics of neutral and cationic forms of the phenazine dye neutral red in n-alcohols, amides and aprotic solvents using picosecond time-resolved fluorescence
depolarization spectroscopy. Both neutral and cationic forms of neutral red experienced more or less the same friction in alcohols, the cationic form experienced 16%-26% more friction in amides and aprotic solvents exceptions being formamide and propylene carbonate. The results were analyzed in terms of the SED hydrodynamic theory and dielectric friction theories of NZ and ZH. Both these theories overestimated the dielectric friction contribution for the neutral red in alcohols. The SED theory with stick boundary condition adequately described the rotational dynamics of neutral red in DMF, DMA, DMP and DMSO. However, it overestimated the friction experienced in formamide, and to a certain extent in propylene carbonate wherein for both forms similar reorientation times were observed. As the cations are strongly solvated by amides, only 60%-70% of the friction experienced in DMF, DMA and DMP can be accounted for by SED theory.

Experimental and computer simulation studies of the rotational relaxation of several polar and neutral organic solutes, viz., oxazine, resorufin, thionine, methoxypyranine, cresyl violet, substituted anthracenes and fluorenes, Resorufamine, DAAQ and TAAQ in polar solvents and electrolyte solutions has been carried out by Balabai et al. [140] to investigate the role of solute-solvent dielectric friction. These studies were used to explore the boundaries of applicability for continuum based models of the dielectric frictional coupling and to identify the important molecular mechanisms that define these boundaries. The study by these authors has probed some limits of continuum based models of the dielectric friction on a rotating molecule in a polar fluid. These studies showed that unassociated polar solvents provide reasonable agreement between the predictions of continuum based models and experimental relaxation times. Despite this apparent success, molecular
dynamics studies reveal that solvent association with the solute molecules provide a mechanism for the frictional coupling which is not accounted for by continuum models. These studies also show that this process creates a link between the mechanical and electrostatic contributions to the frictional coupling. In particular, the electrostatic field of the solute can modify the local structure of the solvent, which modifies the frictional coupling. The molecular dynamics studies showed that this coupling can lead to either an enhancement of the mechanical or a decrease in the friction, depending on the particular system. In associated solvents, the experimental studies identified some important limitations of the continuum model. First, the long range structure of the solvent leads to a modification in the polarization field induced by the solute and hence the dielectric friction. Second, the mechanical component of the frictional coupling can change dramatically and lead to subslip relaxation times. Third, specific association between the solute and the solvent may occur and play an important role in the relaxation. The studies in electrolyte solutions revealed two important effects: ion pairing and dielectric shielding. Both the experimental studies and the molecular dynamic simulations discussed above indicated that the association between solvent and solute would be essential in quantitatively accurate models.

Kumar and Maroncelli [109] made simulations of time-dependent friction controlling rotational, translational and vibrational motions of iodinelike dipolar diatomic solutes in acetonitrile and methanol as a function of solute dipole moment in the range of 0-6.4 D and to investigate the nature of dielectric friction. It is argued that long-range electrostatic forces do not simply add an independent contribution to the friction due to short-ranged or mechanical sources. Rather, these electrical and Lennard-Jones contributions
are found to be strongly anticorrelated and not separable in any useful way. It has also been found that the cross correlation between the mechanical and dielectric components of the friction is not negligible, but is almost equal in magnitude to the dielectric contribution and has a negative sign. Hence the net friction is much smaller than that would be obtained from a simple addition of independent mechanical and dielectric contributions. To ascertain this, Dutt and Raman [25] in their study of rotational dynamics of three structurally similar coumarins; coumarin 6, coumarin 7 and coumarin 30 using steady-state fluorescence depolarization technique found that these coumarins, because of their similarity in shape and size experience almost identical friction in alkanes, which is purely mechanical. However, in alcohols, the observed reorientation times do not follow the trend predicted by the dielectric friction theories of NZ and ZH, based on their dipole moment. They argued that the observed slower rotation of coumarins in alcohols is due to electrostriction effect rather than the dielectric friction as suggested by Kumar and Maroncelli [109].

Fluorescence anisotropy decays of the 7-diethylamino-4-methylcoumarin (C1) in various solvents of different viscosities have been recorded by means of the fluorescence up-conversion and time-correlated single photon counting techniques by Gustavsson et al. [26]. The resulting characteristic times for the rotational diffusion fall into two classes with regards to the viscosity-dependence: n-alcohols and other solvents. The deviation from the SED model in terms of rotation of the coumarin molecule under two different hydrodynamic boundary conditions (stick and slip) in the two solvent classes was discussed. They also predicted much slower reorientational times observed in the case of protic n-alcohols equally well by allowing for solvent attachments and by introducing an additional dielectric
friction. In view of the similarity in the observed and calculated rotational diffusion times, it was felt that the dielectric friction model offers the most realistic picture of the rotational friction of Cl in n-alcohols.

The theoretical approach to study the rotational friction on proteins and macromolecules to derive contributions from at least two distinct sources—hydrodynamic (due to viscosity) and dielectric friction (due to polar interactions) was carried out by Mukherjee and Bagchi [141]. The effect of the latter is taken into account by increasing the size of the protein with the addition of a hydration layer. They calculated the rotational dielectric friction on a protein ($\zeta_{DF}$) by using a generalized arbitrary charge distribution model (where the charges are obtained from quantum chemical calculations) and the hydrodynamic friction with stick boundary condition, by using sophisticated theoretical technique known as tri-axial ellipsoidal method ($\zeta_{TR}$). The calculation of hydrodynamic friction is done with only dry volume of protein (no hydration layer). The authors obtained the total dielectric friction by summing up $\zeta_{DF}$ and $\zeta_{TR}$ that gave a reasonable agreement with the experimental results.

Benzler and Luther [98], studied the rotational reorientation rates of biphenyl and p-terphenyl in n-alkanes at ambient pressure using ultrafast pump-probe polarization spectroscopy. The results showed that the SED theory could describe the experimental results at low viscosities whereas at higher viscosities the experimental results deviate significantly from the hydrodynamic prediction. The breakdown of the hydrodynamic model occurs in solvents whose size is comparable to the size of the rotating molecule. The viscosity of the solvent at which the standard hydrodynamic SED description breaks down is related to the size of the rotating molecule. In a different
approach by Ito et al. [100] the picosecond time-resolved fluorescence depolarization was measured at high pressures for $p$-terphenyl (PTP) in $n$-octane and 1-butanol from which the rotational reorientation time was deduced. A faster rotation than predicted by the modified SED slip hydrodynamic model was observed taking into account the molecular properties of the solvent. Also it was argued that the finite size of the solvent molecule and the free volume of the solvent liquid will break down the continuum model to cause a faster rotational reorientation time than that predicted by the modified SED equation.

The rotational reorientation times of two structurally similar nonpolar molecules, 2,5-dimethyl-1,4-dioxo-3,6-di-phenylpyrrolo-[3,4-c]pyrrole (DMDPP) and 1,4-dioxo-3,6-diphenylpyrrolo[3,4-c] pyrrole (DPP) in alcohols using steady-state fluorescence depolarization technique was reported by Dutt et al. [99]. The rotational dynamics of DMDPP is explained reasonably well by the SED hydrodynamic theory with slip boundary condition. It is argued that the hydrogen bonding between two C=O groups of the probe and solvent molecules could not influence the rotation of DMDPP. However, the reorientation times of DPP are found to be longer by a factor of 2.2 to 2.3 compared to that of DMDPP, and followed a super-stick behavior that has been observed for the first time for a nonpolar solute molecule. This was attributed to the strong hydrogen bonding between the two NH groups of the probe, and the alcoholic solvent molecules.

Goldie and Blanchard [142] report on the rotational diffusion and vibrational population relaxation dynamics of perylene and 1-methylperylene in the primary normal alcohols methanol through $n$-decanol. The results of rotational diffusion dynamics of the two chromophores are the same to within
IV. ROTATIONAL DYNAMICS OF NONPOLAR AND POLAR PROBES

the experimental uncertainty for $n$-propanol through $n$-decanol. A double exponential decay of orientational anisotropy for 1-methylperylene in all the alcohols and for perylene in $n$-propanol through $n$-decanol was observed. The data also reveals a substantial difference in the behavior of perylene in $n$-alkanes and $n$-alkanols. Both chromophores reorient as oblate rotors in the $n$-alkanols, with the aspect ratio of the oblate ellipsoid describing their motion depending on the solvent aliphatic chain length. M. K. Singh [24] studied the rotational reorientation times of a polar molecule neutral red (NR) in $n$-alkanes using steady-state depolarization technique. It is found that the rotational dynamics of NR in alkanes follows slip boundary condition very well. It is also observed that as the size of the solvent molecules exceeds the size of the solute molecule, the probe molecule experiences reduced friction and the experimentally measured reorientation times become shorter.

Dutt [143] studied the rotational dynamics of a nondipolar solute, DMDPP and a dipolar solute, coumarin 6 (C6) in the isotropic phase of a liquid crystal, 4′-methoxybenzylidene-4-$n$-butylaniline (MBBA) to understand the influence of pseudonematic domains on the dynamics of dopant molecules. The reorientation times of both DMDPP and C6 follow the SED hydrodynamic model instead of the Landau-de Gennes model, which is used to describe the rotational relaxation of neat isotropic liquid crystals. A comparison of the data of both DMDPP and C6 in MBBA with that in an isotropic solvent, 1-decanol reveals that the probes rotated considerably slower in the liquid crystal. These results indicate that the ordered local structures of the liquid crystal exert more friction on the rotating solute molecule compared to an isotropic liquid.

In a most recent work from our laboratory [101], the rotational dynamics of two nonpolar laser dyes Exalite392A ($V=609 \, \text{Å}^3$) and Exalite398
(F=928 Å³) as a function of viscosity in alkanes and alcohols by steady-state depolarization technique have been reported. Results were analyzed with the extensively employed SED hydrodynamic theory. Contrary to expectations, subslip behavior has been observed for the Exalite398, which is the largest molecule studied in literature. Both the probes were found to rotate much faster in alcohols than in alkanes. It is found that the experimental results of Exalite398 in both the series of solvents were well explained by the DKS model, which also accounts for the observed faster rotation of the probe in alcohols fairly well. GW theory model is able to predict the results for smaller alcohols though not for larger alcohols.

**IV.5. EXPERIMENTAL METHODS**

The experimental techniques used in the investigation of rotational reorientation times in the present study mainly consist of steady-state fluorescence spectrometry and time-resolved fluorescence spectrometry employing time correlated single photon counting (TCSPC) technique.

**IV.5.1. Steady-state measurements**

The absorption and fluorescence spectra of the present probes under investigation were measured using a Hitachi spectrophotometer (model U-2800) and Hitachi spectrofluorometer (model F-2000). For the steady-state fluorescence anisotropy measurements the same set up (F-2000) is used with polarization accessories. For vertical excitation, the steady-state fluorescence anisotropy can be expressed as [99, 122]

\[
<r> = \frac{I_{||} - GI_{\perp}}{I_{||} + 2GI_{\perp}}
\]  

(4.41)
where \( I_\parallel \) and \( I_\perp \) denote the polarized fluorescence intensities parallel and perpendicular to the polarization of the exciting beam. \( G (= 1.14) [101] \) is an instrumental factor that corrects for the polarization bias in the detection system and is given by

\[
G = \frac{I_{HV}}{I_{HH}}
\]  (4.42)

where \( I_{HV} \) is the fluorescence intensity when the excitation polarizer is kept horizontal and the emission polarizer, vertical and \( I_{HH} \) is the fluorescence intensity when both the polarizers are maintained horizontal.

**IV.5.2. Time-resolved fluorescence measurements**

The fluorescence lifetimes of all the probes were measured employing time correlated single photon counting technique (TCSPC) using the equipment described in detail elsewhere [144]. In brief, the setup includes diode pumped second harmonic radiation of a mode-locked Ti-Sapphire laser as the excitation light source, producing 750-840 nm light pulses with a repetition rate of 85 MHz. The frequency is decreased to 4 MHz by a pulse picker (Spectra Physics, 3980 2S). The second harmonic output was generated by a flexible harmonic generator (Spectra Physics, GWU 23PS). The fluorescence emission from the sample at magic angle \( (54.7^0) \) was counted by a micro-channel plate photomultiplier tube (Hamamatsu R3809U) after being passed through the monochromator and was processed through a constant fraction discriminator (CFD), a time-to-amplitude converter (TAC) and a multichannel analyzer (MCA). The instrument response function for this system is \( \approx 52 \) ps. The fluorescence decay was obtained and was further analyzed by using IBH (UK) software (DAS-6). If the decay of the fluorescence and the decay of the...
anisotropy are represented by single exponentials, then the reorientation time \( \tau_r \) is given by [122]
\[
\tau_r = \frac{\tau_f}{(r_0 / <r>-1)}
\] (4.43)

where \( r_0 \) is the limiting anisotropy when all the rotational motions are frozen and \( \tau_f \) is the fluorescence lifetime.

In case of a prolate-ellipsoid model, the parameter \( f_{\text{stick}} \) is given by [96]
\[
f_{\text{stick}} = \frac{2(\rho^2 + 1)(\rho^2 - 1)^3}{3\rho^2 \ln(\rho + (\rho^2 - 1)^{1/2}) - \rho (\rho^2 - 1)^{1/2}}
\] (4.44)

where \( \rho \) is the ratio of major axis \((a)\) to the minor axis \((b)\) of the ellipsoid. This expression is valid for stick boundary condition. In order to make calculations using SED [Eqn. (4.9)], the volume \((V)\), the axial ratio \((\rho)\), and the boundary condition parameter \((C)\) must be estimated. The value of \( C \) is set equal to unity for stick boundary condition, while, for slip boundary condition, it can be evaluated from the tables of Hu and Zwanzig [55] for the same non-spherical solute molecules.

**IV.5.3. Probes**

The laser grade nonpolar probes Exalite 404 (E404), Exalite 417 (E417) and Exalite 428 (E428) (Exciton Chemical Co., USA) and UVITEX-OB (U-OB) (Ceba Specialty Chemicals, Switzerland) were used as received. For steady-state experiments, the samples were excited at 375 nm and the emission was monitored from 403-422 nm from alkanes to alcohols in case of Exalite probes. The sample solution of U-OB in alkanes and alcohols were excited at 380 nm and the emission was monitored from 422 to 433 nm. The polar probes Coumarin 522B (C522B), Coumarin 307 (C307) and Coumarin 138 (C138)
were from Radiant Dyes Laser GmbH, Germany and used without purification. In alcohols, these samples were excited at 410 nm in case of C522B and C307 and at 375 nm in case of C138. The emission was monitored from 475 to 510 nm for C522B and C307 in alcohols and from 415 to 440 nm in alkanes ($\lambda_{ex} = 375$ nm). In case of C138 the emission was monitored from 434 to 448 nm in alcohols of increasing polarity. All the solvents (HPLC grade Fluka, Germany) were used without further purification. The concentration of all the solutions was kept sufficiently low in order to reduce the effects of self-absorption. Further, all the measurements were performed at 298 K.

The reorientation times ($\tau_r$) of U-OB and coumarins in alcohols were measured by time-resolved fluorescence depolarization method with time correlated single photon counting system, described elsewhere [145, 146]. In this experiment, samples of C522B and C307 were excited at 408 nm and those of U-OB and C138 at 375 nm using a picosecond diode laser (IBH, UK, NanoLED) in an IBH Fluorocube apparatus. In order to obtain the fluorescence anisotropy decay, the analyzer was rotated at regular intervals to get perpendicular [$I_\perp(t)$] and parallel [$I_\parallel(t)$] components. The same IBH (DAS-6) software was used here too to analyze the anisotropy data. All the decays were fitted with a single exponential function with $\chi^2$ lying between 1 and 1.3, indicative of a good fit. The instrument response for the above system is ~90 ps.

The results and discussion of the probes under investigation is organized as Part A and Part B in case of nonpolar and polar molecules, respectively.
CHAPTER IV.A

RESULTS AND DISCUSSION: NONPOLAR PROBES
IV. ROTATIONAL DYNAMICS OF NONPOLAR AND POLAR PROBES

IV.A.1. Rotational dynamics of Exalite laser dyes

The molecular structures of the probes E404, E417 and E428 chosen for the study are shown in Fig.4.1. The absorption and fluorescence spectra of these probes recorded in methanol are depicted in Fig.4.2. The absorption spectra are broad and featureless. However, the emission bands of these dyes exhibit two peaks. Molecular dimensions of these probes were obtained using Corey-Pauling-Koltum (CPK) atomic scaled model [101] and are approximated as prolate ellipsoids keeping the minor axis (2b) fixed for all the probes at 3.4 Å. The major axis (2a) were found to be 14.3 Å (E404), 17.0 Å (E417) and 21.0 Å (E428) and the molecular volumes calculated using Edward’s atomic increment method [147] are 679 Å³, 837 Å³ and 1031 Å³, respectively. The value of initial anisotropy $r_0$, measured at -60°±2° C for these exalite probes dissolved in ethylene glycol (Fluka, Germany), are 0.330±0.003, 0.332±0.004 and 0.340±0.003, respectively, for E404, E417 and E428. The rotational reorientation times ($\tau_r$) calculated using Eqn. (4.43), with the experimentally measured values of steady-state anisotropy ($<r>$) and fluorescence lifetime ($\tau_f$) in alkanes and alcohols are tabulated in Table 4.1 and 4.2, respectively. The exalite molecules are symmetric in structure and the fluorescence decays were expected to be single exponential for a prolate ellipsoid with transition moment along the symmetric axis [128]. A typical fluorescence decay curve of E404 in nonanol is shown in Fig.4.3. In case of a prolate-ellipsoid, the parameter $f_{stick}$ is calculated using Eqn. (4.44).
Figure 4.1: Molecular structures of the exalite dyes (a) E404, (b) E417 and (c) E428
Figure 4.2: Absorption and Fluorescence spectra of (a) E404, (b) E428 and (c) E428
Table 4.1: Steady-state anisotropy ($<r>$), fluorescence lifetime ($\tau_f$) and rotational reorientation time ($\tau_r$) of Exalites in alkanes at 298K. The maximum error in the fluorescence life times is less than ±50 ps.

<table>
<thead>
<tr>
<th>Solvents</th>
<th>$\eta$/mPa s$^a$</th>
<th>$&lt;r&gt;$</th>
<th>$\tau_f$/ ns</th>
<th>$\tau_r$/ ps</th>
<th>$&lt;r&gt;$</th>
<th>$\tau_f$/ ns</th>
<th>$\tau_r$/ ps</th>
<th>$&lt;r&gt;$</th>
<th>$\tau_f$/ ns</th>
<th>$\tau_r$/ ps</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentane</td>
<td>0.23</td>
<td>0.044±0.001</td>
<td>0.74</td>
<td>114±10</td>
<td>0.063±0.002</td>
<td>0.72</td>
<td>169±14</td>
<td>0.111±0.004</td>
<td>0.65</td>
<td>315±28</td>
</tr>
<tr>
<td>Hexane</td>
<td>0.29</td>
<td>0.060±0.002</td>
<td>0.69</td>
<td>153±14</td>
<td>0.083±0.003</td>
<td>0.67</td>
<td>223±18</td>
<td>0.136±0.004</td>
<td>0.62</td>
<td>413±40</td>
</tr>
<tr>
<td>Heptane</td>
<td>0.41</td>
<td>0.073±0.003</td>
<td>0.70</td>
<td>199±16</td>
<td>0.107±0.004</td>
<td>0.67</td>
<td>319±22</td>
<td>0.156±0.003</td>
<td>0.61</td>
<td>517±50</td>
</tr>
<tr>
<td>Octane</td>
<td>0.52</td>
<td>0.093±0.004</td>
<td>0.70</td>
<td>275±25</td>
<td>0.121±0.004</td>
<td>0.70</td>
<td>401±30</td>
<td>0.176±0.003</td>
<td>0.64</td>
<td>687±65</td>
</tr>
<tr>
<td>Nonane</td>
<td>0.66</td>
<td>0.102±0.004</td>
<td>0.72</td>
<td>322±25</td>
<td>0.142±0.005</td>
<td>0.70</td>
<td>523±45</td>
<td>0.193±0.004</td>
<td>0.62</td>
<td>814±78</td>
</tr>
<tr>
<td>Decane</td>
<td>0.84</td>
<td>0.114±0.005</td>
<td>0.79</td>
<td>417±35</td>
<td>0.162±0.005</td>
<td>0.71</td>
<td>677±55</td>
<td>0.212±0.004</td>
<td>0.64</td>
<td>1060±101</td>
</tr>
<tr>
<td>Dodecane</td>
<td>1.35</td>
<td>0.148±0.005</td>
<td>0.78</td>
<td>634±55</td>
<td>0.191±0.005</td>
<td>0.74</td>
<td>1002±88</td>
<td>0.238±0.005</td>
<td>0.64</td>
<td>1493±141</td>
</tr>
<tr>
<td>Tridecane</td>
<td>1.55</td>
<td>0.154±0.005</td>
<td>0.82</td>
<td>718±60</td>
<td>0.199±0.004</td>
<td>0.76</td>
<td>1137±100</td>
<td>0.247±0.004</td>
<td>0.65</td>
<td>1726±155</td>
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<tr>
<td>Pentadecane</td>
<td>2.81</td>
<td>0.201±0.006</td>
<td>0.81</td>
<td>1262±115</td>
<td>0.232±0.007</td>
<td>0.75</td>
<td>1740±120</td>
<td>0.265±0.005</td>
<td>0.64</td>
<td>2261±200</td>
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<tr>
<td>Hexadecane</td>
<td>3.07</td>
<td>0.206±0.007</td>
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<td>1362±113</td>
<td>0.244±0.006</td>
<td>0.75</td>
<td>2080±140</td>
<td>0.272±0.005</td>
<td>0.63</td>
<td>2520±220</td>
</tr>
</tbody>
</table>

$^a$ Viscosity data is from Ref. [101]
Table 4.2: Steady-state anisotropy ($<r>$), fluorescence lifetime ($\tau_f$) and rotational reorientation time ($\tau_r$) of Exalites in alcohols at 298K. The maximum error in the fluorescence life times is less than ±50 ps.

<table>
<thead>
<tr>
<th>Solvents</th>
<th>$\eta$/mPa s$^a$</th>
<th>$&lt;r&gt;$</th>
<th>$\tau_f$/ ns</th>
<th>$\tau_r$/ ps</th>
<th>$&lt;r&gt;$</th>
<th>$\tau_f$/ ns</th>
<th>$\tau_r$/ ps</th>
<th>$&lt;r&gt;$</th>
<th>$\tau_f$/ ns</th>
<th>$\tau_r$/ ps</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>0.55</td>
<td>0.094±0.002</td>
<td>0.80</td>
<td>319±32</td>
<td>0.154±0.003</td>
<td>0.78</td>
<td>675±54</td>
<td>0.173±0.003</td>
<td>0.67</td>
<td>694±63</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1.08</td>
<td>0.124±0.003</td>
<td>0.82</td>
<td>494±48</td>
<td>0.172±0.003</td>
<td>0.80</td>
<td>860±70</td>
<td>0.221±0.004</td>
<td>0.67</td>
<td>1244±110</td>
</tr>
<tr>
<td>Propanol</td>
<td>1.96</td>
<td>0.183±0.004</td>
<td>0.72</td>
<td>896±73</td>
<td>0.196±0.004</td>
<td>0.80</td>
<td>1153±99</td>
<td>0.253±0.005</td>
<td>0.65</td>
<td>1890±172</td>
</tr>
<tr>
<td>Butanol</td>
<td>2.59</td>
<td>0.185±0.006</td>
<td>0.79</td>
<td>1008±89</td>
<td>0.228±0.005</td>
<td>0.78</td>
<td>1710±150</td>
<td>0.264±0.005</td>
<td>0.64</td>
<td>2223±220</td>
</tr>
<tr>
<td>Pentanol</td>
<td>3.55</td>
<td>0.200±0.005</td>
<td>0.77</td>
<td>1185±100</td>
<td>0.234±0.005</td>
<td>0.76</td>
<td>1815±155</td>
<td>0.275±0.005</td>
<td>0.65</td>
<td>2750±225</td>
</tr>
<tr>
<td>Hexanl</td>
<td>4.59</td>
<td>0.215±0.005</td>
<td>0.81</td>
<td>1514±120</td>
<td>0.248±0.004</td>
<td>0.76</td>
<td>2244±201</td>
<td>0.283±0.006</td>
<td>0.64</td>
<td>3178±300</td>
</tr>
<tr>
<td>Heptanol</td>
<td>5.87</td>
<td>0.238±0.006</td>
<td>0.80</td>
<td>2070±182</td>
<td>0.252±0.005</td>
<td>0.75</td>
<td>2363±210</td>
<td>0.289±0.005</td>
<td>0.64</td>
<td>3627±345</td>
</tr>
<tr>
<td>Octanol</td>
<td>7.63</td>
<td>0.251±0.005</td>
<td>0.84</td>
<td>2669±255</td>
<td>0.263±0.005</td>
<td>0.75</td>
<td>2859±250</td>
<td>0.295±0.006</td>
<td>0.63</td>
<td>4130±380</td>
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<tr>
<td>Nonanol</td>
<td>9.59</td>
<td>0.269±0.007</td>
<td>0.87</td>
<td>3879±315</td>
<td>0.268±0.006</td>
<td>0.74</td>
<td>3099±292</td>
<td>0.298±0.005</td>
<td>0.64</td>
<td>4541±410</td>
</tr>
<tr>
<td>Decanol</td>
<td>11.80</td>
<td>0.276±0.006</td>
<td>0.79</td>
<td>4038±330</td>
<td>0.273±0.006</td>
<td>0.80</td>
<td>3702±340</td>
<td>0.300±0.005</td>
<td>0.64</td>
<td>4800±400</td>
</tr>
</tbody>
</table>

$^a$ Viscosity data is from Ref. [101]
Figure 4.3: Fluorescence Decay of E404 in nonanol
IV.A.2. **Exalite 404 (E404)**

Fig.4.4 gives the plots of $\tau$ vs. $\eta$ in alkanes and alcohols for E404, which clearly bring out the feature that, the experimentally determined $\tau$ values increase linearly with $\eta$ in both the solvent systems. In alkanes, they closely follow those predicted by the SED theory with slip boundary condition. However, the $\tau$ values of this molecule measured in alcohols are quite smaller than the $\tau_{slip}$ values. This observation clearly indicates that the rotational dynamics of E404 follows SED hydrodynamics with slip boundary condition in alkanes and tends to follow subslip behavior in alcohols. Further, it is found that E404 rotates slower in alkanes compared to alcohols by a factor of 1 to 1.3. It may be recalled that E392A, another probe from exalite series, followed SED hydrodynamics near stick limit in alkanes [101]. E404 is larger than E392A by a factor of 1.1, and exhibits a behavior opposite to that of E392A, following slip behavior in alkanes. Interestingly, the rotational dynamics of both these probes exhibit subslip behavior in higher alcohols.

Theoretical justification for this approach is provided by the microfriction theories of GW and DKS wherein the solvent size as well as free spaces in the solvent are taken into account. The values using GW theory are calculated using Eqns. (4.11), (4.12) and (4.13). As can be seen from the Fig.4.4, the experimental $\tau$ values are larger than the GW values by a factor varying from 1.9 to 2.6 in alcohols and from 2.8 to 3.4 in alkanes. In view of the large deviation of experimentally measured reorientation times from those calculated theoretically using GW, we also used DKS theory using equations from (4.14) to (4.17). Fig.4.4 depicts clearly the experimental trend of reorientation times following the theoretical predictions of DKS model for
Figure 4.4: Plot of rotational reorientation times of E404 as function of viscosity in (a) alkanes and (b) alcohols. The symbol • represents experimentally measured reorientation times. The stick and slip lines calculated using hydrodynamic theory are represented by solid lines. GW and DKS theories are represented using the symbols Δ and □, respectively.
most of the solvents. Therefore, DKS quasihydrodynamic theory is found to hold good, both qualitatively as well as quantitatively in explaining the observed reorientation dynamics of E404 in alcohols and alkanes.

**IV.A.3. Exalite 417 (E417)**

The rotational reorientation times of E417 as a function of $\eta$ are plotted in Fig.4.5 along with theoretical stick and slip lines. Note that, in alkanes, the rotational reorientation times follow slip hydrodynamic boundary condition, as was noted in case of E404 also. It is also evident from the figure that the probe E417 is following subslip behavior in alcohols from propanol onwards. However, a large nonlinearity is noted in case of E417 on increasing solvent viscosity in alcohols. The slip hydrodynamics overestimates the observed reorientation times by a factor of 1.3 to 2.4 from propanol to decanol in alcohols, whereas it is ~1 for all the solvents in alkanes except in pentadecane, where it is found to be 1.2. GW theory underestimates the experimental values by a factor of 0.3 to 0.8 in alcohols and in alkanes it underestimates by 0.3 to 0.4. It is observed that DKS theory follows the experimental points in alcohols up to butanol, and for higher alcohols a large deviation is observed wherein, it overestimates the experimental values by a factor of 1.2 to 1.9 from pentanol to decanol. It is worth mentioning that the experimental results agree closely with the DKS predictions as well as slip hydrodynamics.

Further, E417 is smaller by a factor of 1.11 compared to E398, the largest molecule studied so far and was reported from our laboratory [101]. Nevertheless, E398 and E417 are observed to behave in a similar way, in the sense that they follow DKS quasihydrodynamics in alkanes. However, the experimentally obtained $\tau_r$ values of E398 were found to deviate remarkably from slip hydrodynamics in alkanes whereas, for E417 the experimental values
Figure 4.5: Plot of rotational reorientation times of E417 as function of viscosity in (a) alkanes and (b) alcohols. The symbol • represents experimentally measured reorientation times. The stick and slip lines calculated using hydrodynamic theory are represented by solid lines. GW and DKS quasihydrodynamic theories are represented using the symbols Δ and □, respectively.
are in good agreement with both SED with slip boundary condition and DKS theory.

IV.A.4. Exalite 428 (E428)

E428 is the largest probe studied so far in literature and as a matter of fact it is larger than E398 by a factor of 1.11. Plots of $\tau_r$ vs. $\eta$ of E428 in alkanes and alcohols along with the calculated stick and slip line are presented in Fig.4.6. In alcohols the experimentally measured $\tau_r$ values increase linearly with $\eta$ from methanol to butanol following slip boundary condition, and from pentanol to decanol a large deviation from linearity is observed indicating a subslip behavior. The ratio of the calculated, using slip boundary condition, to the observed reorientation times are in the range of 0.90 to 2.79, which clearly indicates a significant deviation from slip hydrodynamics in the higher alcohols. However, in alkanes the experimental results clearly follow slip hydrodynamics up to tridecane, while in higher alkanes pentadecane and hexadecane subslip behavior is observed. The slip hydrodynamics mimics the rotational reorientation times fairly well in few solvents though it does not predict the observed nonlinearity with $\tau_r$ vs. $\eta$ in both solvent systems. It is possibly due to the fact that, the solvent size is not considered while calculating using slip boundary condition. It may also be seen from Fig.4.6 that the GW theory underestimates the experimental values by a factor of 0.5 to 1 in alcohols and 0.3 to 0.5 in alkanes. The DKS theory overestimates the experimental trend by a factor of 1.1 to 3.3 in alcohols; nevertheless, the difference is more pronounced in higher alkanes.

An interesting point that emerges from the present study is that, all the three probes are observed to rotate much faster in alcohols compared to alkanes. This can be explained as due to large interstitial gaps that may be
Figure 4.6: Plot of rotational reorientation times of E428 as function of viscosity in (a) alkanes and (b) alcohols. The symbol • represents experimentally measured reorientation times. The stick and slip lines calculated using hydrodynamic theory are represented by solid lines. GW and DKS quasihydrodynamic theories are represented using the symbols △ and □, respectively.
formed in the solvent medium and because of the possible elastic nature of the spatial H-bonding network of large alcohol molecules constituting a supramolecular structure. The elasticity of the spatial network is a driving force for solvophobic interaction, which becomes important for the larger probes. Presumably, these exalite molecules will be located mainly in these solvophobic regions. Thus, they can rotate more freely in these gaps and experience a reduced friction due to a decreased viscosity at the point of contact. This actual viscosity experienced by the probe is highly localized and cannot be measured easily. In such a situation the coupling parameter $C$ is reduced to a much smaller value than $C_{\text{slip}}$ predicted by slip hydrodynamic boundary condition. One of the other plausible reasons is that the Brownian motion, which results from the fluctuating forces in the liquid, is behind the diffusive process. The processes, which are slow compared to solvent fluctuations, would see the full spectrum of the fluctuations and hence, the shear viscosity of the solvent [131]. For example, the fluctuations in $n$-alcohols occur roughly on the 100 ps/mPa s time scale – precisely the time scale of the Debye absorption in these solvents. On the other hand, the processes, which are extremely fast, do not experience the Brownian fluctuating force and are not viscously damped. Thus one expects a reduction in the microscopic friction for probe molecules, which diffuse at a rate comparable to or faster than the solvent fluctuations. This is exactly the type of effect, which would explain the faster rotational diffusion of exalites in $n$-alcohols than in $n$-alkanes. Further, the subslip behavior observed for these probes in polar solvents indicates the existence the nonhydrodynamic forces and thus a straightforward relation between the probe size and the nature of their behavior may not be appropriate.
The experimental data including rotational diffusion times for various neutral solute molecules (including exalites), in alkanes and alcohols, respectively, are collected in Table 4.3 and 4.4. The parameters, necessary to test the validity of molecular models for rotational diffusion, are obtained from Table 4.1 and 4.2 in case of alkanes and alcohols, respectively, for the present exalite probes.

There are many reports on rotational diffusion of small neutral molecules, which exhibit subslip behavior in alcohols. Garg and Smyth [148] have attributed the alcohol molecules to be associated with hydrogen bridges in temporary microcrystalline structures, which in fact are not stable, and at a given instant of time these has a finite length. At each instance some hydrogen bonds are ruptured and others are readily formed. The first dispersion region is connected with the molecules in these microcrystalline structures. The dielectric relaxation process involves the breaking and reforming of the hydrogen bonds with the orientation of dipole moment, and the rate of breaking off is a determining factor for the relaxation time. In order to check whether there is any dielectric friction on these large nonpolar probes in alcohols, we have also calculated dielectric friction contribution to the rotating probe molecule. The excited state dipole moments of exalites [149, 150] were obtained using solvatochormic shift method [151]. It is noted that the combined contribution due to hydrodynamic and dielectric friction will not affect the subslip trend exhibited by the exalite probes in alcohols. Hence, we attribute this unhindered faster rotation to strong hydrogen bonding among the solvent molecules leading to supramolecular structures.

There are several reports in literature where the reorientation times of neutral nonpolar solutes have been measured and analyzed as a function of
Table 4.3: List of normalized rotational diffusion parameters of neutral nonpolar solutes in alkanes, at 25±5°C.

<table>
<thead>
<tr>
<th>Solute</th>
<th>Volume (Å³)</th>
<th>Radius (Å)</th>
<th>Axial ratio</th>
<th>$\tau_r$ (ps/cP)</th>
<th>$\tau_{slip}$ (ps/cP)</th>
<th>$\tau_{stick}$ (ps/cP)</th>
<th>$\tau_r/\tau_{stick}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biphenyl</td>
<td>152</td>
<td>3.31</td>
<td>2.26</td>
<td>24</td>
<td>20</td>
<td>63</td>
<td>0.38</td>
<td>127</td>
</tr>
<tr>
<td>Stilbene</td>
<td>180</td>
<td>3.50</td>
<td>2.82</td>
<td>38</td>
<td>41</td>
<td>94</td>
<td>0.40</td>
<td>91</td>
</tr>
<tr>
<td>DPB</td>
<td>208</td>
<td>3.68</td>
<td>3.40</td>
<td>66</td>
<td>71</td>
<td>140</td>
<td>0.47</td>
<td>88</td>
</tr>
<tr>
<td>PTP</td>
<td>224</td>
<td>3.77</td>
<td>3.03</td>
<td>54</td>
<td>59</td>
<td>128</td>
<td>0.42</td>
<td>90, 131</td>
</tr>
<tr>
<td>Binapthyl</td>
<td>237</td>
<td>3.84</td>
<td>2.36</td>
<td>51</td>
<td>35</td>
<td>102</td>
<td>0.50</td>
<td>171</td>
</tr>
<tr>
<td>PQP</td>
<td>296</td>
<td>4.13</td>
<td>3.77</td>
<td>112</td>
<td>124</td>
<td>226</td>
<td>0.50</td>
<td>131</td>
</tr>
<tr>
<td>DPA</td>
<td>312</td>
<td>4.15</td>
<td>2.55</td>
<td>78</td>
<td>56</td>
<td>147</td>
<td>0.53</td>
<td>131</td>
</tr>
<tr>
<td>BMQ</td>
<td>325</td>
<td>4.27</td>
<td>2.65</td>
<td>131</td>
<td>95</td>
<td>241</td>
<td>0.54</td>
<td>93</td>
</tr>
<tr>
<td>TMQ</td>
<td>359</td>
<td>4.41</td>
<td>2.10</td>
<td>149</td>
<td>71</td>
<td>265</td>
<td>0.56</td>
<td>93</td>
</tr>
<tr>
<td>DMQ</td>
<td>376</td>
<td>4.48</td>
<td>1.82</td>
<td>194</td>
<td>54</td>
<td>282</td>
<td>0.68</td>
<td>93</td>
</tr>
<tr>
<td>TMI</td>
<td>429</td>
<td>4.68</td>
<td>2.43</td>
<td>294</td>
<td>145</td>
<td>416</td>
<td>0.71</td>
<td>93</td>
</tr>
<tr>
<td>E392A</td>
<td>609</td>
<td>5.26</td>
<td>3.59</td>
<td>384</td>
<td>347</td>
<td>435</td>
<td>0.88</td>
<td>101</td>
</tr>
<tr>
<td>QUI</td>
<td>639</td>
<td>5.38</td>
<td>2.09</td>
<td>454</td>
<td>147</td>
<td>554</td>
<td>0.82</td>
<td>93</td>
</tr>
<tr>
<td>E404</td>
<td>679</td>
<td>5.45</td>
<td>4.21</td>
<td>437</td>
<td>362</td>
<td>601</td>
<td>0.73</td>
<td>present work</td>
</tr>
<tr>
<td>BTBP</td>
<td>733</td>
<td>5.59</td>
<td>3.50</td>
<td>430</td>
<td>269</td>
<td>507</td>
<td>0.85</td>
<td>92</td>
</tr>
<tr>
<td>E417</td>
<td>837</td>
<td>5.85</td>
<td>5.00</td>
<td>636</td>
<td>623</td>
<td>944</td>
<td>0.67</td>
<td>Present work</td>
</tr>
<tr>
<td>E428</td>
<td>1031</td>
<td>6.27</td>
<td>6.18</td>
<td>749</td>
<td>1134</td>
<td>1587</td>
<td>0.47</td>
<td>present work</td>
</tr>
</tbody>
</table>
Table 4.4: List of normalized rotational diffusion parameters of neutral nonpolar solutes in alcohols, at 25±5°C.

<table>
<thead>
<tr>
<th>Solute</th>
<th>$\tau_r$ (ps/cP)</th>
<th>$\tau_r/\tau_{\text{stick}}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stilbene</td>
<td>10</td>
<td>0.10</td>
<td>91</td>
</tr>
<tr>
<td>PTP</td>
<td>39</td>
<td>0.30</td>
<td>131</td>
</tr>
<tr>
<td>Binaphyl</td>
<td>36</td>
<td>0.35</td>
<td>174</td>
</tr>
<tr>
<td>PQP</td>
<td>90</td>
<td>0.40</td>
<td>131</td>
</tr>
<tr>
<td>DPA</td>
<td>50</td>
<td>0.34</td>
<td>131</td>
</tr>
<tr>
<td>BMQ</td>
<td>87</td>
<td>0.36</td>
<td>93</td>
</tr>
<tr>
<td>TMQ</td>
<td>117</td>
<td>0.44</td>
<td>93</td>
</tr>
<tr>
<td>DMQ</td>
<td>137</td>
<td>0.49</td>
<td>93</td>
</tr>
<tr>
<td>TMI</td>
<td>194</td>
<td>0.47</td>
<td>93</td>
</tr>
<tr>
<td>E392A</td>
<td>196</td>
<td>0.45</td>
<td>101</td>
</tr>
<tr>
<td>QUI</td>
<td>436</td>
<td>0.79</td>
<td>93</td>
</tr>
<tr>
<td>E404</td>
<td>349</td>
<td>0.58</td>
<td>present work</td>
</tr>
<tr>
<td>BTBP</td>
<td>430</td>
<td>0.85</td>
<td>92</td>
</tr>
<tr>
<td>E417</td>
<td>259</td>
<td>0.27</td>
<td>present work</td>
</tr>
<tr>
<td>E428</td>
<td>357</td>
<td>0.22</td>
<td>present work</td>
</tr>
</tbody>
</table>
solute size and a transition from slip to stick hydrodynamics has been observed with increasing solute size. Ben-Amotz and Drake [92] have reported the rotational dynamics of the neutral large sized probe BTBP ($V=733$ Å$^3$) in series of alcohols and alkanes, and observed that rotational correlation times followed stick boundary condition. Though, BTBP contains the electronegative groups like -O and -N, which are capable of forming hydrogen bond with any solvent, the authors attributed, the stick condition mainly to its volume which is much larger than that of all the solvent molecules employed. Later, Roy and Doraiswamy [93] have studied a series of nonpolar solutes, which do not contain any electronegative groups and they too observed a transition towards the stick boundary condition on increasing the solute size from 2,2′′-dimethyl-$p$-quaterphenyl (BMQ, $V = 325$ Å$^3$) to 3,5,3′′,5′′-tert-$t$-butyl-$p$-quinquephenyl (QUI, $V = 639$ Å$^3$). The above two findings clearly suggest that the transition towards stick condition is directly linked to increase in the solute size as compared to that of the solvent. Therefore, one may expect a stick or even a superstick behavior in case of exalites (E404, E417 and E428) as these are larger than QUI by a factor of 1.1, 1.3 and 1.6, respectively. However, the present situation where the largest probe E428 follows subslip trend in alcohols is surprising and contradicts the predictions of the SED hydrodynamic theory. In such a situation the microscopic friction offered by the solvent molecules reduces well below the macroscopic value, which may result from either dynamic or structural features of the macroscopic solvation environment-giving rise to faster rotation of the probes in hydrogen bonding solvents. As far as the quasihydrodynamics theories are concerned, DKS theory has been successful in explaining the observed trend in alcohols, both qualitatively and quantitatively,
for E404, while it partly explains the rotational diffusion of E417 and E428 in lower alcohols. However, GW theory offers only a qualitative explanation.

On the other hand, rotational reorientation times of these exalite nonpolar probes bequeath interesting results following slip boundary condition in alkanes. It is clear from the Table 4.5 that there is a difference in slope for the two solvent types. Therefore, it is evident that the reorientation times of these exalites are shorter in alcohols than alkanes of comparable viscosity. This difference signifies the presence of nonhydrodynamic effects in one or both of the solvents as described earlier. It is unlikely that nonhydrodynamic behavior resulting from frequency dependence of the solvent friction occurs in alkanes on the 100 ps to 1 ns time scale [152]. These times are much longer than dynamic memory effects in the solvent arising from molecular collisions. These collisional events manifest themselves in the viscoelastic relaxation time, which for an n-alkane is estimated to lie in the subpicosecond to picosecond time domain [153]. Thus one would expect rotational times to be well described by the SED relation with the appropriate boundary condition and the solute shape factor [131] in n-alkanes. The internal mobility also allows the solute molecule to slip better through the surrounding solvent molecules than for a rigid molecular backbone [78]. The slip boundary condition is seen to be reasonable for an uncharged nonpolar molecule diphenylbutadiyne (DPB) in nonpolar solvents [88]. The values of $\tau/\tau_{\text{stick}}$ for DPB and E428 are identical in alkanes, though E428 is about 5 times larger than DPB (Table 4.3), suggesting that the rotation of these probes can well be explained by slip hydrodynamics. Similarly, the studies of a neutral dye BBOT [128], an approximate prolate top, indicate that it rotates in solution more rapidly with slip boundary condition. It was proposed that neutrals would not strongly interact with the solvent, and
Table 4.5: Linear regression results of rotational reorientation of exalites in series of alcohols, alkanes and binary mixture

<table>
<thead>
<tr>
<th>Solutes</th>
<th>Alcohols</th>
<th>Alkanes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Slope (ps/mPa s)</td>
<td>Slope (ps/mPa s)</td>
</tr>
<tr>
<td>E404</td>
<td>349</td>
<td>437</td>
</tr>
<tr>
<td></td>
<td>*360</td>
<td>*454</td>
</tr>
<tr>
<td>E417</td>
<td>259</td>
<td>636</td>
</tr>
<tr>
<td></td>
<td>*362</td>
<td>*677</td>
</tr>
<tr>
<td>E428</td>
<td>357</td>
<td>749</td>
</tr>
<tr>
<td></td>
<td>*510</td>
<td>*901</td>
</tr>
</tbody>
</table>

* The second entry for solute is a slope of the best fit line made to pass through the origin.
slip boundary condition thus were more appropriate. Others have argued [73] that the faster rotation observed for BBOT might be due to the internal mobility of the dye, which could also be one of the possible reasons for the faster rotation observed for the large exalite probes. Further, the GW model predicts very low $\tau_r$ values in alkanes as well as in alcohols and fails to satisfactorily explain the observed results quantitatively. Also, the $C$ values are nearly invariant of the size of the solute. It has been evidenced that the GW theory correctly predicts the observed results for solutes with $\sim 2.5$ Å radius. Therefore, it is adequate for very small solutes such as I$_2$ and NCCCCCN, which rotate very fast and show subslip behavior [154, 155]. Though DKS theory explains the experimentally observed trend up to decane in case of E404 and up to nonane for E428, a better agreement is found for E417 in alkanes. It has been observed [93] that the rotational reorientation times in alkanes are predicted accurately for solutes with radii up to 4.2 Å only, beyond which the theory tends to show poor agreement with the experiment. Our experimental results prove that the DKS theory holds good even for larger probes up to a radius of 6.3 Å in alkanes and brings out the subtle variations in the observed data.

In the present study, a nonlinear dependence of rotational reorientation times on solvent viscosity for these large probes in hydrogen bonding solvents has been observed. The subslip behavior noted for such large probes is surprising and calls for refinement of existing theories which are otherwise unable to explain the results. The quantitative agreement established in case of DKS theory for the rotational diffusion times in alkanes and partly in alcohols might provide a touchstone for an adequate theory of friction on a microscopic scale, which remains to be developed yet.
IV. ROTATIONAL DYNAMICS OF NONPOLAR AND POLAR PROBES

IV.A.5. Rotational dynamics of U-OB

Based on the molecular dimensions \((2a = 12.5 \text{ Å} \text{ and } 2b = 2.7 \text{ Å})\) [128] of U-OB (Fig. 4.7), it is approximated as a prolate ellipsoid. The van der Waals volume of U-OB calculated using Edward's atomic increment method is 383 Å³ [147]. The absorption and emission spectra of U-OB are shown in Fig. 4.8 and a typical fluorescence decay curve is given in Fig. 4.9. The rotational reorientation times of U-OB in alcohols, alkanes and binary mixture of toluene and butanol determined using the measured values of \(\langle r \rangle, r_0\) and \(\tau_f\) [Eqn. (4.43)] are presented in Table 4.6. The \(\langle r \rangle\) values are in the range of 0.019±0.001 to 0.182±0.003 in chosen solvents. A value of 0.360±0.002 for \(r_0\) measured at -60⁰±2⁰ C by using a solution of glycerol (Fluka, Germany), indicates that the absorption and emission dipoles form an angle of 15⁰ with respect to each other. As seen from the Table 4.6 the viscosity of the solvents varies from 0.23 to 3.07 mPa s in alkanes, from 0.55 to 11.80 mPa s in alcohols and from 0.90 to 2.01 mPa s in binary mixtures of toluene and butanol. \(f_{sick}\) is calculated using Eqn. (4.44) for the prolate-ellipsoid.

The rotational reorientation times of U-OB in all the three solvent systems (Table 4.6) were plotted as a function of viscosity, \(\eta\) [Fig. 4.10 (a) and (b)]. Linear regression results of these plots are shown in Table 4.7. Note that a positive intercept at zero viscosity was observed for all the three plots. Such nonzero intercepts have been observed in a number of studies [93, 156, 157] and their significance or otherwise have not been fully understood. The \(\tau_f\) values are found to increase linearly with \(\eta\) in all the three solvent systems. The ratio of the calculated, using slip boundary condition, to the observed reorientation times is in the range of 1.27 to 2.03 for alcohols, 1.07 to 1.5 for...
Figure 4.7: Molecular structure of U-OB

Figure 4.8: Absorption and fluorescence spectra of U-OB in methanol
Figure 4.9: Fluorescence decay curve of U-OB in methanol
Table 4.6: Steady state anisotropy $<r>$, fluorescence lifetime ($\tau_f$) and rotational reorientation times ($\tau_r$) of U-OB at 298 K. The maximum error in the fluorescence lifetime is ±50 ps.

<table>
<thead>
<tr>
<th>Alkanes</th>
<th>η (mPa s)$^a$</th>
<th>$&lt;r&gt;$</th>
<th>$\tau_f$ (ns)</th>
<th>$\tau_r$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentane</td>
<td>0.23</td>
<td>0.019 ± 0.001</td>
<td>0.95</td>
<td>53 ± 14</td>
</tr>
<tr>
<td>Hexane</td>
<td>0.29</td>
<td>0.021 ± 0.002</td>
<td>1.00</td>
<td>62 ± 14</td>
</tr>
<tr>
<td>Heptane</td>
<td>0.41</td>
<td>0.029 ± 0.002</td>
<td>1.00</td>
<td>88 ± 18</td>
</tr>
<tr>
<td>Octane</td>
<td>0.52</td>
<td>0.036 ± 0.002</td>
<td>1.01</td>
<td>112 ± 17</td>
</tr>
<tr>
<td>Nonane</td>
<td>0.66</td>
<td>0.044 ± 0.002</td>
<td>1.04</td>
<td>145 ± 19</td>
</tr>
<tr>
<td>Decane</td>
<td>0.84</td>
<td>0.052 ± 0.002</td>
<td>1.07</td>
<td>181 ± 17</td>
</tr>
<tr>
<td>Dodecane</td>
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<td>281 ± 28</td>
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<td>Tridecane</td>
<td>1.55</td>
<td>0.078 ± 0.002</td>
<td>1.26</td>
<td>349 ± 34</td>
</tr>
<tr>
<td>Pentadecane</td>
<td>2.81</td>
<td>0.106 ± 0.003</td>
<td>1.28</td>
<td>465 ± 51</td>
</tr>
<tr>
<td>Hexadecane</td>
<td>3.07</td>
<td>0.118 ± 0.003</td>
<td>1.33</td>
<td>649 ± 71</td>
</tr>
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<td>Methanol</td>
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<td>1.33</td>
<td>82 ± 21</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1.08</td>
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<td>1.34</td>
<td>211 ± 46</td>
</tr>
<tr>
<td>Propanol</td>
<td>1.96</td>
<td>0.061 ± 0.002</td>
<td>1.35</td>
<td>275 ± 58</td>
</tr>
<tr>
<td>Butanol</td>
<td>2.59</td>
<td>0.085 ± 0.002</td>
<td>1.36</td>
<td>420 ± 59</td>
</tr>
<tr>
<td>Pentanol</td>
<td>3.55</td>
<td>0.094 ± 0.002</td>
<td>1.37</td>
<td>484 ± 63</td>
</tr>
<tr>
<td>Hexanol</td>
<td>4.59</td>
<td>0.112 ± 0.003</td>
<td>1.38</td>
<td>623 ± 81</td>
</tr>
<tr>
<td>Heptanol</td>
<td>5.87</td>
<td>0.122 ± 0.003</td>
<td>1.40</td>
<td>718 ± 72</td>
</tr>
<tr>
<td>Octanol</td>
<td>7.63</td>
<td>0.151 ± 0.003</td>
<td>1.41</td>
<td>1019 ± 102</td>
</tr>
<tr>
<td>Nonanol</td>
<td>9.59</td>
<td>0.166 ± 0.003</td>
<td>1.41</td>
<td>1206 ± 121</td>
</tr>
<tr>
<td>Decanol</td>
<td>11.80</td>
<td>0.182 ± 0.003</td>
<td>1.41</td>
<td>1442 ± 130</td>
</tr>
<tr>
<td>Bu/Tol 9.2 %</td>
<td>2.01$^b$</td>
<td>0.044 ± 0.002</td>
<td>1.36</td>
<td>189 ± 25</td>
</tr>
<tr>
<td>Bu/Tol 19.87%</td>
<td>1.59$^b$</td>
<td>0.041 ± 0.002</td>
<td>1.35</td>
<td>174 ± 17</td>
</tr>
<tr>
<td>Bu/Tol 29.83 %</td>
<td>1.28$^b$</td>
<td>0.037 ± 0.002</td>
<td>1.33</td>
<td>152 ± 15</td>
</tr>
<tr>
<td>Bu/Tol 39.30 %</td>
<td>1.08$^b$</td>
<td>0.036 ± 0.002</td>
<td>1.31</td>
<td>146 ± 13</td>
</tr>
<tr>
<td>Bu/Tol 50.91 %</td>
<td>0.90$^b$</td>
<td>0.035 ± 0.002</td>
<td>1.29</td>
<td>139 ± 14</td>
</tr>
</tbody>
</table>

$^a$ From Ref. [101]
$^b$ From Ref. [172]
Figure 4.10 (a): Plot of rotational reorientation times of U-OB as a function of solvent viscosity in $n$-alcohols and binary mixture of toluene and butanol at 298K. The symbol (•) and (○) represents experimentally measured reorientation times in alcohols and binary mixture, respectively. The dashed line represents a linear best fit through the experimental points in alcohols. The solid lines are the theoretical plots of hydrodynamic models with stick and slip boundary conditions. Reorientation times calculated using GW and DKS theories are given by △ and □, respectively.
Figure 4.10 (b): Plot of rotational reorientation times of U-OB as a function of solvent viscosity in $n$-alkanes at 298K. The symbol (•) represents experimentally measured reorientation times. The dashed line represents a linear best fit through the experimental points. The solid lines are the theoretical plots of hydrodynamic models with stick and slip boundary conditions. Reorientation times calculated using GW and DKS theories are given by ∆ and □, respectively.
Table 4.7: Linear regression results of rotational reorientation of U-OB in series of alcohols, alkanes and binary mixture

<table>
<thead>
<tr>
<th></th>
<th>Alcohols</th>
<th>Alkanes</th>
<th>Binary mixture (toluene + butanol)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Slope (ps/mPa s)</strong></td>
<td><strong>Intercept (ps)</strong></td>
<td><strong>Slope (ps/mPa s)</strong></td>
<td><strong>Intercept (ps)</strong></td>
</tr>
<tr>
<td>119</td>
<td>62</td>
<td>189</td>
<td>17</td>
</tr>
<tr>
<td><strong>122</strong></td>
<td><strong>0</strong></td>
<td><strong>180</strong></td>
<td><strong>0</strong></td>
</tr>
</tbody>
</table>

* The second entry for solute is a slope of the best fit line made to pass through the origin.
alkanes and 1.12 to 3.00 for binary mixtures indicating much faster rotation in contrast to SED slip hydrodynamic prediction. As shown by Fleming et al. [128], the rotational diffusion times of BBOT are nearly the same (≈180 ps/mPa s) both in cyclohexane and ethanol and follow slip behavior. This is also true for the present situation for U-OB in ethanol and dodecane (≈200 ps/mPa s), which have almost similar viscosity. This is due to rapid solvent exchange (weak hydrogen bonds) in which the directional properties of the hydrogen bonds are smeared out. Further, a fluorescence lifetime of 1.34 ns obtained for U-OB in ethanol (η = 1.08 mPa s) at 298K seems reasonable as compared with the previous literature data (τ = 1.17 ns at η = 1.2 mPa s in ethanol) [128]. However, the scenario is different for solvents of higher viscosity. We notice a considerable change in the reorientation times of U-OB on increasing the solvent viscosity. For solvents of lower viscosity till ethanol in alcohols and till octane in alkanes U-OB exhibits a slip behavior. In higher alcohols, alkanes and in binary mixture of toluene and butanol it is surprising to note a much faster rotation than predicted by slip boundary condition, clearly exhibiting subslip trend.

It is worth mentioning here that the first experimental observation of subslip behavior was reported by Canonica et al. [89] for two nonpolar molecules *p*-terphenyl (V=224 Å³) and *p*-quaterphenyl (V=296 Å³). These molecules incidentally possess no hydrogen bonding groups and are normally expected to rotate faster in any solvent system. The authors varied the viscosity by varying temperature from 288 to 323K in paraffin and in mixture of paraffin and *n*-dodecane and argued that the subslip behavior was suggestive of the macroscopic viscosity being greater than microviscosity i.e., the actual viscosity experienced by the rotating molecule. Later, Benzler and Luther [98]
studied the rotational dynamics of these same molecules in alkanes at room temperature and observed a marked deviation from the SED slip hydrodynamics at higher viscosities. They also noted that the viscosity of the solvent at which the standard hydrodynamic SED description breaks down is related to the size of the rotating molecule; in n-alkanes with solvent molecules larger than the probe molecule, simple hydrodynamics failed to explain the experimental results. However, unlike p-terphenyl and p-quaterphenyl, the present probe U-OB has electronegative groups such as -O and -N and is most likely to form hydrogen bonds with the adjacent solvent molecules. In addition, the size of the probe molecule is larger by a factor of 2 to 11 in alcohols, 1 to 4 in alkanes and almost 4 in binary solvents which should clearly explain the SED description at least by slip behavior. The estimated hydrogen bond strength for U-OB is less than 3 kcal/mol, which is classified as weak hydrogen bond and therefore, the time scale of the solvent exchange must vary with the charge and polarizability of the solute molecule [128]. Further, a faster rotation of this probe in alcohols compared to alkanes of comparable viscosity indicates the importance of nonhydrodynamic effects in one or both the solvents series. Table 4.8 presents an overview of rotational diffusion times of neutral molecules dissolved in series of alkanes and alcohols reported in literature. The diffusion time ratios clearly indicate a strong deviation from the slip hydrodynamics. For example, stilbene whose rotational time is about 38 ps/mPa s in n-alkanes rotates more than twice as fast in n-alcohols while the largest probes, QUI and BTBP take nearly the same time of about 420 ps/mPa s and 430 ps/mPa s in n-alkanes and n-alcohols, respectively. For the intermediate solute sizes the trend, although not perfect, is towards a smaller difference between the rotation times in alcohols and alkanes. As mentioned
Table 4.8: Rotational diffusion of some neutral solute molecules in series of alkane and alcohol solvents.

<table>
<thead>
<tr>
<th>Solute</th>
<th>Volume (Å³)</th>
<th>Solvent</th>
<th>Diffusion Time (ps/mPa s)</th>
<th>Ratio</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stilbene</td>
<td>180</td>
<td>n-alcohols/ n-alkanes</td>
<td>13/38</td>
<td>0.34</td>
<td>91</td>
</tr>
<tr>
<td>p-Terphenyl</td>
<td>224</td>
<td>n-alcohols/ n-alkanes</td>
<td>39/57</td>
<td>0.68</td>
<td>76</td>
</tr>
<tr>
<td>9,10-Diphenyl anthracene</td>
<td>312</td>
<td>n-alcohols/ n-alkanes</td>
<td>50/78</td>
<td>0.64</td>
<td>131</td>
</tr>
<tr>
<td>BMQ&lt;sup&gt;a&lt;/sup&gt;</td>
<td>325</td>
<td>n-alcohols/ n-alkanes</td>
<td>78/107</td>
<td>0.73</td>
<td>93</td>
</tr>
<tr>
<td>TMQ&lt;sup&gt;b&lt;/sup&gt;</td>
<td>359</td>
<td>n-alcohols/ n-alkanes</td>
<td>110/136</td>
<td>0.81</td>
<td>93</td>
</tr>
<tr>
<td>DMQ&lt;sup&gt;c&lt;/sup&gt;</td>
<td>376</td>
<td>n-alcohols/ n-alkanes</td>
<td>130/174</td>
<td>0.75</td>
<td>93</td>
</tr>
<tr>
<td>U-OB</td>
<td>383</td>
<td>n-alcohols/ n-alkanes</td>
<td>119/189</td>
<td>0.63</td>
<td>Present work</td>
</tr>
<tr>
<td>TMI&lt;sup&gt;d&lt;/sup&gt;</td>
<td>429</td>
<td>n-alcohols/ n-alkanes</td>
<td>179/277</td>
<td>0.65</td>
<td>93</td>
</tr>
<tr>
<td>TP&lt;sup&gt;e&lt;/sup&gt;</td>
<td>496</td>
<td>n-alcohols/ n-alkanes</td>
<td>104/155</td>
<td>0.67</td>
<td>20</td>
</tr>
<tr>
<td>TT&lt;sup&gt;f&lt;/sup&gt;</td>
<td>601</td>
<td>n-alcohols/ n-alkanes</td>
<td>222/259</td>
<td>0.86</td>
<td>20</td>
</tr>
<tr>
<td>Exalite392A</td>
<td>609</td>
<td>n-alcohols/ n-alkanes</td>
<td>196/384</td>
<td>0.51</td>
<td>101</td>
</tr>
<tr>
<td>QUI&lt;sup&gt;g&lt;/sup&gt;</td>
<td>639</td>
<td>n-alcohols/ n-alkanes</td>
<td>418/426</td>
<td>0.98</td>
<td>93</td>
</tr>
<tr>
<td>BTBP&lt;sup&gt;h&lt;/sup&gt;</td>
<td>733</td>
<td>n-alcohols/ n-alkanes</td>
<td>430/430</td>
<td>1.00</td>
<td>92</td>
</tr>
</tbody>
</table>

<sup>a</sup> 2,2′′′-dimethyl-p-quaterphenyl  
<sup>b</sup> 3,3′,2″,3″-tetramethyl-p-quaterphenyl  
<sup>c</sup> 2-methyl-5-tert-butyl-p-quaterphenyl  
<sup>d</sup> 2,5,2′′′,5″″-tetramethyl-p-quinquephenyl  
<sup>e</sup> 2,5,8,11-tetra-tert-butyiperylene  
<sup>f</sup> 2,5,10,13-tetra-tert-butylterrylene  
<sup>g</sup> 3,5,3″,5″″-tetra-tert-butyl-p-quinquephenyl  
<sup>h</sup> N,N′-bis(2,5-di-tert-butylphenyl)-3,4,9,10-perylene dicarboxamide
earlier, the solvent fluctuations in \( n \)-alcohols occur roughly on the 100 ps/mPa s time scale. Smaller solutes, which diffuse in times shorter than or comparable to these fluctuations would experience reduced friction compared to \( n \)-alkanes and so the diffusion time ratio approaches unity. As this ratio becomes \( \geq 1 \), the observed rotational reorientation times approach stick behavior (Table 4.8). Interestingly, the results of U-OB whose diffusion time ratio \( \approx 1 \) follow subslip behavior, and also the probe rotates faster in alcohols than in alkanes.

The pronounced subslip behavior observed in alcohols may represent an additional influence of the local solvation environment offered by \( n \)-alcohols. The hydrophobic solvation environment around nonpolar solutes appears to offer a weaker coupling to the bulk solvent motion than the hydrophilic solvation environment around charged molecules in \( n \)-alcohols. However, the macroscopic hydrodynamic theories are good to within a factor of 2 in many cases [131]. The rotation factor of 3.0 in case of U-OB, below the slip line also explains the faster rotation of U-OB compared to \( p \)-terphenyl and \( p \)-quaterphenyl in binary mixtures.

Binary solvent mixtures are commonly used to customize solvent properties in chemical reactions and chromatography. Upon mixing, the solvent interaction often creates new solvent properties that are not present in the neat solvents. Numerous studies [158-160] have indicated that alcohols are associated through hydrogen-bonded linear chains (with restricted rotation about hydrogen bonds) into variable degrees of polymerization. When toluene is mixed with butanol the presence of \( \pi \)-electrons in toluene results in the formation of weak intermolecular complexes, which in turn leads to faster rotation of the solute due to poor interaction with solvents. This could also be
one of the possible reasons for faster rotation of U-OB in binary mixture than in alcohols and alkanes.

The steady-state anisotropy measurements agree well with the time resolved anisotropy measurements wherein the rotational correlation times deviate remarkably from SED slip hydrodynamics and follow a subslip behavior in higher alcohols. The fluorescence anisotropy decay parameters of U-OB in higher alcohols are summarized in Table 4.9 and anisotropy decay curves are shown in Fig.4.11 in hexanol and decanol. The rotational correlation function decays as a single exponential, as is usually expected for a prolate ellipsoid with transition moment along the symmetry axis \( [100, 128] \), which is of the form

\[
 r(t) = r_0 \exp\left(-t / \tau_R\right)
\]  

(4.45)

where \( \tau_R \) is the rotational reorientation time about the symmetry axis. The initial anisotropies (at zero time) \( r_0 \) of U-OB measured in alcohols are in the range of 0.349 to 0.375, and are comparable to the steady-state \( r_0 \) value of 0.360 (in glycerol at a temperature of -60\(^0\) C). Justus et al. [132] have studied fluorescence anisotropy kinetics of the probe Cl\(_2\)-\( \phi_2 \)-TPD containing two electronegative groups -O and -N, which has the structure and volume \( (V = 397 \text{ Å}^3) \) similar to U-OB, in chloroform. Noticing the stick-limit prolate models overestimating and slip-limit model underestimating the experimental results, they concluded it as a result of internal rotations within the molecules, which shorten the fluorescence anisotropy decay times. This may also account for shorter fluorescence anisotropy decay that we observe for U-OB as compared to Cl\(_2\)-\( \phi_2 \)-TPD falling in subslip limit with increasing solvent viscosity. Theoretical justification for this approach is provided by the microfriction.
Table 4.9: Fluorescence anisotropy decay parameters in alcohols at 298K ($\lambda_{ex}=375$ nm)

<table>
<thead>
<tr>
<th>Solvents</th>
<th>$\eta$/ mPas</th>
<th>$r_0^a$</th>
<th>$\tau_R$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentanol</td>
<td>3.55</td>
<td>0.355</td>
<td>510 ± 50</td>
</tr>
<tr>
<td>Hexanol</td>
<td>4.59</td>
<td>0.365</td>
<td>655 ± 55</td>
</tr>
<tr>
<td>Heptanol</td>
<td>5.87</td>
<td>0.349</td>
<td>780 ± 84</td>
</tr>
<tr>
<td>Octanol</td>
<td>7.63</td>
<td>0.375</td>
<td>1195 ± 67</td>
</tr>
<tr>
<td>Nonanol</td>
<td>9.59</td>
<td>0.362</td>
<td>1306 ± 75</td>
</tr>
<tr>
<td>Decanol</td>
<td>11.80</td>
<td>0.356</td>
<td>1495 ± 77</td>
</tr>
</tbody>
</table>

$^a$ ±10%.
Figure 4.11: Anisotropy decay of U-OB in hexanol (O) and decanol (⊕) at 298K.
theories of GW and DKS, which consider the solvent size as well as free spaces in the solvent.

IV.A.6. Applicability of quasihydrodynamic theories to rotational reorientation of U-OB

In the first place, the GW theory is used to calculate the parameters $\sigma$ and $C_0$ using Eqns (4.11) and (4.12), respectively, and the van der Waals volume of the solvent $V_s$ in different solvent systems employed. The coupling parameter $C_{GW}$, obtained from Eqn. (4.13) varies from 0.21 to 0.34 in alcohols, 0.18 to 0.25 in alkanes and 0.25 to 0.26 in binary mixture of toluene and butanol. The reorientation times calculated using $C_{GW}$ values were plotted as a function of $\eta$ in Figs.4.10 (a) and (b) for alcohols and binary mixtures and alkanes, respectively. The GW theory is able to mimic the nonlinear profile of $\tau$ vs. $\eta$, nonetheless it underestimates the friction experienced by the probe by a factor of 1.1 to 1.7 in alcohols, 2.3 to 3.0 in alkanes and 0.9 to 2.3 in binary mixture. In view of the large deviation between the experimentally measured reorientation times and those calculated theoretically, DKS theory is also employed in the present study. $C_{DKS}$ and $\gamma$ were calculated using Eqns. (4.14) and (4.15) in alcohols, alkanes and binary solvents. $\Delta V$ is calculated using Eqn. (4.16) for alkanes and Eqn. (4.17) is used for alcohols and binary mixtures. Clearly, the DKS theory overestimates the friction experienced by the probe by a factor of 1.4 to 1.7 in alcohols, 1.2 to 1.3 in alkanes and 1.1 to 2.3 in binary mixtures (Figs.10 (a) and (b)). It is interesting to note that, there is an almost perfect coincidence between the predictions of the slip hydrodynamic model and DKS model which is observed for the first time both for alcohols and alkanes. Also the experimental results are in good agreement with both slip and DKS theory up to nonane in alkanes. We may confidently say that the DKS
description of microscopic friction properly accounts for nonpolar solvents up to nonane and for polar solvents up to ethanol both qualitatively as well as quantitatively. However, in higher alcohols, alkanes and binary mixtures the experimentally obtained reorientation times lie in between the theoretical predictions of DKS and GW. The DKS quasihydrodynamic theory has been applied to analyze the observed results and a good agreement between the experiment and theory has been found \[21, 24, 92, 93, 99, 131\], though in few cases it could not predict the experimental results quantitatively. For example, in the study of few quarter and quinquephenyl molecules with radii in the range from 4 to 5 Å, Roy and Doraiswamy \[93\] noted a good correlation between the DKS theory and the experiment up to a solute radius of 4.5 Å. Dutt et al. \[99\] studied the rotational dynamics of 2,5-dimethyl-1,4-dioxo-3,6-diphenylpyrrolo[3,4-c]pyrrole (DMDPP) in a series of alcohols and observed a poor agreement between the experiment and the DKS theory, though, DMDPP has a radius of 4.1 Å. It was argued that the reason for the poor correlation between the theory and experiment could be due to the shape of the molecule.

In case of U-OB, the magnitude of reduction in the microscopic friction coefficient in case of GW is very small compared to DKS theory in all the solvent systems studied, perhaps due to the fact that the GW theory overlooks the cavities or free spaces created by the solvent molecules around the probe molecule. Further, the DKS theory accounts for the degree of contact between the probe in a cavity and the surrounding solvent, whereas the GW theory accounts for a stepwise decrease of angular velocity due to the finite size of the solvent molecules \[103\].

When the rotational motion of solutes containing -O and -N in polar solvents needs to be described, the simple hydrodynamic friction arising out of
the viscosity of the solvent alone is inadequate. An additional contribution due to dielectric friction has to be included [81]. Dielectric friction is calculated with an intention to check the contribution of dielectric friction, if any, to the rotational motion of U-OB. Within a dielectric continuum model for the solvent, the contribution due to dielectric friction to rotational reorientation time is given by [120]

$$\tau_{DF} = \frac{4\pi\mu^2}{3VkT} \frac{\varepsilon - 1}{(2\varepsilon + 1)^2} \tau_D$$

(4.46)

where $\mu$ is the dipole moment of the probe in the excited state, $\varepsilon$ and $\tau_D$ are the dielectric constant and Debye dielectric relaxation time of the solvent, respectively. The equations that are necessary to calculate the experimentally measured ground and excited state dipole moments using solvatochromic and Guggenheim method are taken from the references [151] and [161], respectively. The ground state geometry of U-OB was fully optimized using DFT with popular hybrid B3LYP functional with 6-31g* basis set [162] and is shown in Fig.4.12. The calculated dipole moments are tabulated in Table 3.10 (Chapter III). The values of dipole moments in the ground and excited states using all the three methods are in good agreement. The excited state dipole moment ($\mu_e = 2.94\pm0.1$ D) calculated using solvatochromic method was used to calculate the $\tau_{DF}$. The values of $\varepsilon$ and $\tau_D$ for alcohol solvents at 298K were taken from Ref. [81]. The calculated $\tau_{DF}$ values range from 9 to 913 ps for methanol through decanol. Thus, $\tau_{DF}$ calculated using the Eqn. (4.46) is added to the theoretically calculated reorientation times ($\tau_{SED}$), which perhaps increases the $\tau_r (=\tau_{SED} + \tau_{DF})$ to a larger extent. This suggests that the microscopic friction of the solvent is reduced well below the macroscopic value, which may be resulting from either dynamic or structural features of the
Figure 4.12: Optimized structure of U-OB obtained using B3LYP level theory with the 6-31 G* basis set. The arrow in the figure indicates the direction of dipole moment in the ground state.
macroscopic solvation environment [163]. Also the strong overlap between the slip hydrodynamics and the DKS theory is an indication of the fact that the solute U-OB is rotating unhindered in free spaces created in solvents thereby exhibiting the faster rotations in alcohols. The faster rotation of U-OB in alkanes is normal for a molecule of this size.
CHAPTER IV.B

RESULTS AND DISCUSSION:
POLAR PROBES
IV.B.1. Rotational dynamics of coumarins

Molecular structures of coumarins C522B, C307 and C138 are shown in Fig.4.13 and their absorption and emission spectra in Fig.4.14. The reorientation times of C522B, C307 in alcohols and alkanes and C138 in alcohols that were obtained from the measured values of $\langle r \rangle$, $r_0$ and $\tau_f$ using Eqn. (4.43) are summarized in Table 4.10 and 4.11. The anisotropies ($\langle r \rangle$) range from 0.002±0.001 to 0.065±0.002 for various solute-solvent combinations chosen. The values of $r_0$ for C522B, C307 and C138, respectively, are 0.369±0.004, 0.370±0.003 and 0.365±0.004 measured in glycerol (Fluka, Germany) as mentioned earlier for nonpolar probes. The measured fluorescence and anisotropy decays were found to be single exponentials in all the solvents studied. However, the observation of nonexponential anisotropy decay is more of an exception than a rule. Horng et al. [21] observed biexponential decay for the probe Coumarin 153 (C153) in a number of polar solvents and ascribed such biexponential decay due to the effects of non-Markovian friction on the rotational motion. The measured fluorescence anisotropy parameters of the three coumarins along with their measured lifetime values are summarized in Table 4.12 and typical fluorescence anisotropy decays of C307 are shown in Fig.4.15. It is evident from the Table that the reorientation times of coumarins are in good agreement with steady-state values and $r_0$ values are found to be 9% smaller than the steady-state values. The $\tau_f$ values thus obtained in alkanes show that C522B rotates faster compared to C307 in heptane through hexadecane. Note that from heptane to hexadecane the faster rotation of C522B is reducing from 54% to 7%, systematically, as compared to C307. This could be due to the low steady-state anisotropy value obtained for C522B in alkanes where errors are of the
Figure 4.13: Molecular structures of (a) C522B, (b) C307 and (c) C138
Figure 4.14: Absorption and fluorescence spectra of coumarins (C522B ---, C307 ----, C138 ---).
Table 4.10: Steady-state anisotropy ($<r>$), fluorescence lifetime ($\tau_f$) and rotational reorientation time ($\tau_r$) of coumarins in alcohols at 298K. The maximum error in the fluorescence life times is less than ±50 ps.

<table>
<thead>
<tr>
<th>Solvents</th>
<th>$\eta$/mPa s$^a$</th>
<th>$&lt;r&gt;$</th>
<th>$\tau_f$/ ns</th>
<th>$\tau_r$/ ps</th>
<th>$&lt;r&gt;$</th>
<th>$\tau_f$/ ns</th>
<th>$\tau_r$/ ps</th>
<th>$&lt;r&gt;$</th>
<th>$\tau_f$/ ns</th>
<th>$\tau_r$/ ps</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>0.55</td>
<td>0.004±0.001</td>
<td>4.87</td>
<td>53±13</td>
<td>0.003±0.001</td>
<td>5.10</td>
<td>42±14</td>
<td>0.003±0.001</td>
<td>3.63</td>
<td>30±10</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1.08</td>
<td>0.006±0.001</td>
<td>5.02</td>
<td>83±14</td>
<td>0.006±0.001</td>
<td>5.12</td>
<td>84±14</td>
<td>0.006±0.002</td>
<td>3.63</td>
<td>61±20</td>
</tr>
<tr>
<td>Propanol</td>
<td>1.95</td>
<td>0.009±0.001</td>
<td>5.05</td>
<td>126±14</td>
<td>0.011±0.002</td>
<td>5.13</td>
<td>157±29</td>
<td>0.009±0.002</td>
<td>3.64</td>
<td>92±20</td>
</tr>
<tr>
<td>Butanol</td>
<td>2.59</td>
<td>0.011±0.002</td>
<td>5.08</td>
<td>156±28</td>
<td>0.016±0.002</td>
<td>5.14</td>
<td>232±29</td>
<td>0.011±0.001</td>
<td>3.64</td>
<td>113±10</td>
</tr>
<tr>
<td>Pentanol</td>
<td>3.51</td>
<td>0.013±0.002</td>
<td>5.09</td>
<td>186±29</td>
<td>0.021±0.003</td>
<td>5.14</td>
<td>309±44</td>
<td>0.015±0.003</td>
<td>3.64</td>
<td>156±31</td>
</tr>
<tr>
<td>Hexanol</td>
<td>4.57</td>
<td>0.017±0.002</td>
<td>5.09</td>
<td>246±29</td>
<td>0.027±0.002</td>
<td>5.14</td>
<td>405±30</td>
<td>0.020±0.002</td>
<td>3.65</td>
<td>212±21</td>
</tr>
<tr>
<td>Heptanol</td>
<td>5.97</td>
<td>0.022±0.003</td>
<td>5.10</td>
<td>323±44</td>
<td>0.034±0.003</td>
<td>5.15</td>
<td>521±46</td>
<td>0.025±0.002</td>
<td>3.65</td>
<td>268±21</td>
</tr>
<tr>
<td>Octanol</td>
<td>7.63</td>
<td>0.027±0.002</td>
<td>5.10</td>
<td>403±30</td>
<td>0.041±0.003</td>
<td>5.15</td>
<td>642±47</td>
<td>0.035±0.004</td>
<td>3.68</td>
<td>390±45</td>
</tr>
<tr>
<td>Nonanol</td>
<td>9.59</td>
<td>0.033±0.003</td>
<td>5.10</td>
<td>501±46</td>
<td>0.051±0.003</td>
<td>5.18</td>
<td>828±49</td>
<td>0.037±0.002</td>
<td>3.74</td>
<td>422±23</td>
</tr>
<tr>
<td>Decanol</td>
<td>11.74</td>
<td>0.042±0.003</td>
<td>5.12</td>
<td>658±47</td>
<td>0.065±0.002</td>
<td>5.18</td>
<td>1104±34</td>
<td>0.047±0.003</td>
<td>3.77</td>
<td>477±35</td>
</tr>
</tbody>
</table>

$^a$ Viscosity data is from Ref. [101]
Table 4.11: Steady-state anisotropy ($<r>$), fluorescence lifetime ($\tau_f$) and rotational reorientation time ($\tau_r$) of coumarins in alkanes at 298K for C522B and C307. The maximum error in the fluorescence life times is less than ±50 ps.

<table>
<thead>
<tr>
<th>Solvents</th>
<th>$\eta$/mPa s$^a$</th>
<th>$&lt;r&gt;$</th>
<th>$\tau_f$/ ns</th>
<th>$\tau_r$/ ps</th>
<th>$&lt;r&gt;$</th>
<th>$\tau_f$/ ns</th>
<th>$\tau_r$/ ps</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentane</td>
<td>0.23</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.003±0.001</td>
<td>4.23</td>
</tr>
<tr>
<td>Hexane</td>
<td>0.29</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.003±0.001</td>
<td>4.28</td>
</tr>
<tr>
<td>Heptane</td>
<td>0.41</td>
<td>0.002±0.001</td>
<td>3.98</td>
<td>22±11</td>
<td>0.004±0.001</td>
<td>4.37</td>
<td>48±12</td>
</tr>
<tr>
<td>Octane</td>
<td>0.52</td>
<td>0.003±0.001</td>
<td>4.11</td>
<td>34±11</td>
<td>0.004±0.001</td>
<td>4.51</td>
<td>49±12</td>
</tr>
<tr>
<td>Nonane</td>
<td>0.66</td>
<td>0.004±0.001</td>
<td>4.17</td>
<td>46±12</td>
<td>0.005±0.001</td>
<td>4.63</td>
<td>63±13</td>
</tr>
<tr>
<td>Decane</td>
<td>0.84</td>
<td>0.005±0.001</td>
<td>4.20</td>
<td>58±12</td>
<td>0.006±0.001</td>
<td>4.60</td>
<td>76±13</td>
</tr>
<tr>
<td>Dodecane</td>
<td>1.35</td>
<td>0.006±0.001</td>
<td>4.26</td>
<td>70±12</td>
<td>0.007±0.002</td>
<td>4.79</td>
<td>92±26</td>
</tr>
<tr>
<td>Tridecane</td>
<td>1.55</td>
<td>0.007±0.001</td>
<td>4.31</td>
<td>83±12</td>
<td>0.008±0.002</td>
<td>4.80</td>
<td>106±27</td>
</tr>
<tr>
<td>Pentadecane</td>
<td>2.81</td>
<td>0.009±0.001</td>
<td>4.38</td>
<td>110±12</td>
<td>0.009±0.002</td>
<td>4.80</td>
<td>120±27</td>
</tr>
<tr>
<td>Hexadecane</td>
<td>3.07</td>
<td>0.010±0.001</td>
<td>4.52</td>
<td>126±13</td>
<td>0.010±0.002</td>
<td>4.86</td>
<td>135±27</td>
</tr>
</tbody>
</table>

$^a$ Viscosity data is from Ref. [101]
Table 4.12: Fluorescence anisotropy decay parameters of coumarins in alcohols at 298K.

<table>
<thead>
<tr>
<th>Solvents</th>
<th>C522B</th>
<th>C307</th>
<th>C138</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \eta/\text{mPa s} )^a</td>
<td>( &lt;r_0&gt;^a )</td>
<td>( \tau / \text{ps} )</td>
</tr>
<tr>
<td>Butanol</td>
<td>2.59</td>
<td>0.338</td>
<td>150±25</td>
</tr>
<tr>
<td>Pentanol</td>
<td>3.51</td>
<td>0.348</td>
<td>179±28</td>
</tr>
<tr>
<td>Hexanol</td>
<td>4.57</td>
<td>0.369</td>
<td>240±35</td>
</tr>
<tr>
<td>Heptanol</td>
<td>5.97</td>
<td>0.375</td>
<td>311±30</td>
</tr>
<tr>
<td>Octanol</td>
<td>7.63</td>
<td>0.365</td>
<td>395±25</td>
</tr>
<tr>
<td>Nonanol</td>
<td>9.59</td>
<td>0.370</td>
<td>480±38</td>
</tr>
<tr>
<td>Decanol</td>
<td>11.74</td>
<td>0.376</td>
<td>630±40</td>
</tr>
</tbody>
</table>

\(^a±10\%\).
Figure 4.15: Fluorescence anisotropy decay of C307 in pentanol (O) and decanol (Δ) with the fitted curve
order of 50% and 30% for heptane and octane, respectively. In alcohols, it is interesting to note that, the probe C138 rotates almost twice as fast from propanol to decanol compared to C307. In other words, C138 is experiencing almost same mechanical friction ($\tau_r$) as that of C522B and twice as C307 from propanol to decanol. In other words, among the three molecules, C307 shows greater interaction owing to its greater polarity. The probes C522B and C138 coincidentally have shown similar interactions. The aminomethyl group in C138 being free contributes more to the charge separation through resonance-whereas in C522B, this resonance contribution is sluggish, comparatively. However, the presence of -CF$_3$ in the latter increases the charge separation leading to a better interaction with the hydrogen bonding solvents. Replacement of -CF$_3$ by cyclic alkyl group in C138 would not have any greater contribution towards its polarity. Hence, the presence of two different groups with contradicting properties leads to the coincidental similarities in reorientation dynamics of C522B and C138. The normalized rotational reorientation times (at unit viscosity) are smaller in alkanes compared to alcohols, which indicates that the probes C522B and C307 rotate faster in alkanes compared to alcohols. The reorientation times of the three probes thus obtained in alcohols follow the trend $\tau_r^{C307} > \tau_r^{C522B} \geq \tau_r^{C138}$.

IV.B.2. Hydrodynamic model

The limiting values of the reorientation times using SED theory with stick and slip boundary conditions were calculated as follows: Based on the van der Waals increments [147], the molecular volumes of C522B, C307 and C138 were determined as 223 Å$^3$, 217Å$^3$ and 210Å$^3$, respectively. The longest end-to-end distance was taken as the long axis (2a) of the molecule. The thickness
of the probes (c) was taken, as suggested by Waldeck and Fleming [80] for an aromatic molecule giving a half axis of 1.9 Å. The axis perpendicular to the long axis i.e., the short in-plane axis was obtained using the expression

\[ V = \frac{4\pi}{3} abc \]  

(4.47)

where \( V \) corresponds to the volume calculated using Edward's atomic increment method [147], \( a, b \) and \( c \) being the half-axes. The estimated axial radii and the van der Waals volumes of the probes are given in Table 4.13.

Owing to the fact that all the three dimensions of the present coumarin probes are different, they are modeled as asymmetric ellipsoids [25]. The friction coefficients with stick boundary condition along the three axes were obtained by interpolating the numerical tabulations of Small and Isenberg [125], while those with a slip boundary condition were obtained from the numerical tabulations of Sension and Hochstrasser [124]. From the friction coefficients \( \zeta \), the diffusion coefficients \( D \), were calculated using the Eqn. (4.40) through which the reorientation times were obtained [Eqn. (4.39)] with the assumption that the transition dipole is along the long axis (Fig.4.16). The reorientation times calculated with stick and slip boundary conditions together with the shape factor, \( f \) and \( C_{\text{slip}} \), are tabulated in Table 4.13. It may be noted that, \( \tau/\eta \) values for all the three probes studied are identical.

Fig.4.17 gives a plot of \( \tau \) vs. \( \eta \) for all the three molecules in alcohols and for C522B and C307 in alkanes along with the stick and slip lines, as C138 did not dissolve in alkanes. With all the three probes having almost identical volumes, it may be interesting to check for the friction experienced by each of them in alcohols. Note that the experimentally measured reorientation times for the three probes lie between slip and stick hydrodynamic in case of alcohols.
Table 4.13: Properties of the solute used in the study

<table>
<thead>
<tr>
<th>Solute</th>
<th>Axial radii/Å³</th>
<th>$V$/Å³</th>
<th>$\beta^a$</th>
<th>$\theta$</th>
<th>$\tau_r\eta^{-1}$/ps (mPa s)$^{-1}$</th>
<th>$C_{slip}$</th>
<th>Slip</th>
<th>Stick</th>
<th>$\mu_e/D$</th>
<th>$\mu_e/D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coumarin 522B</td>
<td>6.1x4.6x1.9</td>
<td>223</td>
<td>1.03</td>
<td>13</td>
<td>1.85</td>
<td>0.15</td>
<td>15</td>
<td>100</td>
<td>2.47$^b$</td>
<td>5.15$^b$</td>
</tr>
<tr>
<td>Coumarin 307</td>
<td>6.3x4.3x1.9</td>
<td>217</td>
<td>1.00</td>
<td>13</td>
<td>1.91</td>
<td>0.18</td>
<td>18</td>
<td>101</td>
<td>1.82$^b$</td>
<td>4.50$^b$</td>
</tr>
<tr>
<td>Coumarin 138</td>
<td>6.5x4.1x1.9</td>
<td>210</td>
<td>0.97</td>
<td>14</td>
<td>1.98</td>
<td>0.22</td>
<td>22</td>
<td>101</td>
<td>2.20$^c$</td>
<td>3.42$^c$</td>
</tr>
</tbody>
</table>

$^a$ $\beta$ is the volume correction factor, which is defined as the ratio of the volume of the solute to the average volume of the three solutes.

$^b$ from the ref [166]

$^c$ from the ref [167]
Figure 4.16: The B3LYP/6-31g* optimized structures of the coumarins (a) C522B (b) C307 and (c) C138 along with the direction of transition moment.
Figure 4.17: A plot of $\tau_\text{r}$ vs. $\eta$ for the three coumarins in alcohols (●), and alkanes (〇) in case of C522B and C307
IV. ROTATIONAL DYNAMICS OF NONPOLAR AND POLAR PROBES

However, in alkanes we observe, as the size of the solvent molecule becomes equal to and larger than the size of the solute molecule, the probe molecules experience a reduced friction. For C522 ($V=223 \, \text{Å}^3$), the experimentally observed $\tau_r$ values are higher than the slip hydrodynamics by a factor of 3.7 to 4.6 from heptane ($V=130 \, \text{Å}^3$) to decane ($V=181 \, \text{Å}^3$), whereas from dodecane ($V=215 \, \text{Å}^3$) to hexadecane ($V=283 \, \text{Å}^3$) it is from 2.6 to 3.6. An interesting point to be noted is that, in case of C307 ($V=217 \, \text{Å}^3$), for a ratio of van der Waals volume of the solvent to probe ($V_s/V_p$) less than 1 (i.e., from pentane, $V=96 \, \text{Å}^3$ to decane), the probe is experiencing higher friction following stick hydrodynamics and from dodecane to hexadecane the probe experiences a reduced friction as the ratio of $V_s/V_p$ increases from 1 to 1.3. Earlier, Benzler and Luther [98] measured the reorientation time of biphenyl ($V=150 \, \text{Å}^3$) and $p$-terphenyl ($V=221 \, \text{Å}^3$) in $n$-alkanes, and observed a nonlinearity in the plot of $\tau_r$ vs. $\eta$ from decane onwards in case of biphenyl and from tetradecane onwards, in the case of $p$-terphenyl. Singh [24] studied reorientation times of the probe neutral red ($V=234 \, \text{Å}^3$) which experienced a reduced friction from tetradecane to hexadecane following subslip behavior. Note that C522B and C307 have almost identical volumes as compared to neutral red and $p$-terphenyl and thus a similar rotational relaxation in alkanes may be expected. From the logarithmic fits of the data, the relationship between $\tau_r$ and $\eta$ for the three probes in alkanes and alcohols were obtained, and summarized in Table 4.14. It may be inferred from this Table that these probes follow different correlations with viscosity in alkanes and alcohols. The degree of nonlinearity is not significant in case of alcohols compared with the alkanes. However, there is little or no theoretical justification for these fits and thus may be considered to be purely empirical in nature.
Table 4.14: The relation between $\tau_r$ and $\eta$ obtained from the logarithmic fits of data in alkanes and alcohols for the three coumarins

<table>
<thead>
<tr>
<th>Solute</th>
<th>Alkanes</th>
<th>Alcohols</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coumarin 522B</td>
<td>(50±3)$\eta^{(0.77±0.07)}$</td>
<td>(87±4)$\eta^{(0.81±0.03)}$</td>
</tr>
<tr>
<td>Coumarin 307</td>
<td>(72±4)$\eta^{(0.54±0.03)}$</td>
<td>(80±2)$\eta^{(1.00±0.01)}$</td>
</tr>
<tr>
<td>Coumarin 138</td>
<td>-</td>
<td>(52±2)$\eta^{(0.92±0.03)}$</td>
</tr>
</tbody>
</table>
The coupling parameter $C_{GW}$, obtained from Eqn. (4.13) varies from 0.17 to 0.29 for the three probes in alcohols, while in case of C522B and C307 in alkanes it is from 0.15 to 0.21. Though the GW theory is able to mimic the nonlinear profile of $\tau_r$ vs. $\eta$, it clearly underestimates the average friction experienced by the probes by a factor of 2.9, 4.1 and 2.3 in alcohols for C522B, C307 and C138, respectively. In alkanes, it underestimates that by a factor of 3.2 to 4.8 in case of C522B and C307. It is also noted that the probes experience reduced friction as the size of the solvent increases. A number of reports [90-97] have noted faster rotation of many probes in alcohols when compared to alkanes, which has been explained as due to higher free volume in alcohols compared to alkanes with the help of DKS theory. Had there been no electrical interaction between the coumarins and alcohols, a faster rotation of the coumarins would have been observed in alcohols compared to alkanes, but an opposite trend observed experimentally indicates the presence of electrical friction [25]. Before evaluating the dielectric friction quantitatively, the contribution due to mechanical friction must be estimated with a reasonable degree of accuracy. SED theory with a slip hydrodynamic boundary condition is often used to calculate the mechanical friction in case of medium-sized solute molecules. However, in the present study the solvent size increases by more than 5 times in alcohols from methanol to decanol. Hence, DKS quasihydrodynamic theory is found to be more appropriate, when size effect is taken into account. Eqn. (4.17) is used to calculate $\Delta V$ in associative solvents like alcohols, because $C_{DKS}$ obtained in this manner gave a better agreement with the experimental results [25, 96, 99, 106, 164].
In the present situation the mechanical friction calculated using DKS theory contributes about 10%-20% to the total friction experienced by the probes C522B and C307 and about 25% - 34% in case of C138 in alcohols. Since the DKS theory predicts the friction on the probe molecule, taking into consideration the relative size of the probe and solvent as well as the free volume of the solvent, we feel that the friction estimated from DKS theory be necessarily included in the calculations though it is underestimating the experimentally observed trend by a factor of 5.64 to 7.57, 5.25 to 9.60 and 2.97 to 3.98, respectively, for C522B, C307 and C138. The mechanical friction calculated using slip hydrodynamics did not vary much from the friction estimated by GW theory. Hence to justify, the mechanical friction calculated using slip hydrodynamics is taken, which accounts for about 15% - 30% of the total friction experienced by C522B and C307 and about 39% - 55% in case of C138 in alcohols. Mechanical friction experienced by coumarins in alcohols was also estimated from the experimentally observed relationship of $\tau_r$ and $\eta$ in alkanes. Alkanes offer more mechanical friction to the rotating probe than alcohols as observed from a number of diffusion studies involving nonpolar probes [25]. In the present case, the mechanical friction experienced by the C522B and C307 in alkanes is about 30%-55% and 37%-47% more than that calculated using slip hydrodynamic theory, while it is about 32%-68% and 45%-52% with DKS theory, respectively. Having evaluated the mechanical friction, we now turn our attention to the dielectric friction contribution. Since, in the present study our aim is to compare the dielectric friction contribution to
the total friction experienced by the three coumarins, it is imperative to determine the mechanical friction fairly accurately.

IV.B.3. Dielectric Friction

The dielectric friction is one of the important mechanisms that hinders the rotation of the polar molecules in polar solvents. Eqn. (4.18) implies that the difference between total friction and mechanical friction can be approximated as contribution due to dielectric friction. Both Nee-Zwanzig (NZ) [85] and van der Zwan-Hynes (ZH) [60] models were used to calculate the dielectric contribution.

IV.B.3.1. Nee-Zwanzig model

NZ theory assumes the solute to be a point dipole located inside a spherical cavity of radius \( a \) and the solvent is treated as a continuous dielectric medium characterized by a frequency dependent dielectric constant. If \( \mu \) is the dipole moment of the solute, \( \varepsilon_0 \) and \( \varepsilon_\infty \) are the zero- and high-frequency dielectric constants of the solvent, respectively, then the dielectric friction, \( \tau_{DF} \) experienced by the solute in the limit of zero-frequency is given by [85, 165] Eqn. (4.19). The excited state dipole moments and dielectric properties in alcohols using Eqn. (4.19) were obtained from our earlier study [166] of C522B and C307, while for C138, they are taken from Ref. [167]. We have used two different values of \( a \) in the calculation. First value of \( a \) was taken from the van der Waals volume obtained for the solutes, treating them as spherical molecules and the second value of \( a \) was taken from the half length of the long axis as given in Table 4.13. These two values signify two extreme limits that can be used to calculate the dielectric friction contribution. But the
general practice is to model the molecule as a sphere and determine its radius from the molecular volume [122, 133]. From the experimentally measured reorientation time, \( \tau_{DF} \) was obtained using the relations, \( \tau_{DF}^{\text{Exp}} = \tau_r - \tau_r^{\text{Slip}} \) and \( \tau_{DF} = \tau_r^{\text{Exp}} - \tau_r^{\text{DKS}} \) for all the three coumarins whereas, \( \tau_{DF} = \tau_r^{\text{Exp}} - \tau_r^{\text{Alkanes}} \) is used additionally in case of C522B and C307. To compare the theoretically calculated dielectric friction with the experimentally observed one, \( \tau_{DF} \) was plotted as a function of \( A \), where

\[
A = \frac{(\varepsilon_{\infty} + 2)(\varepsilon_0 - \varepsilon_{\infty})}{(2\varepsilon_0 + \varepsilon_{\infty})^2} \tau_D
\]  

(4.48)

Fig.4.18 shows a plot of \( \tau_{DF} \) vs. \( A \) for C522B, C307 and C138 using different relations of dielectric frictions. From the figure it is clear that the NZ theory for both the values of \( a \) (van der Waals radii and half length of the long axis), overestimates the dielectric friction contribution. This has reflected in the dipole moments obtained from the slopes of the plot of \( \tau_{DF} \) vs. \( A \) for the experimentally observed dielectric friction, as listed in Table 4.15. Although, three different methods were used to obtain the dielectric friction contribution \( (\tau_{DF}^{\text{Exp}} = \tau_r - \tau_r^{\text{Slip}}, \tau_{DF} = \tau_r^{\text{Exp}} - \tau_r^{\text{DKS}} \text{ and } \tau_{DF} = \tau_r^{\text{Exp}} - \tau_r^{\text{Alkanes}} ) \), the difference between these slopes is not significant and is within the limits of experimental errors. Also when one considers the excited state dipole moments of the present probes, the dielectric friction experienced by them should follow the order \( \tau_{DF}^{C522B} > \tau_{DF}^{C307} > \tau_{DF}^{C138} \). But it is interesting to note that the experimental trends followed are: \( \tau_{DF}^{C307} > \tau_{DF}^{C522B} > \tau_{DF}^{C138} \text{, } \tau_{DF}^{C307} \approx \tau_{DF}^{C522B} < \tau_{DF}^{C138} \text{ and } \tau_{DF}^{C307} > \tau_{DF}^{C522B} \) when dielectric contributions, respectively, with slip, DKS and alkanes, are considered.
Figure 4.18: A plot of experimentally measured dielectric friction $\tau_{DF}$ as a function of $A$, where $A = [(\varepsilon_\infty + 2)^2(\varepsilon_0 - \varepsilon_\infty)/(2\varepsilon_0 + \varepsilon_\infty)^2]\tau_D$. $\tau_{DF}$ was obtained from the experimentally measured reorientation times using three different methods $\tau_{DF} = \tau_{r,Exp} - \tau_{r,Slip}$, $\tau_{DF} = \tau_{r,Exp} - \tau_{r,DKS}$ in case of all the three coumarins and they plotted as open triangle and circles, respectively, and $\tau_{DF} = \tau_{r,Exp} - \tau_{r,Alkanes}$ is used in case of C522B and C307 with filled circles. The dotted lines are calculated ones using Eqn. (4.19). The upper and lower lines correspond to two values $a$ of as explained in the text.
Table 4.15: Excited state dipole moments obtained from the slope of the plot $r_{DF}$ vs. $A$ using NZ theory

<table>
<thead>
<tr>
<th>Solute</th>
<th>$\mu/\text{D}^a$</th>
<th>$\mu/\text{D}^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coumarin 522B</td>
<td>$4.1\pm0.2 \ (1.8\pm0.1^c)$</td>
<td>$8.5\pm0.6 \ (3.7\pm0.3^c)$</td>
</tr>
<tr>
<td>Coumarin 307</td>
<td>$5.6\pm0.3 \ (3.9\pm0.4^c)$</td>
<td>$12.3\pm0.9 \ (8.7\pm0.6^c)$</td>
</tr>
<tr>
<td>Coumarin 138</td>
<td>$3.2\pm0.2$</td>
<td>$7.5\pm0.4$</td>
</tr>
</tbody>
</table>

*a* Dipole moments obtained taking van der Waals radius of the probe molecule (*a*)

*b* Dipole moments obtained taking half length of the long axis (*a*)

*c* Dipole moment values obtained from the slopes of $r_{DF}$ vs $A$ in case of Alkanes
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IV.B.3.2. van der Zwan-Hynes model

Eqn. (4.22) was used to calculate dielectric friction contribution using ZH model. In the calculation of $\tau_L$, $\varepsilon_\infty$ was taken as the square of the refractive index and was assumed to be independent of temperature. $\Delta \nu$ values for C522B and C307 were taken from Ref. [166] and for C138, it varied from 4821 cm$^{-1}$ to 5207 cm$^{-1}$ in alcohols. The observed dielectric friction $\tau_{DF}$, obtained using Eqn. (4.22) was plotted as a function of $\Delta \nu \tau_L$ (Fig.4.19). The experimentally observed dielectric frictions using the three relations (as was done in case of NZ model) have also been used here and are plotted in the figure. It is observed that the theoretically calculated dielectric friction (shown as dotted lines in the figure) using ZH theory overestimates the experimentally observed dielectric friction contribution as was also noted in the case of NZ theory. From the slopes of the plots of $\tau_{DF}$ vs. $\Delta \nu \tau_L$, $\mu^2/\langle \Delta \mu \rangle^2$ values were obtained and summarized in Table 4.16 along with the experimentally calculated $\mu^2/\langle \Delta \mu \rangle^2$ values. When compared with $\mu^2/\langle \Delta \mu \rangle^2$ values calculated from Table 4.13, the observed trend should be in the order: $\tau_{DF}^{C138} > \tau_{DF}^{C522B} > \tau_{DF}^{C307}$, nevertheless, from the slopes of Fig.4.19, it is observed that $\tau_{DF}^{C307} > \tau_{DF}^{C522B} > \tau_{DF}^{C138}$. It is seen from the table that the $\mu^2/\langle \Delta \mu \rangle^2$ values are greater by a factor of 52, 5 and 12, respectively, for C138, C307 and C522B with respect to dielectric friction using slip and DKS theories, whereas in case of alkanes it varies from 11 to 61, for C307 and C522B. The large difference in $\mu^2/\langle \Delta \mu \rangle^2$ values using dielectric friction in alkanes and that obtained with ZH theory may account for the fact that higher mechanical friction offered by the alkanes is much more than the dielectric friction in case of C307 and C522B.
Figure 4.19: A plot of experimentally measured dielectric friction $\tau_{DF}$ as a function of $\Delta \nu \tau_\nu$. $\tau_{DF}$ was obtained from the experimentally measured reorientation times using three different methods i.e., $\tau_{DF} = \tau_r^{Exp} - \tau_r^{Slip}$, $\tau_{DF} = \tau_r^{Exp} - \tau_r^{DKS}$ in case of all the three coumarins and are plotted as open triangle and circles, respectively, and $\tau_{DF} = \tau_r^{Exp} - \tau_r^{Altcont}$ is used in case of C522B and C307 with filled circles. The dotted lines are calculated ones using Eqn. (4.22).
Table 4.16: Excited state dipole moments obtained from the slope of the plot $\tau_{DF}$ vs. $\Delta \nu$ $\tau_L$ using ZH theory

<table>
<thead>
<tr>
<th>Solute</th>
<th>$\mu^2/(\Delta \mu)^2a$</th>
<th>$\mu^2/(\Delta \mu)^2b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coumarin 522B</td>
<td>0.30±0.02 (0.06±0.01°)</td>
<td>3.69±0.08</td>
</tr>
<tr>
<td>Coumarin 307</td>
<td>0.53±0.03 (0.26±0.01°)</td>
<td>2.82±0.05</td>
</tr>
<tr>
<td>Coumarin 138</td>
<td>0.15±0.01</td>
<td>7.86±0.22</td>
</tr>
</tbody>
</table>

* Obtained from the slope of the plot $\tau_{DF}$ vs $\Delta \nu$ $\tau_L$.

* Calculated from the dipole moment values listed in Table .

* Dipole moment values obtained from the slopes of $\tau_{DF}$ vs $\Delta \nu$ $\tau_L$ in case of Alkanes.
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It is clear from the above discussion that both the theories fail to predict the observed behavior, even qualitatively. One important point that emerges is that the NZ model predicts a reduced friction for C138 based on its low excited state dipole moment in comparison with C522B and C307, whereas, the opposite trend is predicted by ZH theory, based on their $\mu^2/\langle\Delta\mu\rangle^2$ and $\Delta\nu$ values and, the experimentally observed trend is closer to the predictions of ZH theory.

The failure of dielectric friction theories can be understood in many ways. It is seen (Table 4.13) that the experimentally observed dipole moment values in alcohols calculated using solvatochromic technique increase, as the probe size increases. Hence, one can easily predict the probe C522B to show higher rotational relaxation times and experience larger dielectric friction compared to C307 and C138. It is interesting to observe a reverse trend where C307 is experiencing higher dielectric friction and rotating about 40% and 50% slower in alcohols from pentanol to decanol as compared to C522 and C138. The reason for this is that in C307, the nitrogen atom is part of secondary amino group whereas in C522B it is part of tertiary amino group. In such case, the former can better contribute to hydrogen bonding leading higher dielectric friction. Dutt et al. [84] have studied the dielectric friction contribution in case of two similar probes-neutral and cationic forms of neutral red in series of alcohols, amides and aprotic solvents using NZ and ZH theories. The van der Waals volumes of these two probes were 234 and 237 Å³, respectively, which are almost equal to those of the present coumarin molecules. Both neutral ($\mu_e = 8$ D) and cationic forms were found to experience more or less same friction in alcoholic solvents. Also it is noted that [25], the probe coumarin7 (C7) ($V = 297$ Å³, $\mu_e = 9.6$ D) having lower dipole moment compared to Coumarin6 (C6)
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(V = 303 Å³, μₑ = 12.0 D), rotates about 20% faster. This was attributed to the presence of -NH group in C7 forming a hydrogen bond with alcohol solvents, which hinders the molecular rotation. This argument was also supported by the previous studies [99, 104, 168, 169] of rotational dynamics of two structurally similar nonpolar probes DPP and DMDPP in hydrogen bonding solvents. The probe DPP with two NH groups was found to rotate two to three times slower than its dimethyl counterpart DMDPP wherein two N-CH₃ groups replace the two NH groups. However, coumarin30 (C30), in which the NH group is replaced by the N-CH₃ also experienced the same friction as comarin7. With this, they concluded that the friction experienced by C6 and C7 is not due to hydrogen bonding. Incidentally a similar trend is observed in the present study where the probe C522B (V = 223 Å³, μₑ = 5.15 D) is rotating much faster compared to C307 (V = 217 Å³, μₑ = 4.50 D). Also it is noted that the dipole moment values of C6 and C7 are larger by more than 50% in comparison with C522B and C307. This clearly rules out the possibility of the observed dielectric friction arising out of solute-solvent hydrogen bonding, incase of C522B and C307.

Since the agreement between SED and NZ predicted rotational times and observations, various improvements in the original Nee-Zwanzig description have been incorporated in the recent past. Showing unambiguously that the NZ formalism for dielectric friction is only a special case of dielectric continuum predictions of solvation dynamics, Maroncelli [165] noted that the NZ formalism, as described by Eqn. (4.19) is invalid. His remark is of importance for weakly polar solvents but since nuclear polarization is dominant in polar solvents we have used Eqn. (4.19) directly to calculate dielectric friction. Waldeck and coworkers [14, 22, 82, 170] applied the extended charge
distribution (AW model) [86, 87] to explain the dielectric friction experienced by a number of polar molecules in polar solvents. This model was intended to improve the microscopic effects of dielectric friction regarding a larger solute molecule and to successfully explain the fact that the molecules having no permanent dipole moment experience more dielectric friction than the molecules having a permanent dipole moment. However, it has not been successful in modeling the friction experienced by the probes in associative solvents like alcohols. Another important aspect of the failure of dielectric friction model, is the inseparability of mechanical and dielectric friction theories [107, 110, 111] as discussed earlier in which the cross correlation between mechanical and dielectric components, i.e., the net friction is smaller than that would be obtained from a simple addition of these two independent terms. However, the dielectric contribution calculated using NZ and ZH (both van der Waals radius and length of long axis) overestimate the experimentally observed trend. The results also showed that the probes C522B and C307 are rotating faster in alkanes compared to alcohols thus ruling out the possibility of dielectric friction, and the observed interaction could be due to “electrostriction” [109]. The possible reason for the “electrostriction” is explained in terms of solvent molecules that are arranged to maintain electrical interactions with the solute, which are attractive, because of their polar nature. These electrostatic interactions form the main origin of slow diffusion and increase the density around the solute molecule, thereby, increasing the mechanical friction further. This enhanced mechanical friction, arising out of “electrostriction” slows down the rotation of the solute in alcohols than the dielectric friction.
IV. C. REFERENCES


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